# REMOVAL OF PERMETHRIN AND BIFENTHRIN INSECTICIDES FROM RUNOFF WATER BY ACTIVATED CARBON ADSORPTION

By

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## Abstract

Among the hundreds of pesticides and insecticides, pyrethroids-particularly permethrin and bifenthrin, have become very popular due to their high toxicity to insects and low toxicity to humans, leading to extensive use in both agriculture and urban areas. Pyrethroids have no discharge limits because of this, leading to a negative impact on surrounding ecosystems due to their high toxicity to fish and aquatic life. Due to their low solubility and long half-lives, they are prominent in the environment long after application with a high potential for getting transported in runoff water to nearby water bodies. In this study, DSR-C reactivated carbon from Calgon Carbon was tested as an adsorbent for permethrin and bifenthrin from deionized water. Pyrethroid samples were extracted from water by liquid-liquid extraction and analyzed using a UV-vis spectrophotometer. Isotherm data was best represented by the Langmuir model suggesting single-layer adsorption with an adsorption capacity of 149 mg/g for permethrin and 0.822 mg/g for bifenthrin. Permethrin adsorption was studied further in solutions containing 200 mg/L of sulfate and 10 mg/L of nitrogen, phosphorus, and potassium fertilizer nutrients to simulate realistic agricultural runoff conditions. Across all three water matrices used (DI water, 10 mg/L N-P-K, and 200 mg/L sulfate), kinetic data for permethrin adsorption was best represented by the pseudo-second order kinetic model with similar kinetic rates and equilibrium capacities. Isotherm data represented by the Langmuir model resulted in an average adsorption capacity of 155 ± 39 mg/g across three different water matrices. Adsorption with DSR-C is an effective treatment process for permethrin in agricultural runoff water.

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# Chapter 1 – Introduction

## 1.1 Problem Overview

Pesticides and insecticides are commonly used in agriculture to improve crop efficiency and, in urban environments, to minimize disease and infection spreading. Among the hundreds of pesticides and insecticides, pyrethroids—particularly permethrin and bifenthrin among many others—have become very popular due to their high toxicity to insects and low toxicity to humans, leading to extensive use in both agriculture and urban areas. Pyrethroids have minimal regulations because of this, but most people fail to realize the impact these chemicals can have on the surrounding ecosystems. Pyrethroids are highly toxic to fish and aquatic life, and due to their highly stable structures, they are prominent in the environment for months after initial use. Pyrethroids get carried away in runoff water during storms, after which they contaminate surrounding water bodies and cause secondhand damage to aquatic communities.

Pyrethroids are 1000 times more toxic to fish than to birds and mammals due to causing oxidative stress. They affect the gills, muscles, and livers of fish, and can even alter their protein structure and damage their DNA. These effects were evident in various fish species including trout, tilapia, and carp (Yang et al., 2020). When embryo-larval zebrafish were given sub-lethal concentrations of bifenthrin (50-200 μg/L), various developmental issues were evident. Measurements and observations were taken at various time points from 24-96 hours after dosing, and the zebrafish were seen to have slower and impaired swimming, as well as having developed a curved body axis. Zebrafish dosed with 150 μg/L or greater also experienced endocrine disruption (Jin et al., 2009). If pyrethroids continue to contaminate aquatic bodies, drastic decreases in fish populations could be seen leading to disruptions in the entire ecosystem food chain.

California is one of the biggest agricultural states in the US and, thus, one of the greatest pyrethroid-using states. In 2019 alone in California, 2.5 million acres of agriculture were treated with the pyrethroid lambda-cyhalothrin, placing it at number three in the state when ranking all pesticides for usage. The crops that used the most lambda-cyhalothrin were pistachio with 465,000 acres treated, alfalfa with 325,000 acres treated, and rice with 168,000 acres treated. Bifenthrin was the second most used pyrethroid to treat 335,000 acres of pistachio (Henderson, 2019). When sampling storm drain outfalls around residential neighborhoods of Sacramento, California, bifenthrin was found in every sample with concentrations up to 73 ng/L. Concentrations increased during heavy storms, with stormwater runoff leading to as many pyrethroids detected in 3 hours as 6 months of irrigation would create (Weston et al., 2009). Of all pyrethroids available, when studying urban runoff around San Francisco, bifenthrin was the number one most detected in water. It was even the most detected of all pesticide varieties, not just pyrethroids, with most of it accumulating in the storm drains (Ensminger & Kelley, 2009).

Due to their low solubility and long half-lives, pyrethroids can readily be found in surface water around their application areas. When simulated rainfall was applied to potted *Ilex cornuta* plants treated with bifenthrin, 604 µg/L of bifenthrin was detected in the drainage water on the first day, and 135 µg/L was still detected in the drainage water on the second day (Hinz et al., 2020). Their longevity on concrete surfaces is what makes them so prevalent in runoff water. When pyrethroids were applied to concrete and then the concrete was rinsed with water, pyrethroids were still detected 7 months after treatment even during hot and dry summer conditions (Jiang et al., 2012).

Many treatment methods have been tested to remove pyrethroids from water, and sorption is the most common. Various granulated materials have been tested, such as treated patellidae shells (TPS), which are composed of calcium carbonate. TPS was effective at removing bifenthrin from water in fixed bed column tests. TPS was also found to have good regenerative properties, proving effecting for up to five cycles of reuse (Bakka et al., 2020). Granulated cork was also tested at larger diameters of 1-4 mm for equilibrium and kinetic experiments. Batch experiments showed better sorption than activated carbon (80% removal as opposed to 70%), and the optimal particle size was 1-2 mm (Domingues et al., 2005). To get a more detailed idea of how activated carbon works, another group used activated carbon made from the inner stem bark of the *C. Verum* tree to remove deltamethrin from water. The activated carbon they prepared had an adsorption capacity of 89 mg/g (Langmuir model) and kinetics that followed the pseudo-second-order model (Ettish et al., 2022). In a simulated drainage ditch, bifenthrin and lambda-cyhalothrin were detected at 666 and 374 μg/L, respectively, located 200 m downstream from the application site at 3 hours after application at the head of the drainage ditch (Bennett et al., 2005). This emphasizes the importance of developing treatment methods that can be applied directly to the source of pollution to minimize threats to downstream aquatic ecosystems.

### 1.2 Goals, Objectives, Research Questions, and Hypotheses

**Goals and Objectives:** The goal of this research is to provide information that could improve existing best management practices (BMP) aimed at reducing pyrethroid contamination in aquatic ecosystems. This research will be of interest to anyone implementing an activated carbon treatment system for agricultural runoff water to help reduce concentrations of pyrethroid insecticides that dissipate downstream.

These objectives are relevant to the goal:

- Determine the adsorption rate and capacity for permethrin and bifenthrin, the two most widely used pyrethroids, using granular activated carbon
- Determine if adsorption rate and capacity are adversely affected by N-P-K fertilizer nutrients and sulfate-based salinity, which are benign components of agricultural runoff

The first research question focuses on the fundamental process for activated carbon adsorption of pyrethroids.

**RQ 1:** What are the adsorption mechanisms for permethrin and bifenthrin?

**Hypothesis:** Pyrethroids, such as permethrin and bifenthrin, will display multi-layer adsorption to activated carbon particles.

**Justification:** Due to their hydrophobicity causing high association with sample containers (Hladik et al., 2009), it is anticipated that more pyrethroids will be able to conjugate on top of one another after the entire surface area of the activated carbon becomes occupied.

The second and third research questions examine the influence of runoff water constituents on adsorption. Nutrients are often applied to agricultural fields and urban landscapes along with pesticides, so they may be present in runoff water. Sulfate is another common ion in water. In particular, it is found in relatively high concentrations in the Colorado River, which is used for agricultural irrigation in the western US.

**RQ 2:** How does pyrethroid adsorption change in the presence of nutrients in the forms of urea, phosphate, and potassium?

**Hypothesis:** Experiments performed in an aqueous matrix containing 10 mg/L of common fertilizer nutrients in the form of urea, phosphate, and potassium will show slightly lower pyrethroid adsorption capacity and a slower rate, but the change will not be significant enough to recommend against using activated carbon in runoff treatment. SEM-EDS analysis performed after adsorption will show negligible amounts of N, P, and K adsorbed to the surface.

**Justification:** Previous studies have shown that phosphate is able to adsorb well to peanut shell derived biochar in ranges from 70-150 mg/g by ligand exchange (Liu et al., 2022). However, since the highest levels of phosphate naturally occurring in runoff water rarely exceed 10 mg/L (Krimsky et al., 2021), there will not be enough phosphate to cause significant interference. Urea, the most common form of nitrogen in fertilizers, only displayed adsorption at roughly 1.4 mg/g of activated carbon (Kameda et al., 2020). This value is also quite low compared to previous literature on pyrethroid adsorption, so nitrogen as urea is not expected to interfere significantly. Urea quickly breaks down into ammonium ($NH_4$) which has been determined to adsorb to activated carbon at 17 mg/g (Long et al., 2008). The highest levels of potassium found in agricultural runoff are also around 10 mg/L (Bertol et al., 2007). When studying the adsorption of potassium onto various textured soils, a maximum adsorption capacity of 0.33 mg/g was determined by the Langmuir model (Kibreselassie et al., 2018), so once again it will not be high enough to substantially affect pyrethroid adsorption. Potassium and ammonium will display weak ion exchange bonding to the activated carbon surface due to being cations with a charge of +1. Phosphate shows higher adsorption due to being an anion with a charge of -3. Since any adsorption of N-P-K will be through weaker ion exchange bonds, they are unlikely to interfere with the hypothesized multi-layer adsorption of permethrin.

**RQ 3:** How does pyrethroid adsorption change in the presence of sulfate?

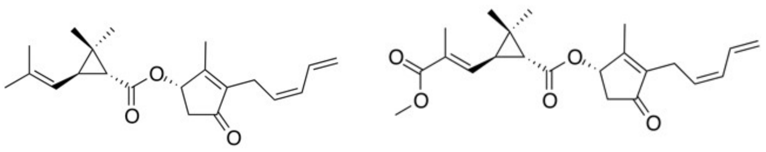
**Hypothesis:** Sulfate will show a more noticeable amount of interference on pyrethroid adsorption to activated carbon because it is a divalent anion and found at relatively high concentrations. SEM-EDS analysis performed after adsorption will show higher amounts of S adsorbed than N, P, or K.

**Justification:** The levels of sulfate naturally occurring in runoff water surpass 200 mg/L, far exceeding the levels of urea, phosphate, and potassium found (Schelz & Moran, 2005). Sulfate has also been found to adsorb to activated carbon at rates up to 57 mg/g (Sadeghalvad et al., 2021). The high presence of sulfate in the water along with its relatively moderate adsorption rate due to being an anion with a charge of -2 is anticipated to interfere and decrease the adsorption of pyrethroids to activated carbon.

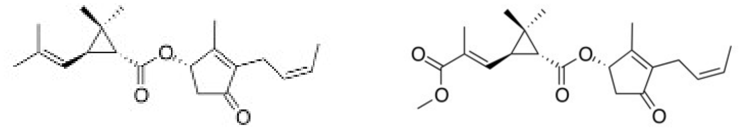
# Chapter 2 – Literature Review

## 2.1 Organic Pyrethrins

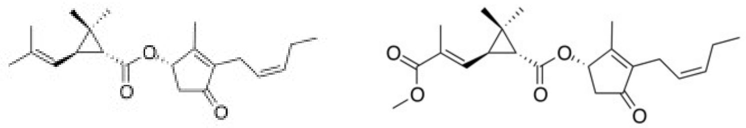
Pyrethroid insecticides are synthetic variations of a naturally occurring insecticide, pyrethrin. Pyrethrin is a natural compound that can be extracted from the chrysanthemum flower, and it has been used in its original form as a pesticide for thousands of years. The Chinese powdered chrysanthemum flowers and applied it around their homes to get rid of insects, and in the 1800s it was discovered that the compound pyrethrin is what gave the powdered flower its insecticidal properties. There are six naturally occurring pyrethrin esters that are formed from the combination of two possible acid moieties and three possible alcohol moieties. These six active ingredients occur in varying ratios in nature (Spurlock & Lee, 2008) and they are known as pyrethrin I & II, cinerin I & II, and jasmolin I & II. Since pyrethrin I & II are the most potent, the group of all six active ingredients are commonly referred to as simply “pyrethrin” (Grdiša et al., 2013).



Pyrethrin I Pyrethrin II



Cinerin I Cinerin II



Jasmolin I Jasmolin II

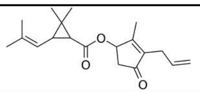
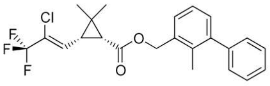
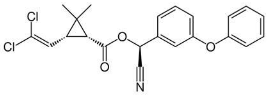
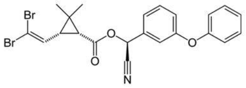
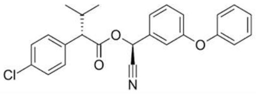
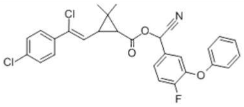
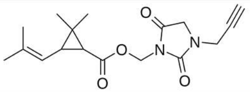
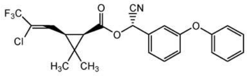
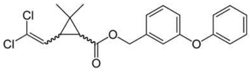
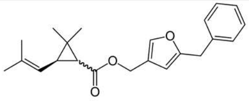
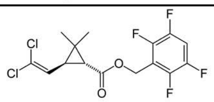
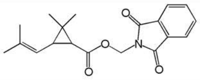
Figure 2-1: Naturally occurring pyrethrins and their molecular structures

## 2.2 Synthetic Pyrethroids

Synthetic pyrethroids were created by modifying portions of the original pyrethrin molecule, and then experimenting to verify its efficiency. The structural modifications of both the acid and alcohol moieties have resulted in hundreds of superior pyrethroids with over 30 varieties on the market today (Ujihara, 2019). In 1949, the first pyrethroid allethrin was created by removing one vinyl group from the unstable diene structure (Ujihara, 2019), and it is still in worldwide commercial use today (de Boer et al., 2019). Another early breakthrough compound was deltamethrin, which became popular soon after introduction in 1974 because it was 100 times more potent than DDT, with the added benefit of accumulating less in the environment (Khambay & Jewess, 2005).

Structural modifications to the alcohol part of the pyrethrin molecule improved the speed at which target insects were affected. For example, tetramethrin has fast action against flies, and imiprothrin has fast action against cockroaches (Ujihara, 2019). When modifications were done to the chrysanthemic acid portion of the molecule, it improved photostability. Photostability is important because it prolongs the life and effectiveness of the molecule when applied in agriculture amidst long days of sunlight exposure. Permethrin was the first photostable pyrethroid available on the market in the early 1970's (Spurlock & Lee, 2008) which is now one of the best-selling insecticides to date. Once new pyrethroids were created, new modifications and substitutions were done to existing pyrethroids, such as replacing the E vinyl chloride in cypermethrin with $CF_3$ or a 4-chlorophenyl group to create cyhalothrin and flumethrin, which are especially effective against a particular species of tick (Khambay & Jewess, 2005). Hundreds of other modifications have been done to give pyrethroids other useful properties, such as being highly non-polar in order to not dissolve water and having a low vapor pressure to not evaporate easily (Laskowski, 2002). This ensures that they will still be effective after rainfall and they can also withstand long days of sun exposure.

Table 2-1: Common pyrethroids with their molecular structures, discovery date, and usage

| Pyrethroid | Date discovered[a] | Molecular Mass (g/mol) | lbs applied in California, 2021[b] |
|---|---|---|---|
|  Allethrin | 1949 | 242.3 | 2.48 |
|  Bifenthrin | 1978 | 422.9 | 425,966 |
|  Cypermethrin | 1972 | 416.3 | 18,985 |
|  Deltamethrin | 1972 | 505.2 | 73,676 |
|  Esfenvalarate | 1975 | 419.9 | 33,165 |
|  Flumethrin | 1977 | 391.3 | N/A |
|  Imiprothrin | 1977 | 339.4 | N/A |
|  Lambda-cyhalothrin | 1977 | 449.9 | 173,094 |
|  Permethrin | 1972 | 391.3 | 203,283 |
|  Resmethrin | 1965 | 316.3 | 5.29 |
|  Tefluthrin | 1979 | 389.3 | N/A |
|  Tetramethrin | 1693 | 300.4 | 22 |

[a]Ujihara (2019), [b]CDPR (2021)

## 2.3 Pyrethroid Use and Environmental Fate

### 2.3.1 Pyrethroids in Agriculture

California is one of the biggest agricultural states in the US and, thus, one of the greatest pyrethroid-using states. In 2019 alone in California, 2.5 million acres of agriculture were treated with lambda-cyhalothrin, placing it at number three in the state when ranking all pesticides for usage. The crops that used the most lambda-cyhalothrin were pistachio with 465,000 acres treated, alfalfa with 325,000 acres treated, and rice with 168,000 acres treated. Bifenthrin was the second most used pyrethroid to treat 335,000 acres of pistachio (Henderson, 2019).

The most used pyrethroid in the US today is permethrin, with an estimated 2 million pounds applied annually (Shrestha et al., 2022). Permethrin was first registered for use on cotton, and now it is widely used in all agricultural and residential settings. Sixty percent of permethrin is used for pest mitigation on cotton plants, with other crops such as soy, maize, tobacco, and coffee using lesser amounts (WHO, 1990).

### 2.3.2 Pyrethroid Occurrence and Fate in the Environment

Pesticides, through various pathways such as runoff or drift, can inadvertently reach places distant from their application sites. In storm drain outfalls from the residential neighborhoods of Sacramento, California, bifenthrin was found in every sample up to 73 ng/L in water and 1211 ng/g on suspended sediment. Permethrin and cypermethrin were also frequently detected, in concentrations up to 125 ng/L and 23 ng/L, respectively. Concentrations increased during heavy storms, with stormwater runoff leading to as many pyrethroids detected in 3 hours as 6 months of irrigation would create (Weston et al., 2009). Of all pyrethroids available, when studying urban runoff around San Francisco, bifenthrin was the number one most detected in water. It was even the most detected of all pesticide varieties, not just pyrethroids, with most of it accumulating in the storm drains (Ensminger & Kelley, 2009). In addition to accumulating in runoff water, pyrethroids also have high affinity to soil particles. The San Joaquin Valley in California had high concentrations of bifenthrin and cyhalothrin found in their streambed sediments. (Domagalski et al., 2010).

Although most papers currently only review pyrethroid usage in California, pyrethroids are in fact used and detected all over the United States. When sampling streambed sediments from 7 locations around the United States, bifenthrin was detected in 41% of samples. The Dallas/Fort Worth sampling site had the highest concentration of pyrethroids including cyhalothrin, cypermethrin, permethrin, and resmethrin, with concentrations appearing in 89% of samples (Kuivila et al., 2012). Another group collected sediment samples from 36 streams in 25 states around the US, and bifenthrin and permethrin were the two most commonly detected. At least one pyrethroid was detected in 78% of collected sediment samples in concentrations from 0.3 to 180 ng/g, and some samples even had up to seven pyrethroids detected at once. Samples were collected from both urban and agricultural sites, and the highest detected concentrations were split evenly between both sites. Predicted toxicity for both sites was attributed to bifenthrin more than any other pyrethroid detected (Hladik & Kuivila, 2012). To get even wider of a range, one study took a global approach and collected samples from South America, Asia, Europe, Australia, and Africa. They detected pyrethroids in ranges up to 100 ng/g in the soil and identified bifenthrin and cypermethrin as the main toxicity contributors to benthic invertebrates

(Li et al., 2017). This supports the estimation that pyrethroids are one quarter of pesticides used globally, with over 400 tons used per year (de Boer et al., 2012).

Due to their chemical properties such as low solubility and long half-lives, pyrethroids can readily be found in surface water around their application areas. Bifenthrin and permethrin have low solubility limits due to their high log $K_{ow}$ values of 6.0 and 6.5, respectively. Their longevity on concrete surfaces is what makes them so prevalent in runoff water. When pyrethroids were applied to concrete and then the concrete was rinsed with water, permethrin was detected at 5,300 µg/L and bifenthrin was detected at 82 µg/L one day after treatment. Even during hot and dry summer conditions, pyrethroids were still detected 7 months after treatment (Jiang et al., 2012).

Table 2-2: Chemical properties of bifenthrin and permethrin

| Pyrethroid | Solubility in water at 25° C (mg/L) | Half-life in soil (days) | Half-life in water (days) | log $K_{ow}$ at 20° C | $K_{oc}$ |
|---|---|---|---|---|---|
| Bifenthrin[a] | <0.001 | 122–345 | 276–416 | 6.0 | $1.31 \times 10^5 - 3.02 \times 10^5$ |
| Permethrin[b] | 0.0055 | 39.5 | 19–27 hours | 6.5 | $1.00 \times 10^5$ |

[a]Johnson (2010), [b]Toynton (2009)

## 2.4 Pyrethroid Toxicity

The greatest reason why pyrethroids are so successful is their insect to mammal toxicity ratio. Pyrethroids are 2250 times more toxic to insects than to vertebrates because of the more sensitive sodium channels (Chrustek et al., 2018). Pyrethroids work by binding to and disrupting the voltage gated sodium channels inside the nerves of the insect. This leads to the voltage in their nervous system getting excited, which quickly leads to paralysis and ultimately their death. Sometimes when lab measurements of the lethal dose required to kill 50% of the population ($LD_{50}$) are made, paralyzed insects are regarded as dead but eventually make a full recovery over the following days. However, this does not limit the efficiency of pyrethroids in field application because during paralysis the insects will die regardless through desiccation or predation (Khambay & Jewess, 2005). Pyrethroids have also been shown to cause fertility and immunity issues in mammal test subjects but at much higher doses upwards of many grams/kilogram of bodyweight (Chrustek, 2018). No conclusive data has been found on the neurotoxic effects of low-level pyrethroid exposure in humans (Kolaczinski & Curtis, 2004).

The issue with pyrethroids arises when non-target organisms are affected, particularly aquatic communities. Since the chemical properties of pyrethroids like low solubility, long half-life, and photostability make them so long lasting in the environment, they easily get caught in runoff water and later accumulate in storm drains and make it to surrounding water bodies like lakes and streams. This is an issue because pyrethroids are 1000 times more toxic to fish than to birds and mammals by causing oxidative stress. This affects the gills, muscles, liver, and can even alter their protein and damage their DNA. These effects were evident in various fish species including trout, tilapia, and carp (Yang et al., 2020). When embryo-larval zebrafish were given sub-lethal concentrations of bifenthrin (50–200 µm), various developmental issues were evident. Measurements and observations were taken at various time points from 24–96 hours after dosing, and the zebrafish were seen to have slower and impaired swimming, as well as a curved body axis. Zebrafish dosed with 150 µg/L or greater also experienced endocrine disruption (Jin et al., 2009). If pyrethroids continue to contaminate aquatic bodies, drastic decreases in fish populations could be seen leading to disruptions in the entire ecosystem food chain.

Amphipod crustaceans are also affected by pyrethroid contamination of aquatic sediments, such as *Hyalella Azteca.* This species was tested for pyrethroid toxicity, and it was found that the lethal concentration required to kill 50% of the population ($LC_{50}$) for bifenthrin was 0.18 µg/g, lambda-cyhalothrin was 0.45 µg/g, deltamethrin was 0.79 µg/g, and permethrin was 4.87 µg/g. Growth inhibition was still seen at concentrations down to one-third of the $LC_{50}$. Pyrethroids in the interstitial water where these amphipods reside was the greatest source of toxicity (Amweg et al., 2005). In addition to being detrimental to aquatic communities in surrounding areas, pyrethroids also harm microbial communities within the target application site. Cypermethrin, deltamethrin, esfenvalareate, and permethrin were applied to soil and the effects on microbial communities were observed. These chemicals decreased the growth of nitrifying and ammonifying bacteria, causing an imbalance in nutrients available for uptake by plants. Beneficial soil invertebrates such as earthworms are also harmed. Earthworms provide texture and aeration to soil which facilitates root growth and nutrient uptake for plants (Galadima et al., 2021). Although the target organism interfering with crop growth will be easily eliminated by pyrethroid application, secondary beneficial organisms can also be affected, which will eventually provide sub optimal growing conditions.

Table 2-3: $LD_{50}$ of bifenthrin and permethrin for varying species

| | Bifenthrin[a] | Permethrin[b] |
|---|---|---|
| $LD_{50}$ insect | 0.015 µg/bee | 0.029 µg/bee |
| Species | Bee (*Apis mellifera)* | Bee *(Apis mellifera)* |
| $LD_{50}$ fish | 0.1-0.18 µg/L | 2.5 µg/L |
| Species | Rainbow trout *(Onchorynchus mykiss)* | Rainbow trout *(Onchorynchus mykiss)* |
| $LD_{50}$ bird | 1.8 g/kg | 13.5 g/kg |
| Species | Bobwhite quail *(Colinus virginianus)* | Japanese quail *(Coturnix japonica)* |
| $LD_{50}$ mammal | 0.4 g/kg | 3.8 g/kg |
| Species | Rat *(Rattus norvegicus)* | Rat *(Rattus norvegicus)* |

[a]Johnson (2010), [b]Toynton (2009)

## 2.5 Regulations

Due to their low toxicity to humans, regulations on pyrethroids are rather flexible. Pyrethrins were first registered with the EPA in the 1950s, permethrin was registered in 1968, and bifenthrin was registered in 1989. The EPA has put certain recommendations for pyrethroid packaging, such as having an illustration on the label to show that they should not be disposed of down the drain. Pyrethroids also have certain usage recommendations, such as using only when wind speeds are less than 10 mph, and not using them in slanted areas with high runoff possibility (Friedman et al., 2020). No official discharge limits have been established for commercial or residential pyrethroid usage. The world health organization (WHO) has recommended acceptable daily intakes of pyrethroids for humans, and the values have been updated over the years. The current recommended daily intake for permethrin is 0.05 mg/kg/day, and for bifenthrin it is 0.02 mg/kg/day (WHO, 2005).

## 2.6 Components of Agricultural Runoff Water

For optimal crop yield and plant strength, fertilizer nutrients must be added to the soil in agricultural sites. These nutrients found in agricultural soil later get transported in runoff water and can be detected downstream. The three most common fertilizer nutrients are nitrogen (N), phosphorus (P) and potassium (K) and they are generally referred to as "NPK". Some common ways that nitrogen can be added to soil are in the form of anhydrous ammonia, urea, ammonium nitrate, or ammonium sulfate. Phosphate can be added in various forms such as diammonium phosphate or monoammonium phosphate. Potassium is added in forms of potassium chloride, potassium sulfate, potassium hydroxide, or potassium nitrate (Vitosh, 1996).

NPK nutrients can be found downstream in varying concentrations, depending on application and location. When sampling stream flows from across the United States, agricultural sites had the highest total nitrogen concentrations on the order of 10 mg/L (Dubrovsky et al., 2010). Soybean agricultural runoff water under different tillage/agricultural conditions resulted in maximum potassium concentrations of 9.0 mg/L detected (Bertol et al., 2007). Across different seasons and application conditions in Florida, the highest concentrations of phosphate found in surface runoff were 10 mg/L (Krimsky et al., 2021).

Another common constituent of agricultural runoff water is sulfate, which is a major contributor to salinity in the Colorado River. The Colorado River is the main source of water used for irrigation in Southern California (Bauder et al., 2023). The Colorado River flows through the middle of Canyonlands National Park in Southeast Utah. Water samples collected from all areas of Canyonlands National Park contained sulfate in concentrations up to 200 mg/L (Schelz & Moran, 2005).

## 2.7 Common Treatment Processes

Various stormwater treatment processes can be implemented, and the method is usually chosen by considering the target pollutant, discharge limits, and affordability. Pollutants with a larger particle size can be removed by sedimentation or physical filtration (Clark & Pitt, 2012). The chemical properties of the target pollutant also play a role in deciding which treatment process to apply. For example, pollutants that are highly volatile can be removed through air stripping. Microorganisms can be neutralized through disinfection by chlorine, ozone, or ultraviolet light (Clark & Pitt, 2012).

### 2.7.1 Pyrethroid Treatment Processes

Of all the treatment processes tested to remove pyrethroids from water, sorption is the most implemented. Various granulated materials have been tested, such as treated patellidae shells (TPS), which are composed of calcium carbonate. The high specific surface area of 158 $m^2/g$ made it effective at removing bifenthrin from water in fixed bed column tests. Researchers were able to achieve an adsorption capacity of 25.3 mg/g using a flow rate of 8 mL/min and a bed depth of 4 cm, particle size range of 50–100 µm, and flow concentration of 20 mg/L. They also found TPS to have good regenerative properties, proving effecting for up to five cycles of reuse (Bakka et al., 2020). Granulated cork was also tested at larger diameters of 1–4 mm for equilibrium and kinetic experiments. Batch experiments showed better sorption than activated carbon (80% removal as opposed to 70%), and the optimum particle size was 1–2 mm (Domingues et al., 2005). Another group used activated carbon made from the inner stem bark of the *C. Verum* tree to remove deltamethrin from water. The activated carbon they prepared had a surface area of 1000–2000 $m^2$/g, a pore volume of 0.47–1.22 mL/g, and a pore diameter of approximately 2 nm. They used Langmuir's model to find a maximum adsorption capacity of 89 mg/g during adsorption testing (Ettish et al., 2022).

In addition to just removal of pyrethroids by sorption, other remediation processes have been studied to decompose the pyrethroid molecule entirely. Ozone was also shown to be effective at cleansing rice grains contaminated with bifenthrin and deltamethrin. A continuous ozone flow of 1.0 L/min at a concentration of 3 mg/L resulted in 92% removal after ten hours of treatment, without altering the quality of the rice grains (de Ávila et al., 2017). UV treatment was shown to be more effective than ozone, and one group was able to decompose fenvalerate by 99% in under 10 minutes. What was even more efficient than either UV or ozone alone was using a combination of the two. The UV/ozone combination was able to achieve 99% decomposition of fenvalerate in under 5 minutes of reaction time (Tran et al., 2014).

### 2.7.2 Nutrient Treatment Processes

Sorption has also been tested to remove other constituents of runoff water such as fertilizer nutrients and sulfate. Urea, a common form of nitrogen applied to agriculture, was found to adsorb to activated carbon at roughly 1.4 mg/g (Kameda et al., 2020). Potassium was found to adsorb across a variety of textured soils, with a maximum adsorption capacity of 0.33 mg/g (Kibreselassie et al., 2018). When testing peanut shell-derived biochar produced under different conditions, the best performing samples adsorbed phosphorus at a maximum of 150 mg/g (Liu et al., 2022). Sulfate adsorption was tested across varying carbon-based adsorbents, and a mean adsorption capacity of 40 mg/g was determined. Activated carbon derived from rice straw had the highest sulfate adsorption capacity of 56.5 mg/g. Activated carbon derived from coconut shell had the poorest sulfate adsorption capacity at just 7.9 mg/g (Sadeghalvad et al., 2021).

# Chapter 3 – Removal of Permethrin and Bifenthrin Insecticides from Runoff Water by Activated Carbon Adsorption

## Abstract

Among the hundreds of pesticides and insecticides, pyrethroids-particularly permethrin and bifenthrin, have become very popular due to their high toxicity to insects and low toxicity to humans, leading to extensive use in both agriculture and urban areas. Pyrethroids have no discharge limits because of this, leading to a negative impact on surrounding ecosystems due to their high toxicity to fish and aquatic life. Due to their low solubility and long half-lives, they are prominent in the environment long after application with a high potential for getting transported in runoff water to nearby water bodies. In this study, DSR-C reactivated carbon from Calgon Carbon was tested as an adsorbent for permethrin and bifenthrin from deionized water. Pyrethroid samples were extracted from water by liquid-liquid extraction and analyzed using a UV-vis spectrophotometer. Isotherm data was best represented by the Langmuir model suggesting single-layer adsorption with an adsorption capacity of 149 mg/g for permethrin and 0.822 mg/g for bifenthrin. Permethrin adsorption was studied further in solutions containing 200 mg/L of sulfate and 10 mg/L of nitrogen, phosphorus, and potassium fertilizer nutrients to simulate realistic agricultural runoff conditions. Across all three water matrices used (DI water, 10 mg/L N-P-K, and 200 mg/L sulfate, kinetic data for permethrin adsorption was best represented by the pseudo-second order kinetic model with similar kinetic rates and equilibrium capacities.  Isotherm data represented by the Langmuir model resulted in an average adsorption capacity of 155 ± 39 mg/g across three different water matrices. Adsorption with DSR-C is an effective treatment process for permethrin in agricultural runoff water.

**Keywords:** adsorption; permethrin; bifenthrin; activated carbon; pyrethroid

## 3.1 Introduction

Pesticides and insecticides are commonly used in agriculture to improve crop efficiency and, in urban environments, to minimize disease and infection spreading. Among the hundreds of pesticides and insecticides, pyrethroids—particularly permethrin and bifenthrin among many others—have become very popular due to their high toxicity to insects and low toxicity to humans, leading to extensive use in both agriculture and urban areas. Pyrethroids have minimal regulations because of this, but most people fail to realize the impact they can have on the surrounding ecosystems. Pyrethroids are highly toxic to fish and aquatic life, and due to their highly stable structures, they are prominent in the environment for months after initial use. Pyrethroids get carried away in runoff water during storms, after which they contaminate surrounding water bodies and cause secondhand damage to aquatic communities. Pyrethroids are detrimental to aquatic life due to causing oxidative stress and damaging the gills, muscles, and livers of fish, and sometimes even altering their protein structure and DNA (Yang et al., 2020). Sub-lethal concentrations of bifenthrin as low as 50 μg/L cause developmental issues in embryo-larval zebrafish such as impaired swimming and a curved body axis (Jin et al., 2009). If pyrethroids continue to contaminate aquatic bodies, drastic decreases in fish populations could be seen leading to disruptions in the entire ecosystem food chain.

California is one of the biggest agricultural states in the US and, thus, one of the greatest pyrethroid-using states. In 2021 alone in California, 426,000 lbs of bifenthrin, 203,000 lbs of permethrin, and 173,000 lbs of lambda-cyhalothrin were applied both by agricultural professionals and residential homeowners (CDPR, 2021). Permethrin was first registered for use on cotton, but now it is applied to a variety of other crops such as soy, maize, tobacco, and coffee (WHO, 1990). Bifenthrin is the second most used pyrethroid, used to treat a variety of products such as cereal, corn, alfalfa, hay, fruits, and vegetables (Johnson (2010). Due to the low solubility and long half-lives of pyrethroids, they are prominent in the environment long after application. Water samples from storm drain outfalls around neighborhoods of Sacramento, California contained bifenthrin and permethrin in concentrations up to 73 ng/L and 125 ng/L, respectively. Concentrations increased during heavy storms, with stormwater runoff leading to as many pyrethroids detected in 3 hours as 6 months of irrigation would create (Weston et al., 2009). In sediment samples from 36 streams across the entire United States, bifenthrin and permethrin were the two most detected pyrethroids in concentrations up to 180 ng/L (Hladik & Kuivila, 2012). Agricultural runoff water also contains other non-toxic components, such as dissolved nutrients and ions originating from fertilizers. Nitrogen, phosphorus, and potassium are the three most common fertilizers nutrients used to allow plants optimal growing conditions (Vitosh, 1996). Another common component of agricultural runoff water, especially in Southern California, is sulfate-based salinity originating from the Colorado River (Bauder et al., 2023).

Various stormwater treatment processes can be implemented, and methods are usually chosen by considering the target pollutant and affordability. Ozone was shown to be effective at cleansing rice grains contaminated with bifenthrin and deltamethrin. A continuous ozone flow of 1.0 L/min at a concentration of 3 mg/L resulted in 92% removal after ten hours of treatment, without altering the quality of the rice grains (de Ávila et al., 2017). UV treatment was shown to be more effective than ozone, and one group was able to decompose fenvalerate by 99% in under 10 minutes. What was even more efficient than either UV or ozone alone was using a combination of the two. The UV/ozone combination was able to achieve 99% decomposition of fenvalerate in under 5 minutes of reaction time (Tran et al., 2014). Sorption has been tested on various granulated materials, such as treated patellidae shells (TPS), which are composed of calcium carbonate. The high specific surface area of 158 $m^2/g$ made it effective at removing bifenthrin from water in fixed bed column tests with an adsorption capacity of 40.53 mg/g, as well as good regenerative properties, proving effecting for up to five cycles of reuse (Bakka et al., 2020). Granulated cork was also tested at larger diameters of 1-4 mm for equilibrium and kinetic experiments. Batch experiments showed better sorption than activated carbon and an optimal particle size of 1-2 mm (Domingues et al., 2005). Activated carbon prepared from the inner stem bark of the *C. Verum* tree was found to be effective at removing deltamethrin from water, with a maximum adsorption capacity of 89 mg/g determined during kinetic studies (Ettish et al., 2022).

In this study, reactivated carbon sourced from previously used granular activated carbon was tested for its adsorption potential of permethrin and bifenthrin, two of the most common pyrethroids used today. Kinetic and isotherm adsorption models were applied to both pyrethroids as they were adsorbed from deionized water. Afterwards, the adsorption potential for permethrin was studied further in two new water matrices containing fertilizer nutrients and sulfate-based salinity, to assess if the effectiveness of activated carbon is compromised by benign components of agricultural runoff water. SEM imaging and EDS elemental analysis were performed on the activated carbon surface before and after adsorption to identify elements present in the samples, further supporting the results of the adsorption experiments.

## 3.2 Materials and Methods

### 3.2.1 Methodology

Batch adsorption tests were performed to determine the adsorption rate and capacity of pyrethroids to activated carbon. Figure 3.0 illustrates the laboratory process of a sample from start to finish. First, a microbalance was used to weigh granular activated carbon into an empty, labeled vial. Then, water (either deionized, nutrient laden, or sulfate laden) was added to the vial at either 15 or 20 mL. Then a glass syringe was used to spike in the commercial pyrethroid solution. After the vial and all its contents was prepared, it was sealed tightly and placed into an orbital shaker for their respective time requirements depending on the experiment being conducted.

After the predetermined reaction time is reached, the samples are removed from the shaker and filtered into a new vial through a wire mesh to remove the activated carbon. Then, a liquid-liquid extraction is performed to extract the pyrethroids from the water into ethyl acetate. Ethyl acetate samples are then ready to be analyzed on the UV-vis spectrophotometer.

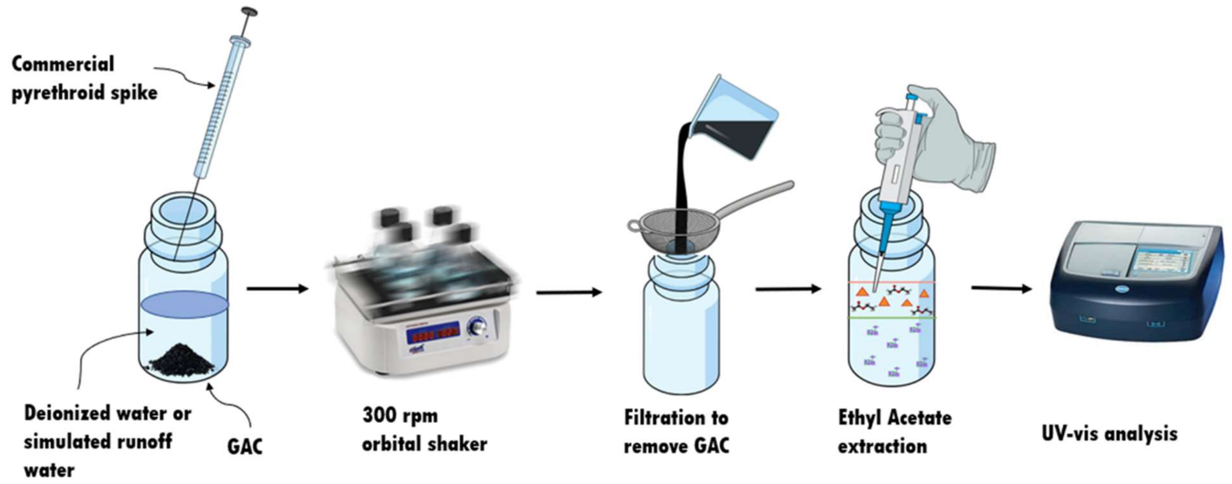


Figure 3.0: Laboratory process of carrying out adsorption experiments.

Kinetic and isotherm models were applied to help determine the adsorption rate and capacity of permethrin and bifenthrin, two of the most common pyrethroid insecticides. Experiments are first performed in deionized water for investigation. Afterwards, the pyrethroid which displays higher adsorption rates is studied further in water samples containing nutrients and ions, simulating realistic agricultural runoff conditions. Experiments are conducted in water containing nitrogen, phosphorus, and potassium (N-P-K) fertilizer nutrients as well as in water containing high sulfate concentrations to assess any potential interferences in adsorption.

### 3.2.2 Chemicals and Reagents

To stay consistent with the forms of pyrethroid insecticides commonly available on the market, Durvet Permethirn (10%) and Ike's Total Pest Control (7.9% Bifenthrin) were used for spiking all samples in this experiment. DSR-C reactivated carbon was obtained from Calgon

Carbon. Potassium chloride (ACS grade) was obtained from Ward's Science and urea (ACS grade) was obtained from J.T. Baker. Sodium sulfate (99%), sodium chloride (99%), ethyl acetate (99.9%), and methanol (ACS grade) were obtained from VWR. Ammonium phosphate monobasic (ACS grade) was obtained from Fisher Scientific.

### 3.2.3 Equipment

USA standard testing sieves by Newark were used to sieve the activated carbon, and a Symphony ultrasonic cleaner by VWR was used for cleaning the activated carbon. Stainless steel wire cloths from McMaster-Carr were used for filtering the activated carbon after cleaning and sample reaction. An XPR micro-analytical balance by Mettler Toledo was used for weighing the activated carbon with a precision of 0.1 mg, and the SK-O330-M orbital shaker by ONiLAB was used for sample oscillation. A Hach DR6000 UV-vis spectrophotometer was used for liquid-phase pyrethroid analysis, and a Jeol JSM-IT200 scanning electron microscope was used to observe the surface morphology and microstructure of the activated carbon.

### 3.2.4 Preparation of Activated Carbon

The activated carbon to be used for this experiment was acquired from Calgon Carbon, a supplier based in Pennsylvania, USA. Upon recommendation from the technical marketing manager, the DSR-C reactivated carbon was selected for these experiments due to its high surface area and low cost due to being reactivated. It was specifically designed for the removal of organic contaminants from water, with high density and durability to withstand multiple cycles of use and reactivation.

A porcelain mortar and pestle were used to crush the activated carbon before sieving to isolate multiple size ranges. Sieves # 20 (850 µm), # 35 (500 µm), # 60 (250 µm), and # 325 (45 µm) were used. Multiple rounds of crushing and sieving were performed to collect activated carbon in three size ranges of 850-500 µm, 500-250 µm, and 250-45 µm. Any activated carbon that did not make it through the first sieve (larger than 850 µm) was put back in the mortar for crushing, and anything collected in the bottom pan (smaller than 45 µm) was discarded. Three different size ranges of activated carbon were stored in separate vials for further use and analysis.

#### 3.2.4.1 Ultrasonic Sonication

Even after using a sieve to separate the activated carbon into different size groups, it is possible that two or more smaller particles were stuck together and got incorrectly mixed into the larger size group. Therefore, each size group of particles was separated into individual smaller portions and subjected to ultrasonic sonication in an ethyl alcohol medium to separate all small particles from one another and cleanse the sample of impurities. After sonication, the sample was placed on a wire mesh above a vacuum filtration apparatus to isolate the desired particles while allowing the ethyl alcohol and smaller particles to be removed. A 35x35 mesh, 60x60 mesh, and 325x325 mesh stainless steel wire cloth from McMaster-Carr were used to filter the 850–500 µm, 500–250 µm, and 250–45 µm size ranges, respectively. Then the activated carbon was dried in a vacuum oven at 80 °C for 2 hours to allow evaporate the remaining ethyl alcohol. This process ensures that the activated carbon used throughout the experiment only contains particles of the desired size range and no impurities or smaller particles will pass through the wire mesh filter and continue reacting with the sample after collection.

### 3.2.4.2 Flowrate Testing and Selection of Particle Size

When it comes to the implementation of on-site remediation efforts, the particle size of the adsorbent must be considered to create the most efficient design for a storm water filtration system. Generally, a finer particle size of adsorbent results in faster adsorption kinetics, as well as a higher adsorption capacity per mass of adsorbent used due to the increase in surface area. However, as the particle size decreases, the permeability of a filter constructed with said particles will also decrease. If the permeability of the filter is too low, the runoff water will get backed up behind the filter and ultimately spill over the top, resulting in minimal pyrethroid removal. If the particle size is too large, permeability of the barrier would be high, but adsorption rates might be too low, leading to an ineffective design.

A gravity flowrate column test was conducted for each activated carbon size range by packing a 1-cm wide burette with 10 $cm^3$ of activated carbon. A ball of glass fiber was placed at the bottom of the column to prevent any activated carbon from flowing out of the system. A tube attached to a peristaltic pump fed water in through the top of the column to maintain a constant 15 cm of water above the activated carbon. The bottom of the column was then opened and held over a graduated cylinder for a controlled amount of time, and the volume of water collected after each trial was recorded. The column packed with 500-850 µm granules had an average flowrate of 5.1 mL/min, the column packed with 250-500 µm granules had an average flowrate of 3.5 mL/min, and the column packed with 45-250 µm granules had a flowrate of 0 mL/min. To provide data applicable to stormwater treatment, activated carbon granules between 250-500 µm were selected for this experiment because they provide a good flowrate while maintaining a smaller particle size for better adsorption performance.

### 3.2.5 Adsorption Experiments

#### 3.2.5.1 Preparation of Water Matrix

Experiments with permethrin and bifenthrin were first conducted in deionized water before creating two new water matrices designed to simulate realistic runoff water conditions. Water samples containing 300 ppm of bifenthrin had a pH of 6.2, and water samples containing 400 ppm of permethrin had a pH of 6.4. The pH of stormwater generally remains between values of 6.5 to 9.0 (Salehi et al., 2020). Due to the pKa of permethrin and bifenthrin being extremely low at -3.7 and -7.1, respectively (Knox et al., 2024), the water was not buffered since variability due to protonation/deprotonation would not be possible under the conditions of this experiment or natural runoff water conditions.

The fertilizer nutrient laden water was prepared to target the high end of nitrogen, phosphate, and potassium naturally found in runoff water of 10 mg/L of nitrogen (Dubrovsky et al., 2010), 10 mg/L of phosphate (Krimsky et al., 2021), and 9.0 mg/L of potassium (Bertol et al., 2007). A one-liter stock containing 10 mg/L of nitrogen, phosphorus, and potassium was prepared by adding urea (11.8 mg), ammonium phosphate monobasic (37.2 mg), and potassium chloride (19.1 mg) to deionized water.

The sulfate laden water was prepared to target the high end of sulfate found in the Colorado River, which is the main source of water used for irrigation in Southern California (Bauder et al., 2023). Water samples from the Colorado River frequently contain sulfate in concentrations up to 200 mg/L (Schelz & Moran, 2005). A one-liter stock containing 200 mg/L of sulfate was prepared by adding sodium sulfate (296 mg) to deionized water.

### 3.2.5.2 Kinetic and Isotherm Experiments

Adsorption experiments were conducted using 10–50 mg of 250–500 µm activated carbon granules in a 20 mL vial containing water and 6 mg of pyrethroids. First, a micro-analytical balance was used for weighing the activated carbon, which was then put into a vial. Next, water (either deionized, nutrient laden, or sulfate laden) was added to each vial, and then a glass syringe was used to add Durvet Permethrin or Ike's Total Pest Control to each vial. Permethrin samples were prepared in 15 mL of water with a concentration of 400 mg/L by spiking in 50 µL of pure stock (10% permethrin by mass), and bifenthrin samples were prepared in 20 mL of water with a concentration of 300 mg/L by spiking in 60 µL of pure stock (7.9% bifenthrin by mass). These concentrations were determined by considering the density of permethrin (1.19 g/cm$^3$) and bifenthrin (1.26 g/cm$^3$). After samples were prepared, the vials were sealed tightly and placed into an orbital shaker at 300 rpm and room temperature (23 ± 1 °C).

Kinetic experiments all used the same mass of activated carbon with varying reaction times, and isotherm experiments used varying masses of activated carbon with the same reaction time. For kinetic experiments, each sample contained 40 ± 0.1 mg of activated carbon. Permethrin samples were removed from the shaker at 7-time increments leading to equilibrium at

24 hours, and bifenthrin samples were removed from the shaker at 11-time increments leading to equilibrium at 96 hours. For isotherm experiments, each sample contained activated carbon in increments of 10, 20, 30, 40, and 50 ± 0.1 mg. All permethrin and bifenthrin isotherm samples each reacted in the shaker for their respective equilibrium times of 24 and 96 hours before removal and analysis.

### 3.2.5.3 Adsorption Kinetic Models

Various kinetic models can be applied to the resulting data to give kinetic rate constants and help determine the adsorption mechanisms and equilibrium capacity. In this study, the Lagergren pseudo first-order kinetic model and the pseudo second-order kinetic model were applied to each dataset after completion of adsorption kinetic experiments due to providing better parameter estimation and interpretability than first order or second order kinetic models alone. Pseudo kinetic models are a better fit when there are rate limiting steps and one driving force dominates over the other. In the case of these experiments, two driving forces in effect are the adsorption capacity and the concentration of the adsorbent.

The Lagergren pseudo-first order model assumes that the rate of adsorption is directly proportional to concentration of the adsorbate (Sahoo & Prelot, 2020). In this case, the adsorption speed is controlled by the availability of active sites on the surface of the carbon granules, and the amount of pyrethroids in the solution. If kinetic data fit this model well, it suggests that the underlying assumptions of the pseudo-first order model correctly describe pyrethroid adsorption onto activated carbon.

The linear form of the Lagergren pseudo-first order kinetics model can be determined by:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$$

where

$t$ = time

$q_e$ = amount adsorbed at equilibrium (mg/g)

$q_t$ = amount adsorbed at time t (mg/g)

$k_1$ = equilibrium rate constant (L/hour)

The pseudo second-order kinetic model assumes that chemisorption is the rate-limiting step over the whole range of adsorption (Sahoo & Prelot, 2020). In this case, the adsorption rate is not dependent on the concentration of pyrethroids in the solution, but only on the adsorption capacity of the activated carbon itself. If kinetic data fit this model well, it suggests that chemical sorption is the driving mechanisms behind pyrethroid removal from water samples.

The linear form of the pseudo-second order kinetics model can be determined by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where

$t$ = time

$q_e$ = amount adsorbed at equilibrium (mg/g)

$q_t$ = amount adsorbed at time t (mg/g)

$k_2$ = equilibrium rate constant (g/mg hour)

### 3.2.5.4 Adsorption Isotherm Models

Adsorption isotherm models can be applied to experimental data to help describe how an adsorbent interacts with the adsorbate. Adsorption isotherm models explore the relationship between the amount of contaminant adsorbed per gram of adsorbent, and the concentration remaining in the solution, all while reacting for the same length of time at the same temperature. The parameters determined by adsorption isotherm models can provide clues to the adsorption mechanisms and capacity of the compounds in question. In this study, the Freundlich isotherm model and two forms of the Langmuir isotherm model were applied to each dataset to determine which better describes the relationship between activated carbon and pyrethroid insecticides.

The Freundlich model is used to describe multilayer adsorption on a heterogenous adsorbent surface, assuming different binding energies at each adsorption site (Sahoo & Prelot, 2020). The Freundlich constants $K_F$ and 1/n represent the adsorption capacity and intensity of system.

The linear form of the Freundlich isotherm can be determined by:

$$\log(q_e) = \log(K_F) + \left(\frac{1}{n}\right)\log(C_e)$$

where

$q_e$ = amount adsorbed at equilibrium (mg/g)

$C_e$ = equilibrium concentration (mg/L)

$K_F$ = Freundlich capacity constant

1/n = Freundlich intensity constant

The Langmuir model describes the relationship between the concentration of adsorbate and the extent of surface coverage. It assumes that the entire surface of the adsorbent is homogenous, and monolayer adsorption occurs (Sahoo & Prelot, 2020). The calculated Langmuir constants help determine the adsorption capacity as well as the energy of adsorption. In this experiment, two different forms of the Langmuir model were applied to datasets.

The first linear form of the Langmuir isotherm model can be determined by:

$$\frac{1}{q_e} = \frac{1}{K_L Q_m C_e} + \frac{1}{Q_m}$$

and the second linear form of the Langmuir isotherm model can be determined by:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m}$$

where

$q_e$ = amount adsorbed at equilibrium (mg/g)

$Q_m$ = maximum adsorption capacity (mg/g)

$C_e$ = equilibrium concentration (mg/L)

$K_L$ = Langmuir energy constant (L/g)

### 3.2.6 Sample Processing for Analysis

#### 3.2.6.1 Sample Extraction

Immediately after removing samples from the shaker, they were filtered with a 60-mesh stainless steel wire cloth (~230 µm holes) into a new vial to remove the activated carbon granules and stop the adsorption process. Then, 5.4 g of sodium chloride were added to the 15 mL permethrin samples, and 7.2 g of sodium chloride were added to the 20 mL bifenthrin samples to ensure the samples reach their saturation point. Then the samples were sealed tightly, vigorously shaken and inverted for two minutes, allowing the salt to dissolve.

After the salt dissolved, 5 mL of ethyl acetate was added to the 15 mL permethrin samples, and 15 mL of ethyl acetate was added to the 20 mL bifenthrin samples, which were transferred to 40 mL vials. The samples were then sealed once more and shaken for two minutes. Due to the density difference between ethyl acetate and water, the ethyl acetate portion settled upwards and sat above the water. Due to the high salinity of the water, the pyrethroids displayed a much higher affinity to the ethyl acetate phase and migrated to the upper portion. The uppermost ethyl acetate (1.8 mL from permethrin samples and 7.5 mL from bifenthrin samples) was then carefully removed by pipette and stored in a separate vial, leaving the lower portion as a buffer to ensure no water was taken up accidentally.

### 3.2.6.2 Sample Analysis

Pyrethroid samples in ethyl acetate were analyzed on a Hach DR6000 UV-Vis spectrophotometer. The UV-Vis spectrophotometer was calibrated with eight calibration standards to enable accurate detection within the concentration ranges of 1 to 100 ppm, and 1 to 400 ppm, respectively, for both permethrin and bifenthrin. Permethrin displayed maximum UV absorbance at a wavelength of 266 nm, and a calibration with a correlation coefficient ($R^2$) of 0.9988 was achieved. Bifenthrin displayed a maximum UV absorbance at a wavelength of 253 nm, and a calibration with a correlation coefficient ($R^2$) of 0.9982 was achieved.

Every calibration standard was first spiked into deionized water, before being filtered and extracted into ethyl acetate to incorporate the recovery factor into the analysis. After extraction, permethrin samples were diluted before analysis by transferring 420 µL from the storage vial to a volumetric flask and then adding ethyl acetate until the final volume reached 5 mL. The samples were then transferred to a new vial for storage before analysis. Since bifenthrin samples were extracted into a larger volume of ethyl acetate and the UV-Vis detection range was also higher, no further dilution was needed before bifenthrin analysis.

For analysis, samples were transferred to a 3 mL quartz cuvette which was then inserted into the UV-vis spectrophotometer to detect absorbance of the corresponding wavelength. After a reading was acquired, the quartz cuvette was rinsed with ethyl acetate before transferring the next sample for analysis.

### 3.2.6.3 Quality Assurance/Quality Control

Preliminary quality assurance trials tested the extraction recovery of spiked permethrin samples in deionized water under different extraction conditions to determine which action most affects recovery/loss of analyte. Samples extracted in the original vial (no transferring involved) had an average recovery of 85.2%. Samples poured into a new vial for extraction had an average recovery of 84.2%. Samples transferred to a new vial with a plastic syringe had an average recovery of 84.6%. Samples transferred to a new vial with a plastic syringe and 5 µm nylon syringe filter had an average recovery of 77.2%. As expected, samples that were filtered had a lower extraction recovery and samples extracted in the original vial had the highest recovery rate. All samples analyzed through the entire experiment from this point forward were filtered into a new vial by pouring the sample through a 60-mesh stainless steel wire cloth before extraction regardless of whether they contained activated carbon or not, to ensure consistency across all samples.

Quality control samples were included in every batch in the form of positive controls, negative controls, and experimental duplicates. Positive controls were spiked with the same amount of permethrin/bifenthrin and were subjected to the same amount of time in the shaker but contained no activated carbon. This was to ensure that any decreases in permethrin/bifenthrin seen were due to adsorption to the activated carbon as opposed to decomposition through hydrolysis, volatilization, or photodegradation. Two negative controls were included in every batch; a sample containing only water and activated carbon with no pyrethroids spiked in, and a total blank containing only water. These samples were also subjected to the same amount of time in the shaker before being extracted and analyzed to ensure that there was no contamination originating from the activated carbon or any step in the sample handling process. Every experimental sample in each batch was prepared in duplicate to ensure reliability and reproducibility of experimental data, and to minimize the impact of random error.

### 3.2.7 SEM-EDS Analysis

After adsorption experiments, the used activated carbon was collected and air dried for further analysis including scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). SEM was used to generate up-close, high-resolution images of the activated carbon granules. EDS was used to determine the elemental composition of the activated carbon granules. By detecting characteristic X-ray emissions from the surface of the activated carbon, EDS helped identify and quantify elements present in the sample, including trace elements and impurities in either the activated carbon or pyrethroid industrial stocks.

## 3.3 Results and Discussion

### 3.3.1 Permethrin and Bifenthrin Adsorption Kinetics in DI water

Permethrin and bifenthrin samples containing 40 ± 0.1 mg of activated carbon reacted in the shaker for varying times leading up to 24 and 96 hours, respectively, until equilibrium was reached. Figure 3.1 shows the effect of reaction time on permethrin and bifenthrin adsorption from DI water. Permethrin adsorption kinetics follow a logarithmic trend, with concentrations quickly decreasing in the early stages of the reaction and eventually stabilizing towards the end of the reaction at roughly 25% of the starting concentration. Permethrin samples reached kinetic equilibrium between 8–24 hours, which is a bit slower than the equilibrium time of 90 minutes determined when testing adsorption onto zinc-oxide nanoparticles (Moradi et al., 2014). However, Moradi et al. used a much lower initial concentration of 0.1 ppm as opposed to 400 ppm used in this study, explaining why a much quicker equilibrium was reached. Bifenthrin adsorption kinetics also follow a logarithmic trend, but adsorption is drastically lower, even with a longer equilibrium time. Bifenthrin samples containing granular activated carbon (GAC) had just marginally lower concentrations than bifenthrin positive control samples containing no GAC. The lower adsorption rates seen for bifenthrin may be due to proprietary ingredients in the formula of Ike's Total Pest Control. A proprietary blend known as "AU-335" makes up 22% of Ike's Total Pest Control composition (Ike's, 2021). This may be purposely designed to reduce sorption and effectively remain in the environment longer. For Durvet Permethrin, 80-90% of the composition is kerosene (Durvet, 2020). This solvent is meant to increase the solubility of the insecticide in water and does not seem to interfere with adsorption to activated carbon.

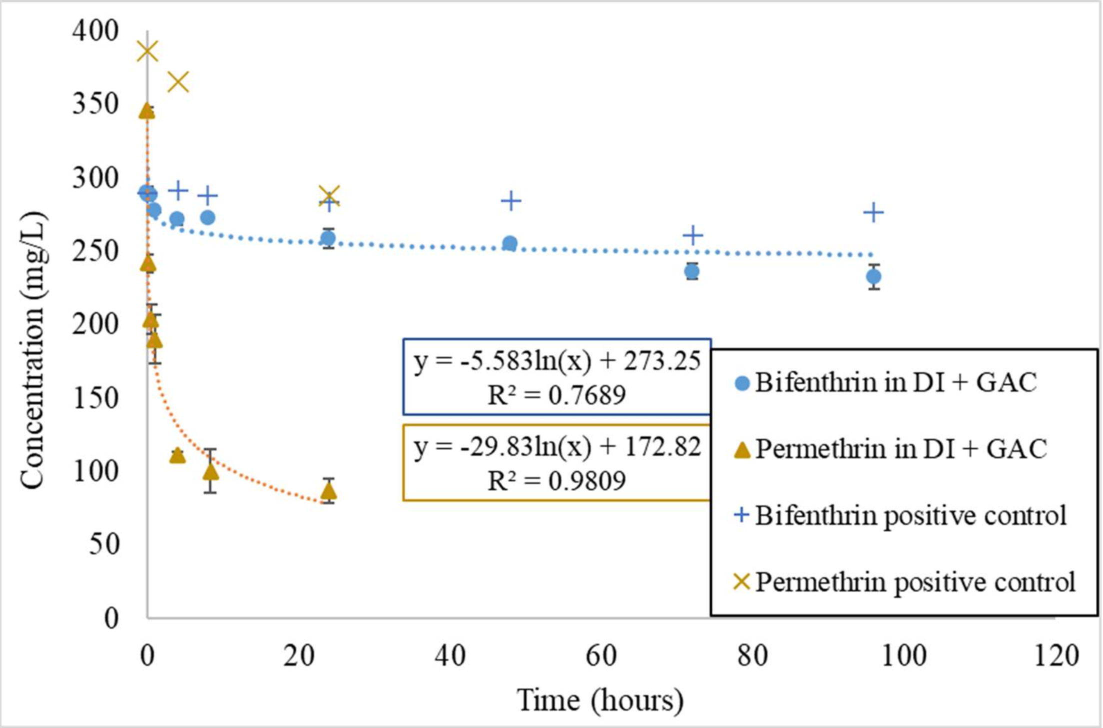


Figure 3.1: Removal of permethrin and bifenthrin from deionized (DI) water over time in the presence of granular activated carbon (GAC). Error bars represent one standard deviation for duplicate samples.

The Lagergren pseudo first-order and the pseudo second-order kinetic models were applied to the resulting data to better understand the adsorption kinetics. Figure 3.2 shows the Lagergren pseudo first-order model applied to both bifenthrin and permethrin and Figure 3.3 shows the pseudo second-order model applied to both datasets. Permethrin samples align better with the pseudo second-order model, as determined by the higher correlation coefficient. This suggests that permethrin adsorption to activated carbon occurs through chemical bonds between the permethrin molecules and the carbon surface. However, several researchers have agreed upon the idea that application of kinetic models alone cannot be used for prediction of adsorption mechanisms (Andrunik & Bajda, 2021). Bifenthrin samples align better with the pseudo first-order model, suggesting that adsorption is driven by the concentration of bifenthrin in the solution. Table 3-1 shows relevant parameters for the two kinetic models applied to permethrin and bifenthrin adsorption. The equilibrium rate constant ($k_1$) determined by the pseudo first-order model was an order of magnitude higher for permethrin than bifenthrin (0.326 L/hr compared to 0.0249 L/hr) as well as the equilibrium rate constant ($k_2$) determined by the pseudo second-order model (0.0204 g/mg·hr compared to 0.00424 g/mg·hr). The amount adsorbed at equilibrium ($q_e$) was also higher for permethrin across both models, which supports the results seen in Figure 3.1, depicting substantial permethrin adsorption and minimal bifenthrin adsorption over time.

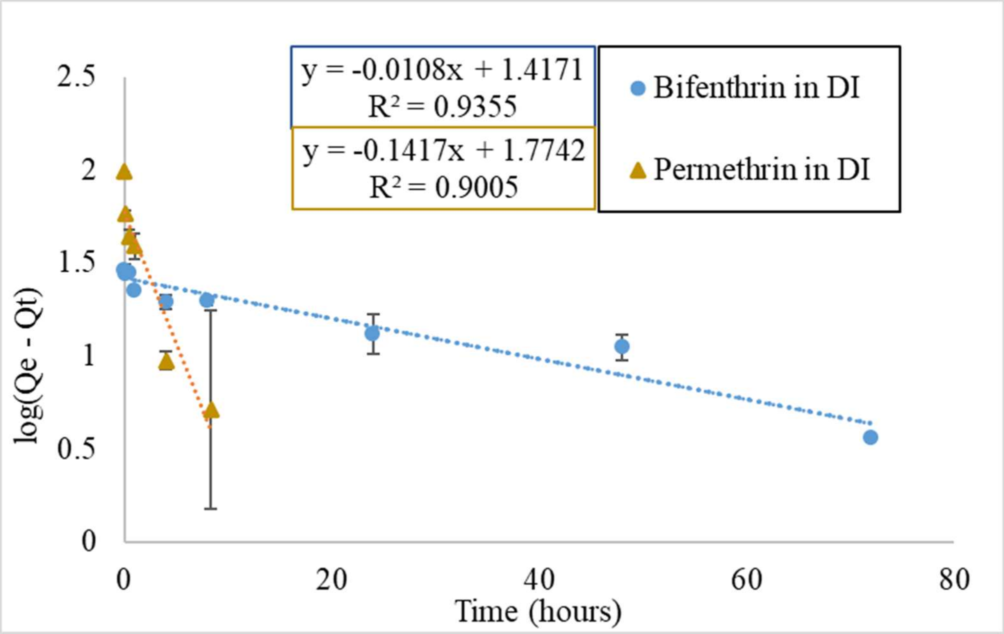


Figure 3.2: Lagergren pseudo first-order kinetic model for permethrin and bifenthrin in deionized (DI) water. Error bars represent one standard deviation for duplicate samples.

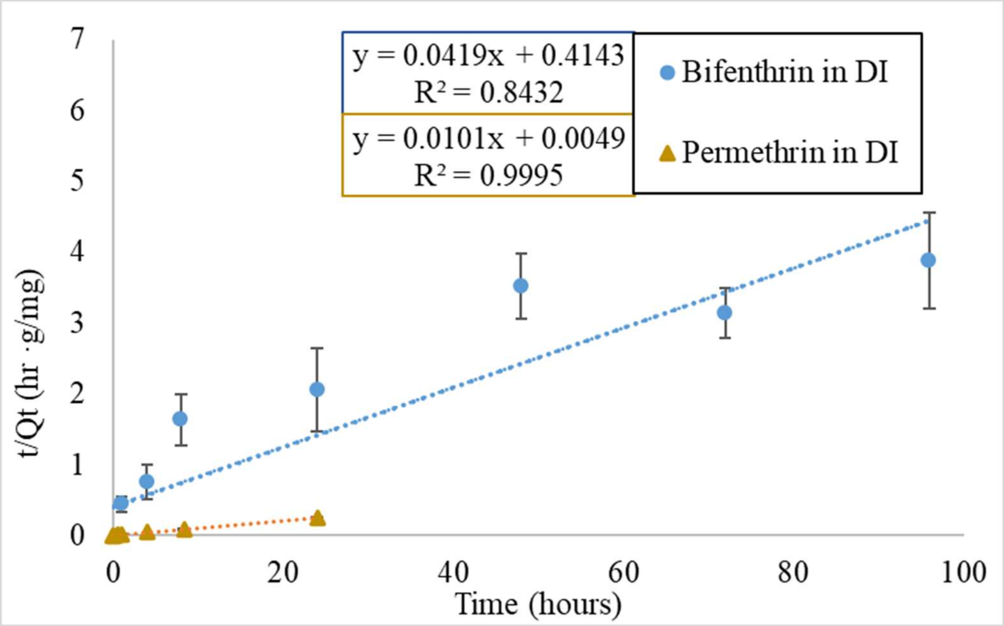


Figure 3.3: Pseudo second-order kinetic model for permethrin and bifenthrin in deionized (DI) water. Error bars represent one standard deviation for duplicate samples.

Table 3-1: Adsorption kinetic models and parameters for permethrin and bifenthrin in deionized (DI) water. Average values are shown as the average ± standard deviation.

| **Model and parameters** | **Permethrin** | | **Bifenthrin** | |
|---|---|---|---|---|
| | **set 1** | **set 2** | **set 1** | **set 2** |
| **Pseudo first-order** | | | | |
| $q_e$ (mg/g) | 66.8 | 55.9 | 25.3 | 26.5 |
| Avg $q_e$ (mg/g) | 59.5 ± 7.7 | | 26.1 ± 0.8 | |
| $k_1$ (L/hr) | 0.457 | 0.270 | 0.0235 | 0.0240 |
| Avg $k_1$ (L/hr) | 0.326 ± 0.132 | | 0.0249 ± 0.0003 | |
| $R^2$ | 0.980 | 0.777 | 0.815 | 0.923 |
| Avg $R^2$ | 0.901 ± 0.144 | | 0.936 ± 0.77 | |
| **Pseudo second-order** | | | | |
| $q_e$ (mg/g) | 102.0 | 96.2 | 26.1 | 21.6 |
| Avg $q_e$ (mg/g) | 99.0 ± 4.2 | | 23.9 ± 3.2 | |
| $k_2$ (g/mg·hr) | 0.0192 | 0.0225 | 0.00425 | 0.00420 |
| Avg $k_2$ (g/mg·hr) | 0.0204 ± .0024 | | 0.00424 ± 0.00004 | |
| $R^2$ | 0.999 | 1.000 | 0.851 | 0.827 |
| Avg $R^2$ | 1 ± 0.001 | | 0.843 ± 0.017 | |

### 3.3.2 Permethrin and Bifenthrin Adsorption Isotherms in DI water

Permethrin and bifenthrin samples containing activated carbon ranging from 10 – 50 mg (in 10 ± 0.1 mg increments) were all subjected to the determined equilibrium time of 24 hours and 96 hours, respectively. For every isotherm batch conducted, the positive controls were analyzed and used as the starting concentration to account for any potential losses through hydrolysis, photodegradation, or adsorption to container walls. Figure 3.4 shows the amount of pyrethroids detected in the solution (as a percentage of the starting concentration) as the activated carbon dosage in each sample increases. Permethrin adsorption follows a negative exponential trend, with concentrations decreasing to roughly 25% of their starting concentrations as the activated carbon dosage increases to 50 mg. Bifenthrin shows poor adsorption, with the lowest concentration detected when 30 mg of activated carbon was used, and then increasing concentrations were detected when more activated carbon was used. This coincides with the poor adsorption kinetics seen for bifenthrin leading up to 96 hours.

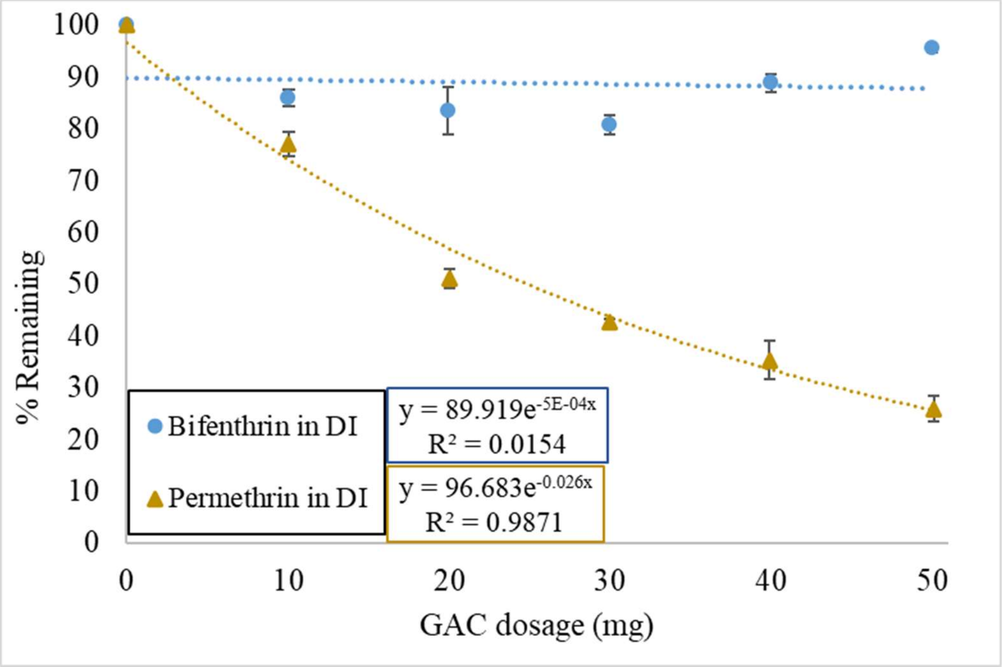


Figure 3.4: Effect of granular activated carbon (GAC) mass on permethrin (initial concentration 400 ppm) and bifenthrin (initial concentration 300 ppm) removal in deionized (DI) water. Error bars represent one standard deviation for duplicate samples.

Three adsorption isotherm models were applied to the resulting isotherm data: the Freundlich linear model and the Langmuir type I and type II linear models as seen in Figure 3.5, Figure 3.6, and Figure 3.7. Both permethrin and bifenthrin datasets best fit the Langmuir type II model, as determined by the higher correlation coefficients ($R^2$). This suggests that monolayer adsorption occurs over a homogenous adsorbent surface as opposed to the Freundlich model, which would suggest multi-layer adsorption over a heterogenous surface. Relevant parameters are shown in Table 3-2 for the three different models. The Langmuir energy constant ($K_L$) was higher for permethrin at 0.0104 L/g compared to -0.00441 L/g for bifenthrin, and the maximum adsorption capacity ($Q_m$) was determined to be 149 mg/g for permethrin and 0.822 mg/g for bifenthrin, coinciding with the adsorption seen in Figure 3.4. Although the bifenthrin adsorption capacity is quite low compared to permethrin, it is of a similar order of magnitude as previous research findings. Doningues et al. (2005) used Langmuir's model to determine a bifenthrin adsorption capacity of 0.294 mg/g to activated carbon and 0.260 mg/g to granulated cork. Bakka et al. (2020) obtained a higher bifenthrin adsorption capacity of 25.3 mg/g to treated patellidae shells. This may be due in part to using 99.9% bifenthrin for experiments as opposed to a proprietary industrial formula, as well as using a smaller adsorbent particle size of 50–100 µm.

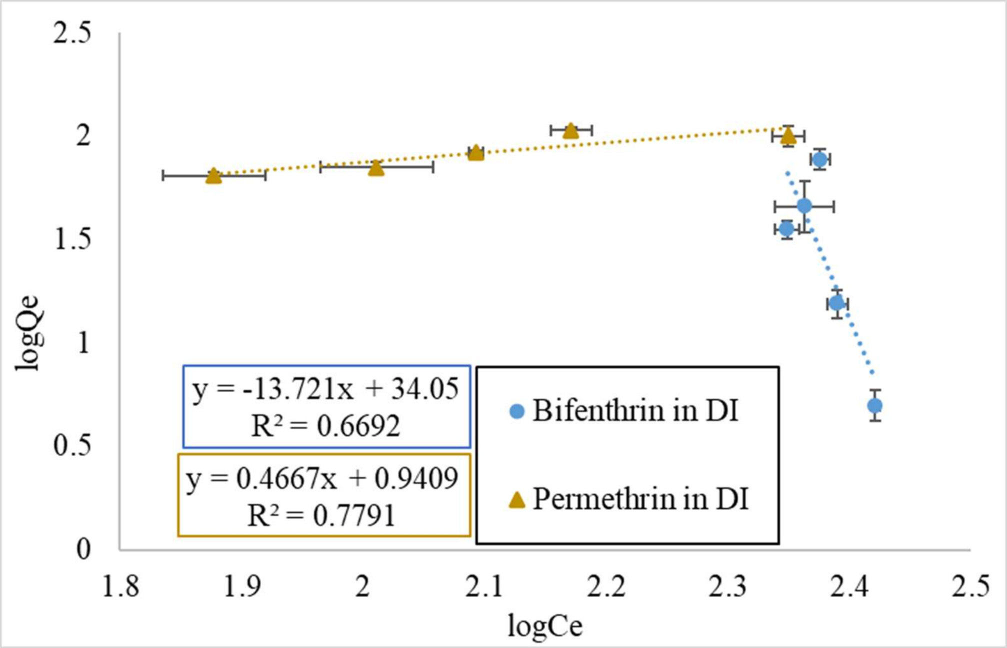


Figure 3.5: Freundlich isotherm model for permethrin and bifenthrin in deionized (DI) water.

Error bars represent one standard deviation for duplicate samples.

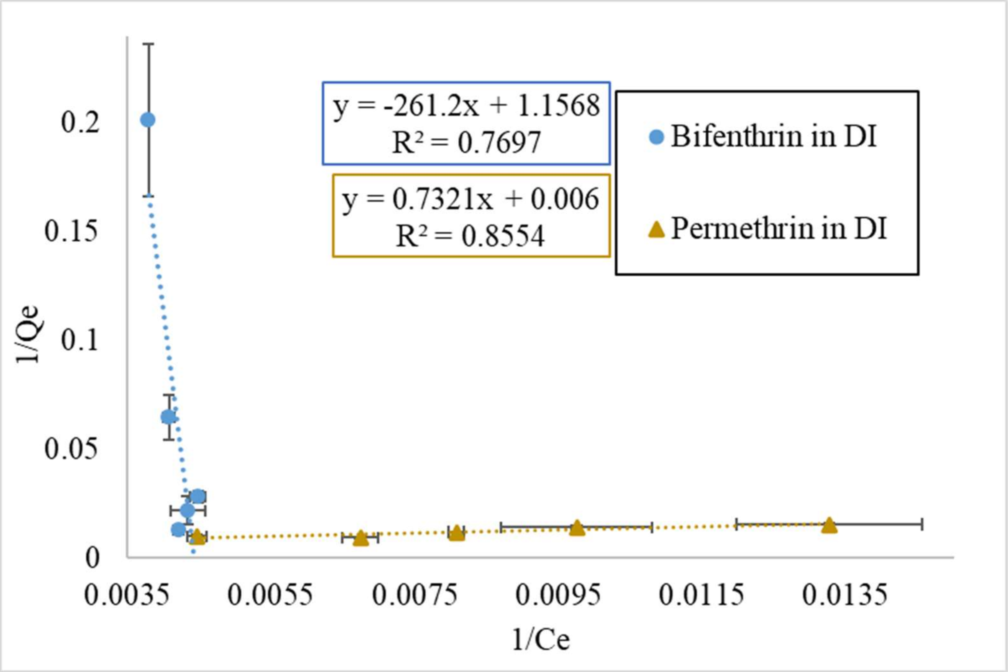


Figure 3.6: Langmuir type-I isotherm model for permethrin and bifenthrin in deionized (DI) water. Error bars represent one standard deviation for duplicate samples.

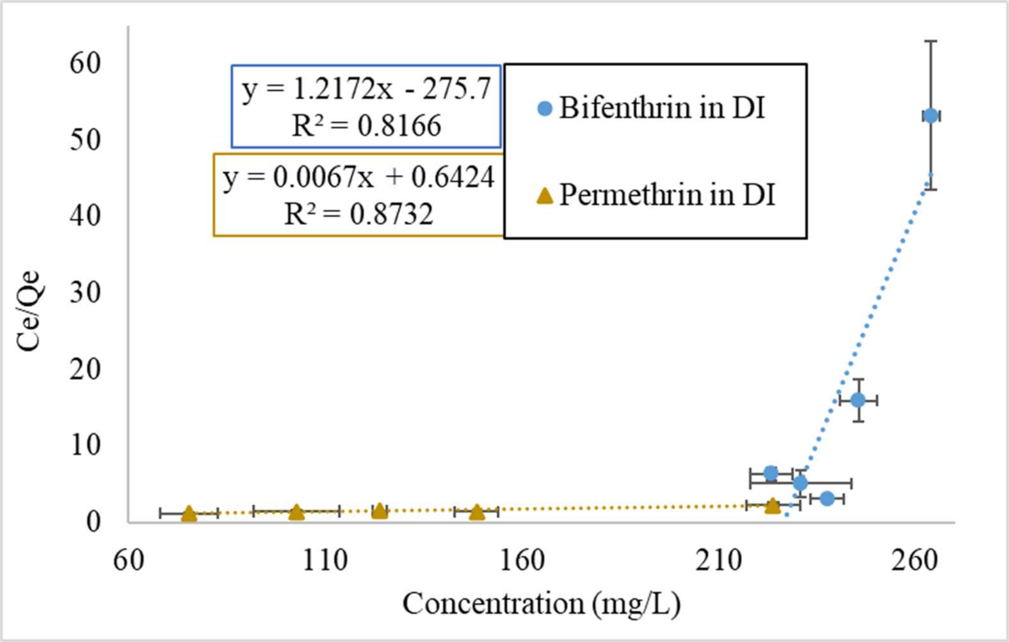


Figure 3.7: Langmuir type-II isotherm model for permethrin and bifenthrin in deionized (DI) water. Error bars represent one standard deviation for duplicate samples.

Table 3-2: Adsorption isotherm models and parameters for permethrin and bifenthrin in deionized (DI) water. Average values are shown as the average ± standard deviation.

| **Model and parameters** | **Permethrin** | | **Bifenthrin** | |
|---|---|---|---|---|
| | **set 1** | **set 2** | **set 1** | **set 2** |
| **Freundlich** | | | | |
| $K_F$ | 14.6 | 5.67 | 1.00E+30 | 2.03E+34 |
| Avg $K_F$ | 8.73 ± 6.32 | | 1.12E+34 ± 1.43E+34 | |
| 1/n | 0.355 | 0.561 | -12.0 | -13.8 |
| Avg 1/n | 0.467 ± 0.146 | | -13.7 ± 1.3 | |
| $R^2$ | 0.618 | 0.831 | 0.574 | 0.728 |
| Avg $R^2$ | 0.779 ± 0.151 | | 0.669 ± 0.109 | |
| **Langmuir type I** | | | | |
| $Q_m$ (mg/g) | 127 | 222 | 0.923 | 0.960 |
| Avg $Q_m$ (mg/g) | 167 ± 68 | | 0.864 ± 0.027 | |
| $K_L$ (L/g) | 0.0147 | 0.00507 | -0.00444 | -0.00448 |
| Avg $K_L$ (L/g) | 0.00820 ± 0.00682 | | -0.00443 ± 3.12E-05 | |
| $R^2$ | 0.667 | 0.902 | 0.606 | 0.825 |
| Avg $R^2$ | 0.855 ± 0.166 | | 0.77 ± 0.155 | |
| **Langmuir type II** | | | | |
| $Q_m$ (mg/g) | 120 | 185 | 0.836 | 0.923 |
| Avg $Q_m$ (mg/g) | 149 ± 45 | | 0.822 ± 0.062 | |
| $K_L$ (L/g) | 0.0170 | 0.00700 | -0.00440 | -0.00447 |
| Avg $K_L$ (L/g) | 0.0104 ± 0.0071 | | -0.00441 ± 4.59E-05 | |
| $R^2$ | 0.871 | 0.833 | 0.679 | 0.862 |
| Avg $R^2$ | 0.873 ± 0.027 | | 0.817 ± 0.129 | |

### 3.3.3 Effects of NPK and $SO_4$ on Permethrin Adsorption Kinetics

Permethrin was tested further in varying aqueous conditions made to represent different constituents of agricultural runoff water. In addition to DI water, adsorption kinetics were tested in water containing 200 mg/L of sulfate ($SO_4^{2-}$) and 10 mg/L of nitrogen, phosphorus, and potassium (NPK). As seen in Figure 3.8, adsorption kinetics follow similar logarithmic trends across all three water matrices, with adsorption in NPK being marginally lower. In previous studies, sulfate has been shown to adsorb to various types of activated carbon at varying capacities from 7.9–56.5 mg/g (Sadeghalvad et al., 2021). Urea was found to adsorb to activated carbon at a relatively low rate of 1.4 mg/g (Kameda et al., 2020) and potassium was found to adsorb to textured soils with at a rate of 0.33 mg/g (Kibreselassie et al., 2018). Phosphorus, however, was found to adsorb to peanut shell-derived biochar at a maximum rate of 150 mg/g (Liu et al., 2022). Therefore, the very slight decrease in permethrin adsorption in nutrient laden water may be attributed mostly to the presence of phosphorus.

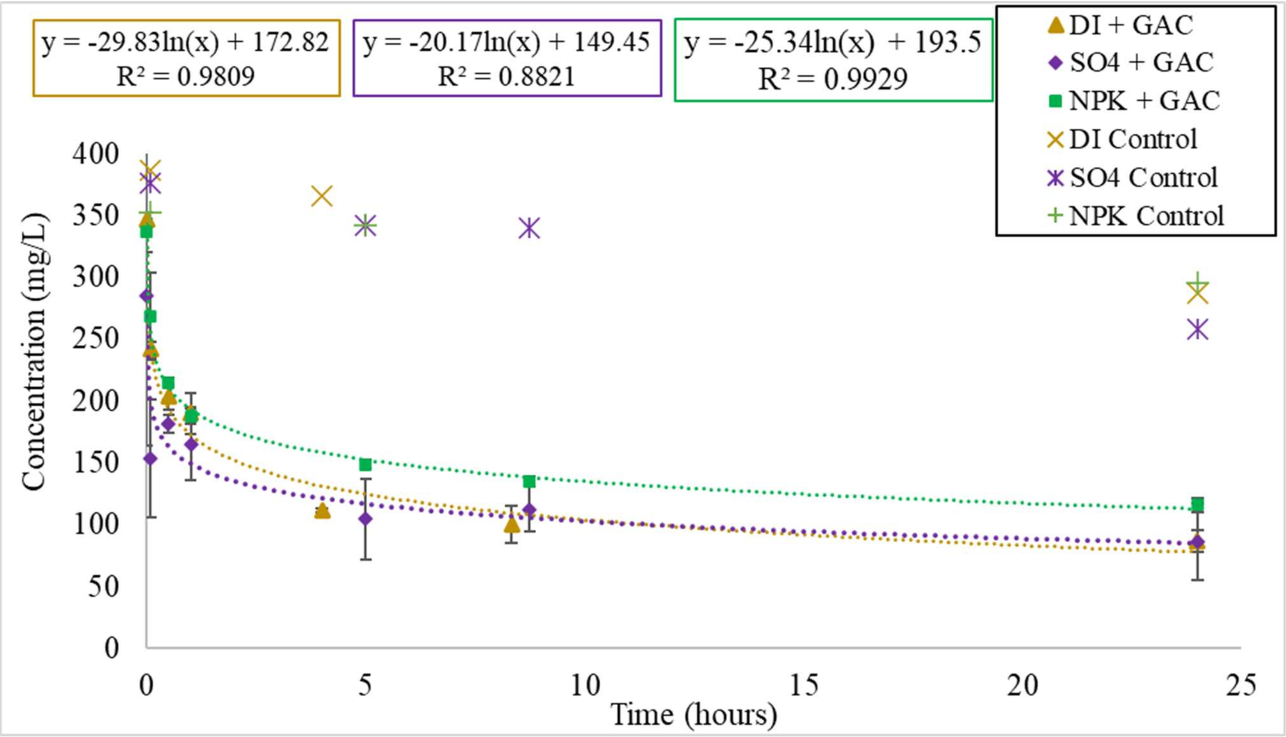


Figure 3.8: Removal of permethrin from varying aqueous conditions over time. Error bars represent one standard deviation for duplicate samples.

The Lagergren pseudo first-order and pseudo second-order kinetic models were applied to the resulting data for permethrin adsorption across three water matrices as seen in Figure 3.9 and Figure 3.10. Table 3-3 shows relative parameters for both kinetic models. The pseudo second-order model had the highest correlation coefficient ($R^2$) across all three aqueous conditions, which means chemisorption may predominate as the driving factor for permethrin adsorption to activated carbon (Andrunik & Bajda, 2021). The equilibrium rate constant ($k_2$) was of a similar magnitude across all water conditions ranging from 0.0240–0.0748 g/mg·hr. The determined equilibrium adsorbed amount ($q_e$) was of similar magnitude for all aqueous conditions but showed slightly higher adsorption in DI water at 96.2 mg/g and slightly lower adsorption in nutrient laden water at 70.4 mg/g.

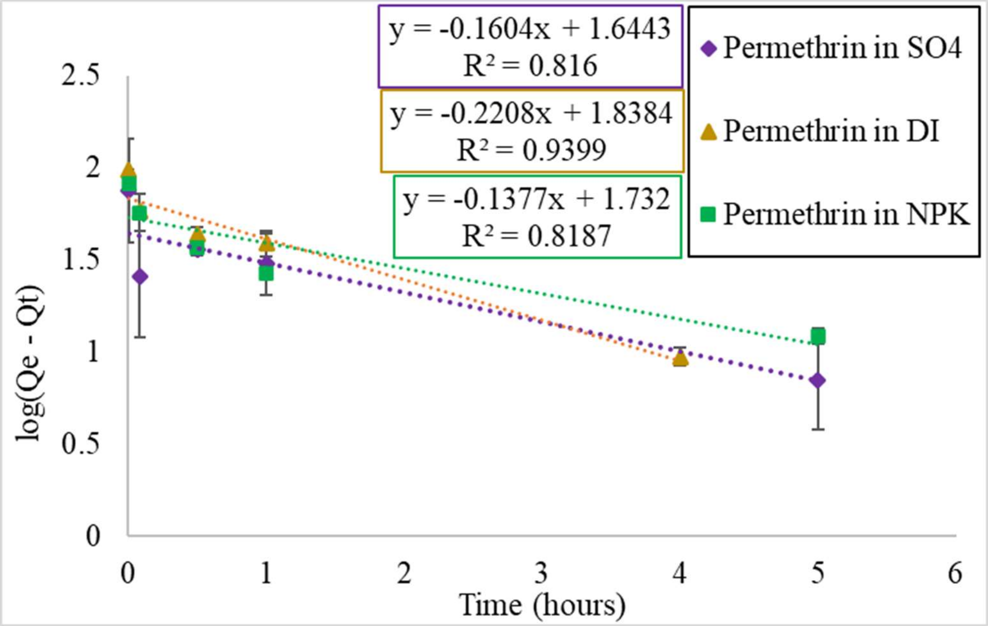


Figure 3.9: Lagergren pseudo first-order kinetic model for permethrin in varying aqueous conditions. Error bars represent one standard deviation for duplicate samples.

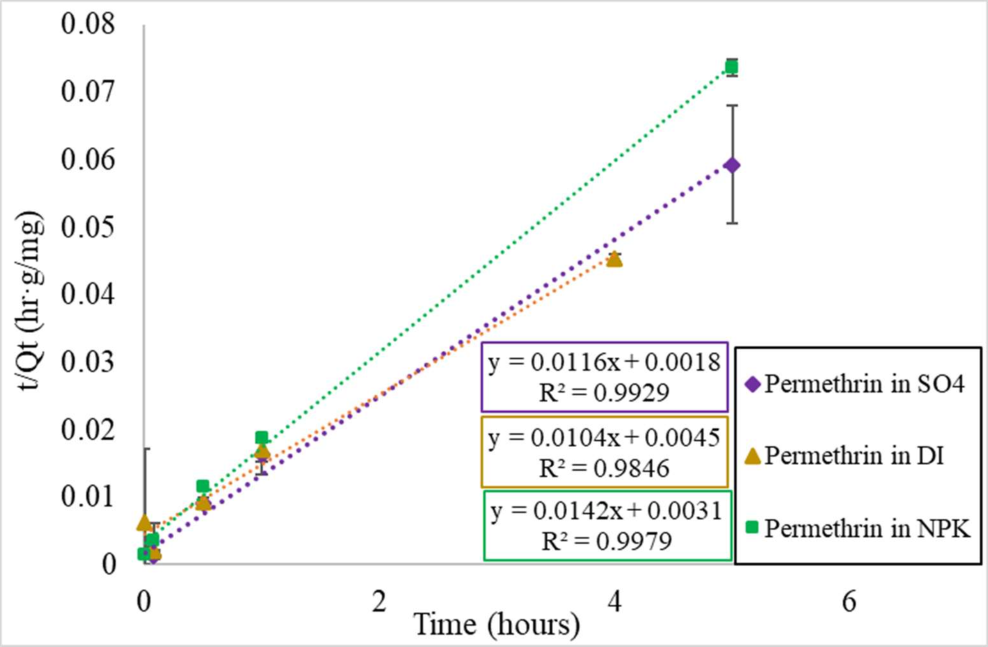


Figure 3.10: Pseudo second-order kinetic model for permethrin in varying aqueous conditions. Error bars represent one standard deviation for duplicate samples.

Table 3-3: Adsorption kinetic models and parameters for permethrin in varying aqueous conditions. Average values are shown as the average ± standard deviation.

| **Model and parameters** | **DI water** | | **SO4 water** | | **NPK water** | |
|---|---|---|---|---|---|---|
| | **set 1** | **set 2** | **set 1** | **set 2** | **set 1** | **set 2** |
| **Pseudo first-order** | | | | | | |
| $q_e$ (mg/g) | 68.3 | 69.3 | 41.0 | 38.3 | 51.4 | 56.1 |
| Avg $q_e$ (mg/g) | 68.9 ± 0.6 | | 44.1 ± 1.9 | | 54.0 ± 3.3 | |
| $k_1$ (L/hr) | 0.484 | 0.534 | 0.190 | 0.360 | 0.295 | 0.338 |
| Avg $K_1$ (L/hr) | 0.509 ± 0.036 | | 0.369 ± 0.121 | | 0.317 ± 0.030 | |
| $R^2$ | 0.920 | 0.948 | 0.963 | 0.508 | 0.760 | 0.850 |
| Avg $R^2$ | 0.940 ± 0.020 | | 0.816 ± 0.322 | | 0.819 ± 0.064 | |
| **Pseudo second-order** | | | | | | |
| $q_e$ (mg/g) | 82.6 | 98.0 | 76.9 | 95.2 | 68.5 | 72.5 |
| Avg qe (mg/g) | 96.2 ± 10.9 | | 86.2 ± 13.0 | | 70.4 ± 2.8 | |
| $k_2$ (g/mg·hr) | -0.488 | 0.0236 | 0.0889 | 0.0613 | 0.0969 | 0.0476 |
| Avg $k_2$ (g/mg·hr) | 0.0240 ± 0.362 | | 0.0748 ± 0.0196 | | 0.0650 ± 0.0349 | |
| $R^2$ | 0.918 | 0.988 | 0.993 | 0.992 | 0.996 | 0.997 |
| Avg $R^2$ | 0.985 ± 0.050 | | 0.993 ± 0.001 | | 0.998 ± 0.001 | |

### 3.3.4 Effects of NPK and $SO_4$ on Permethrin Adsorption Isotherms

Permethrin isotherm trials were also carried out in varying aqueous conditions simulating agricultural runoff water. Figure 3-11 shows the amount of permethrin remaining in the solution as the GAC dosages increase. Across all three different water matrices, adsorption follows a negative exponential trend with very similar values for each water matrix. Due to duplicate samples from different aqueous conditions overlapping the range of one another, it can be said that the presence of sulfate or fertilizer nutrients does not substantially affect adsorption. An analysis of covariance test was conducted to determine if the linear regression plotted from each water matrix was significantly different from one another. The lines were not significantly different from one another (*p*=0.84), further confirming that adsorption is not significantly affected by the presence of nutrients or sulfate ions.

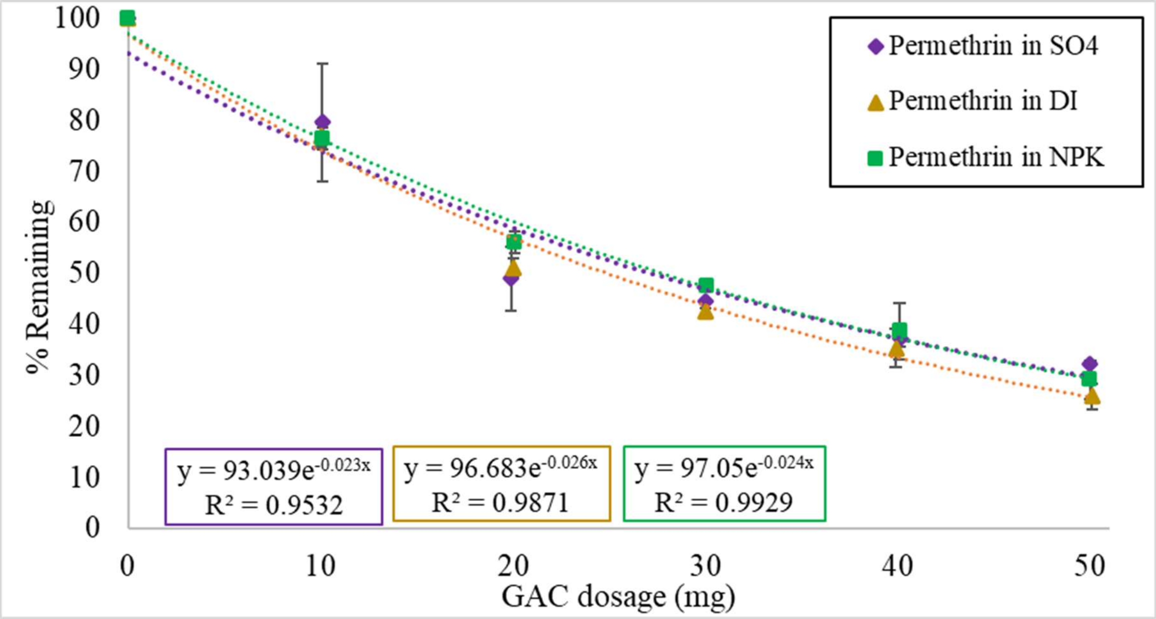


Figure 3.11: Effects of granular activated carbon (GAC) mass on permethrin (initial concentration 400 ppm) removal in varying aqueous conditions. Error bars represent one standard deviation for duplicate samples.

The Freundlich linear isotherm model and Langmuir type I and type II isotherm models were applied to the permethrin isotherm data across three different water matrices as seen in Figure 3.12, Figure 3.13, and Figure 3.14. Relative parameters for the three isotherm models can be found in Table 3-4. For adsorption in DI water and sulfate water, the Langmuir type II isotherm had the highest correlation coefficient ($R^2$). This once again suggests that monolayer adsorption occurs over a homogenous activated carbon surface. However, for permethrin adsorption in nutrient laden water, the Freundlich isotherm model had the highest correlation coefficient. This may suggest multilayer adsorption occurred over a heterogenous surface, although the Freundlich isotherm is empirical and does not make any strict assumptions on adsorption (Andrunik & Bajda, 2021). This may be due to adsorption of nitrogen, phosphorus, and potassium onto the surface of the activated carbon giving the surface a heterogenous consistency. For both Langmuir models across all three water matrices, the maximum adsorption capacity ($Q_m$) was of the same order of magnitude, ranging from 119 to 196 mg/g. The adsorption capacity of permethrin is higher than the adsorption capacity of deltamethrin to activated carbon of 89 mg/g (Ettish et al., 2022). Permethrin and deltamethrin share a very similar molecular structure, but permethrin is slightly smaller with a lower molecular mass (391 g/mol compared to 505 g/mol), which possibly explains the higher adsorption capacity.

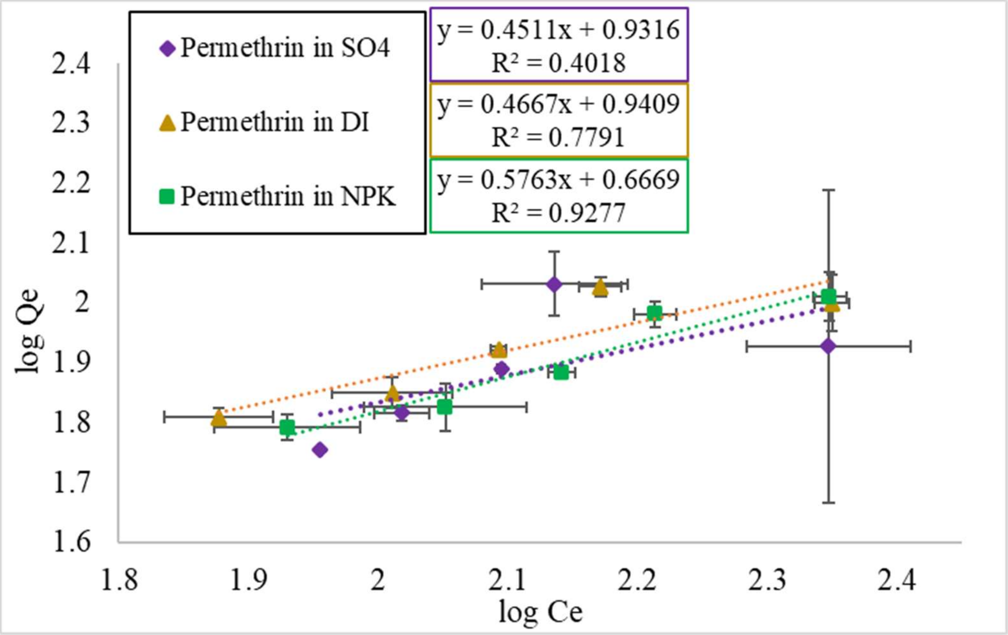


Figure 3.12: Freundlich isotherm model for permethrin in varying aqueous conditions. Error bars represent one standard deviation for duplicate samples.

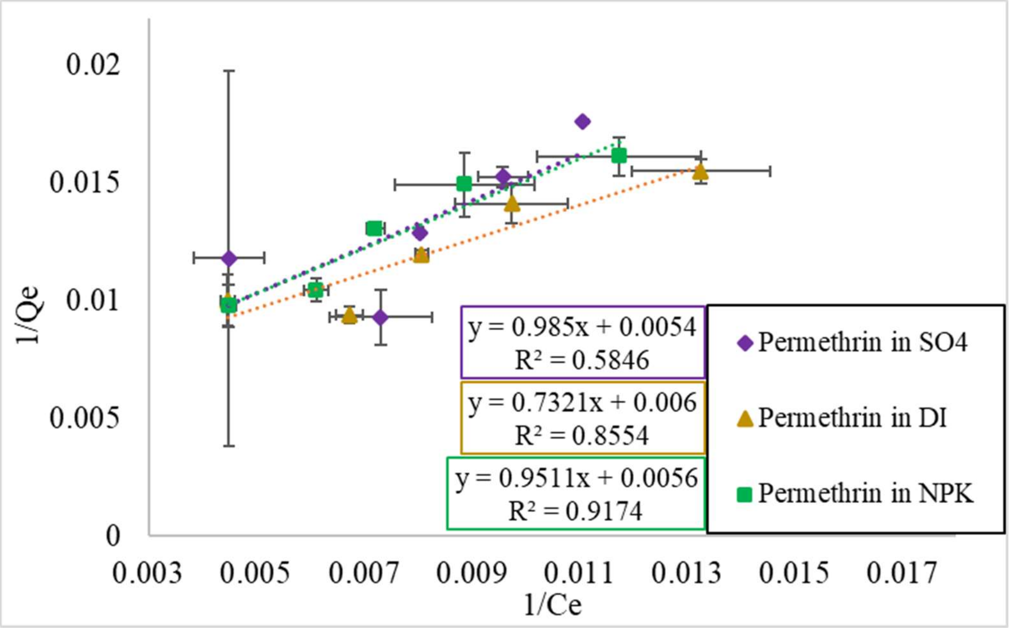


Figure 3.13: Langmuir type-I isotherm model for permethrin in varying aqueous conditions. Error bars represent one standard deviation for duplicate samples.

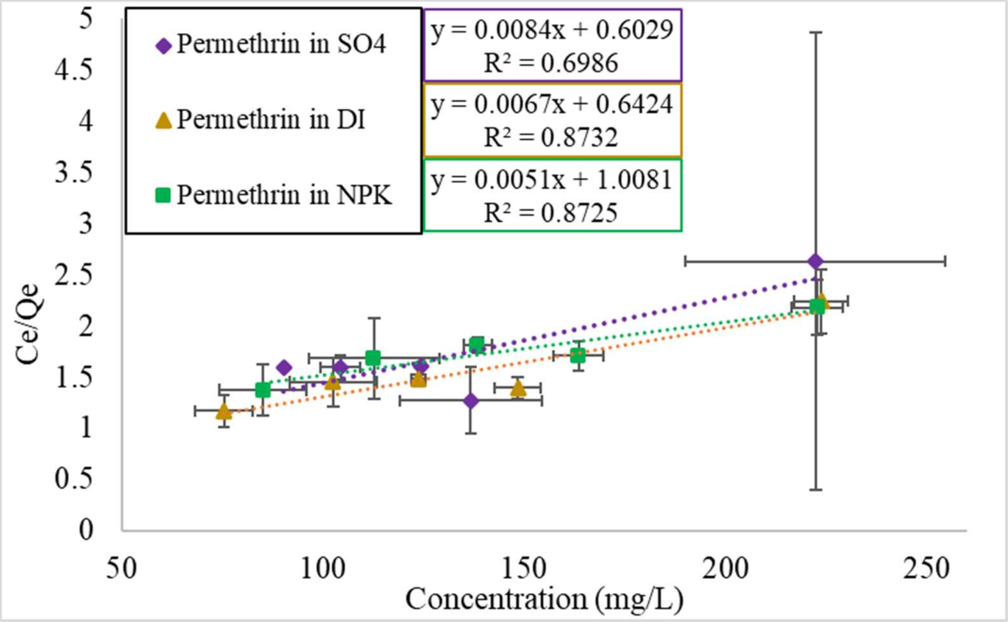


Figure 3.14: Langmuir type-II isotherm model for permethrin in varying aqueous conditions. Error bars represent one standard deviation for duplicate samples.

Table 3-4: Adsorption isotherm models and parameters for permethrin in varying aqueous conditions. Average values are shown as the average ± standard deviation.

| **Model and parameters** | **DI water** | | **SO4 water** | | **NPK water** | |
|---|---|---|---|---|---|---|
| | **set 1** | **set 2** | **set 1** | **set 2** | **set 1** | **set 2** |
| **Freundlich** | | | | | | |
| $K_F$ | 14.6 | 5.67 | 0.900 | 228 | 6.86 | 3.68 |
| Avg $K_F$ | 8.73 ± 6.3 | | 8.54 ± 161 | | 4.64 ± 2.25 | |
| 1/n | 0.355 | 0.561 | 0.927 | -0.243 | 0.507 | 0.613 |
| Avg 1/n | 0.467 ± 0.146 | | 0.451 ± 0.828 | | 0.576 ± 0.075 | |
| $R^2$ | 0.618 | 0.831 | 0.983 | 0.0790 | 0.963 | 0.752 |
| Avg $R^2$ | 0.779 ± 0.151 | | 0.402 ± 0.639 | | 0.923 ± 0.149 | |
| **Langmuir type I** | | | | | | |
| $Q_m$ (mg/g) | 127 | 222 | 2000 | 55.9 | 154 | 204 |
| Avg $Q_m$ (mg/g) | 167 ± 68 | | 185 ± 1370 | | 179 ± 36 | |
| $K_L$ (L/g) | 0.0147 | 0.00507 | 0.000332 | -0.0471 | 0.00876 | 0.00427 |
| Avg $K_L$ (L/g) | 0.00820 ± 0.0068 | | 0.00548 ± 0.660 | | 0.00589 ± 0.00318 | |
| $R^2$ | 0.667 | 0.902 | 0.984 | 0.0510 | 0.933 | 0.786 |
| Avg $R^2$ | 0.855 ± 0.166 | | 0.585 ± 0.660 | | 0.917 ± 0.104 | |
| **Langmuir type II** | | | | | | |
| $Q_m$ (mg/g) | 120 | 185 | 1000 | 42.9 | 182 | 192 |
| Avg $Q_m$ (mg/g) | 149 ± 46 | | 119 ± 677 | | 196 ± 7 | |
| $K_L$ (L/g) | 0.0170 | 0.00700 | 0.000687 | -0.0216 | 0.00638 | 0.00471 |
| Avg $K_L$ (L/g) | 0.0104 ± 0.0071 | | 0.139 ± 0.02 | | 0.00506 ± 0.00118 | |
| $R^2$ | 0.871 | 0.833 | 0.348 | 0.888 | 0.922 | 0.617 |
| Avg $R^2$ | 0.873 ± 0.027 | | 0.699 ± 0.382 | | 0.873 ± 0.216 | |

### 3.3.5 SEM Imaging and EDS Elemental Analysis

#### 3.3.5.1 DSR-C Reactivated Carbon

Scanning electron microscopy (SEM) was used to generate high resolution images of the DSR-C reactivated carbon surface before it was used in adsorption experiments. When viewing the activated carbon granules at a micron scale, micropores and differences in the surface morphology become apparent. Two types of activated carbon granules can be seen in Figure 3.15: some sheared granules with flat surfaces towards the left, and some jagged granules with irregular surfaces towards the right. This difference in morphology between granules was likely caused during the preparation stages, when the mortar and pestle were used to crush larger particles to isolate a smaller size range. The blunt force of the pestle striking a granule of activated carbon may have caused it to split along a smooth surface, resulting in some sheared grains. The jagged grains likely were already at their respective sizes as prepared by Calgon Carbon.

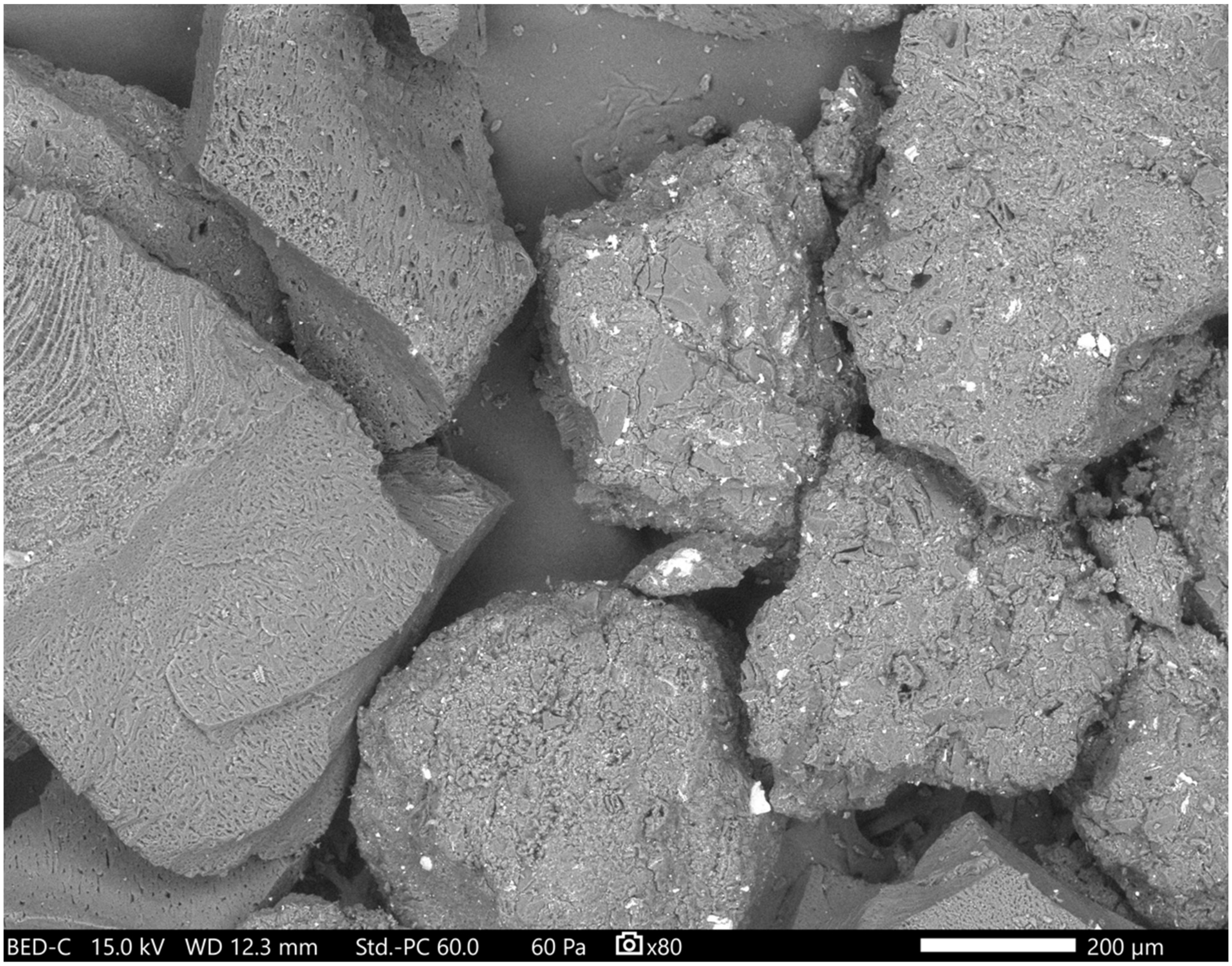
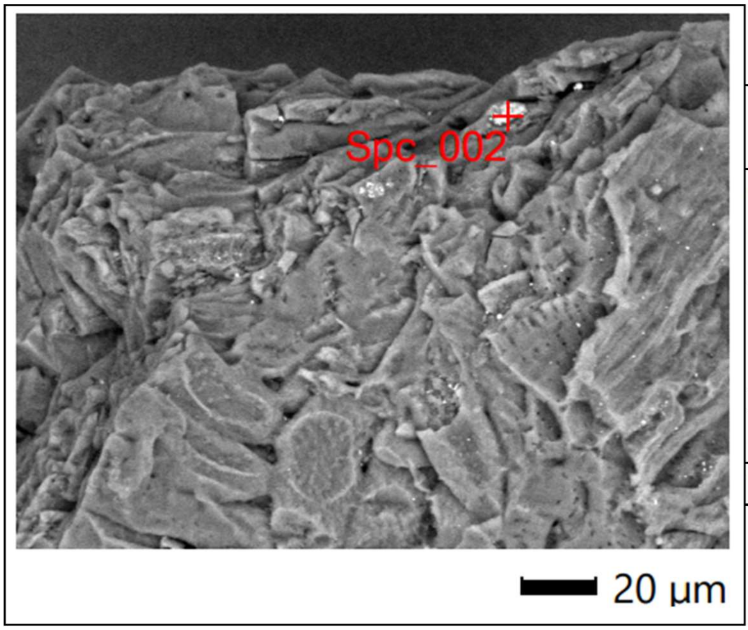


Figure 3.15: SEM image of DSR-C reactivated carbon granules used in this experiment

An energy-dispersive x-ray spectroscopy (EDS) scan was performed to determine the elemental composition of an activated carbon granule before it was used in adsorption experiments. Three scans were done on the same granule of activated carbon. In addition to carbon and oxygen, the sample contained some impurities such as Al, Si, S, and K. This may be due to the activated carbon being previously used and regenerated by Calgon Carbon. Figure 3.16 shows an elemental scan of an activated carbon granule. The elemental composition varied slightly between analysis scans, and in the second analysis silicon was the third most present element detected at 1.77 wt%.

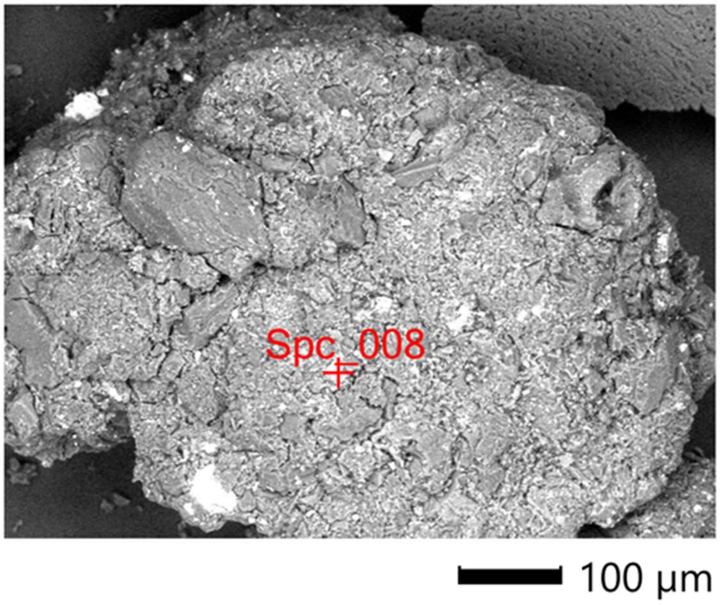


| Element | Mass % | | |
|---|---|---|---|
| | Scan 1 | Scan 2 | Scan3 |
| C | 87.69 | 82.08 | 89.12 |
| O | 11.86 | 15.29 | 9.53 |
| Al | 0.13 | 0.09 | nd |
| Si | nd | 1.77 | 0.15 |
| S | 0.32 | 0.31 | 0.29 |
| K | nd | 0.45 | 0.45 |
| Cu | nd | nd | 0.9 |
| Total | 100.00 | 100.00 | 100.00 |

Figure 3.16: EDS elemental scan of an activated carbon granule pre-permethrin adsorption.

### 3.3.5.2 Activated Carbon Post Permethrin Adsorption in Nutrient Laden Water

SEM-EDS analysis was performed on an activated carbon granule after it was used for adsorbing permethrin in nutrient laden water. Many impurities can be seen on the surface of this granule in the form of white specks. These may signify mineralization of feldspar ($KAlSi_3O_8$, $NaAlSi_3O_8$, $CaAl_2Si_2O_8$) or quartz ($SiO_2$) which are the two most common minerals in Earth's crust. This corresponds with the percentage of elements detected in the first scan of Figure 3.17, where aluminum and silicon were the two most detected elements besides carbon and oxygen. Furthermore, nitrogen, phosphorus, and potassium were also detected, corresponding with the fertilizer nutrients added to the aqueous solution used for the experiment. The elemental composition detected varied between scans due to different points on the granule creating slightly different elemental peaks. The chlorine detected on the surface corresponds to permethrin adsorption, since chlorine is a significant component of the permethrin molecule besides carbon, hydrogen, and oxygen. Although nitrogen, phosphorus, and potassium were detected on the surface of the activated carbon, they were present in small concentrations compared to other trace elements detected such as aluminum, silicon, calcium, iron, sodium, and copper. The miniscule presence of fertilizer nutrients compared to other impurities already present in the activated carbon explains why they did not have a substantial impact on permethrin adsorption.

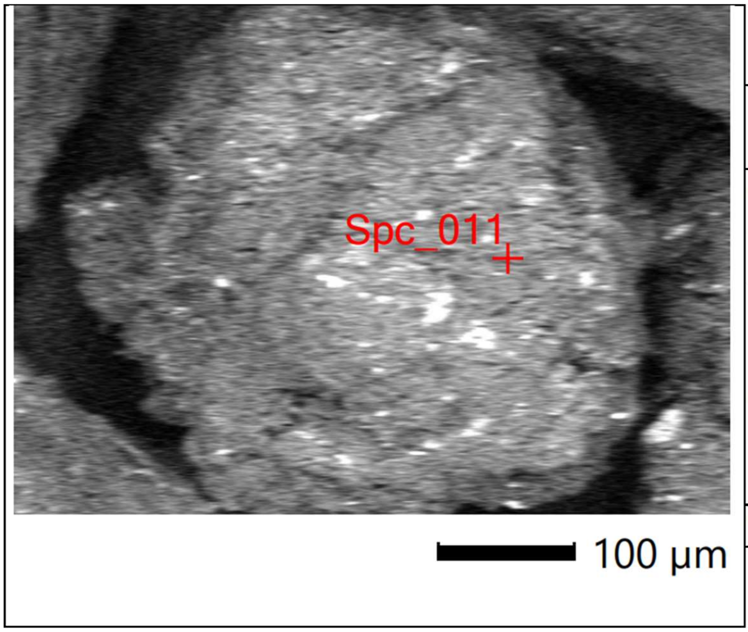


| Element | Mass % | | |
|---|---|---|---|
| | Scan 1 | Scan 2 | Scan 3 |
| C | 68.45 | 83.94 | 82.81 |
| N | 1.07 | nd | nd |
| O | 12.72 | 13.65 | 14.27 |
| Na | 0.41 | nd | nd |
| Al | 3.71 | 1.35 | 1.31 |
| Si | 4.59 | nd | nd |
| P | 0.04 | 0.1 | 0.09 |
| S | 0.32 | nd | 0.67 |
| CI | 0.57 | 0.87 | 0.66 |
| K | 3.53 | 0.09 | 0.019 |
| Ca | 1.66 | nd | nd |
| Fe | 1.49 | nd | nd |
| Cu | 1.44 | nd | nd |
| Total | 100 | 100 | 100 |

Figure 3.17: EDS elemental scan of an activated carbon granule post-permethrin adsorption in nutrient laden water

#### 3.3.5.3 Activated Carbon Post Permethrin Adsorption in Sulfate Laden Water

SEM-EDS analysis was also performed on an activated carbon sample after being used for adsorbing permethrin from sulfate laden water. As seen in Figure 3.18, this granule contained less trace metals than the granule previously analyzed, but it still contained silicon, aluminum, calcium, and copper. More sulfur was detected across all three scans in this granule than the sulfur amounts seen in the pre-adsorption & NPK granules. This corresponds to the sulfate added to the aqueous matrix the activated carbon reacted in. Similar amounts of chlorine were detected in the $SO_4^{2-}$ granule as in the NPK granule, corresponding to the similar permethrin adsorption rates seen in both different water matrices. The second EDS scan performed on this granule detected 25 wt% calcium, which is much higher than detected on any other EDS scan. This may originate from the previous life cycle of the reactivated carbon and a tiny pocket of calcification was picked up on this scan.



| Element | Mass % | | |
|---|---|---|---|
| | Scan 1 | Scan 2 | Scan3 |
| C | 88.01 | 59.28 | 81.76 |
| O | 9.41 | 10.81 | 14.19 |
| Al | 0.48 | 0.55 | 0.62 |
| Si | 0.40 | 0.56 | 0.47 |
| S | 0.79 | 0.55 | 0.87 |
| Cl | 0.54 | 0.56 | 1.54 |
| Ca | 0.37 | 25.33 | 0.54 |
| Cu | nd | 2.36 | nd |
| Total | 100 | 100 | 100 |

Figure 3.18: EDS elemental scan of an activated carbon granule post-permethrin adsorption in sulfate laden water

### 3.4 Conclusions

When comparing permethrin adsorption to bifenthrin adsorption in DI water, there was considerably greater permethrin adsorption. This is demonstrated by the higher equilibrium capacity of 59.5 mg/g for permethrin compared to 26.1 mg/g for bifenthrin determined by the pseudo first-order kinetic model, and 99.0 mg/g for permethrin compared to 23.9 mg/g for bifenthrin determined by the pseudo second-order kinetic model. Isotherm data was best represented by the Langmuir type-II isotherm model, which determined a substantially higher adsorption capacity of 149 mg/g for permethrin compared to 0.822 mg/g for bifenthrin. The poor adsorption potential for bifenthrin may be due to proprietary ingredients in the formula of Ike’s

Pest Control, which may be specifically designed to reduce sorption and allow the solution to be effective in the environment longer.

When comparing permethrin adsorption kinetics across three different water matrices consisting of DI water, sulfate laden water, and nutrient laden water, all datasets best aligned with the pseudo-second order kinetic model. This suggests that chemical bonding is the driving factor for permethrin adsorption to activated carbon. Similar equilibrium rate constants and equilibrium capacities across all three batches suggests that the presence of sulfate or nutrients in the water matrix does not impact permethrin adsorption kinetics. An investigation of adsorption isotherms across all three water matrices produced similar negative exponential trends for permethrin detection. Duplicate samples from each batch overlapped the range of duplicate samples from the other batches, further suggesting that the presence of sulfate or nutrients does not substantially affect adsorption.

SEM-EDS analysis of activated carbon granules before being used for this experiment detected many impurities and trace metals in the sample. This is due to the activated carbon being previously used and regenerated. After being used for permethrin adsorption in nutrient water and sulfate water, fertilizer nutrients and sulfur were detected in the activated carbon granules. However, their presence was small compared to the other trace elements already on the activated carbon surface. This explains why there was no substantial difference in permethrin adsorption after sulfate and nutrients were introduced into the reaction.

## Chapter 4 – Implications and Recommendations for Future Work

Pyrethroid insecticides are widely used in agricultural settings to get rid of unwanted pests. Bifenthrin and permethrin were the two most used pyrethroids in California in 2021, with 426,000 and 203,000 lbs applied, respectively (CDPR, 2021). When studying the adsorption potential of Durvet permethrin to DSR-C reactivated carbon, promising results were found with an adsorption capacity of 155 ± 39 mg/g within 24 hours of reaction time. Ike's Total Pest Control (7.9% bifenthrin as only active ingredient) did not adsorb well, with a much lower capacity of 0.822 mg/g after 96 hours of reaction time. Permethrin adsorption experiments were carried out across varying water conditions designed to replicate realistic agricultural runoff, and no substantial change in adsorption rate or capacity was observed. SEM-EDS analysis was carried out on the activated carbon before and after permethrin adsorption to observe differences in the elemental composition. The number of impurities and trace metals already present in the activated carbon before use outweighed the mass percentage of sulfate or fertilizer nutrients that were added to simulate agricultural runoff, explaining why there was little impact on adsorption capacity when tests were carried out in different water conditions.

Due to the high adsorption capacity of Durvet permethrin across varying agricultural runoff conditions, activated carbon adsorption would be an effective runoff treatment process for reducing permethrin concentrations. If applying Ike's Total Pest Control (7.9% Bifenthrin) to an agricultural site, activated carbon adsorption with DSR-C would not be an effective treatment process for reducing bifenthrin concentration. This is most likely due to the proprietary formula containing ingredients designed to prevent sorption, since bifenthrin was previously determined to adsorb to calcium carbonate with a capacity of 41 mg/g (Bakka et al., 2020). Bakka et al.

carried out experiments using analytical grade bifenthrin (99% purity) which explains why a higher adsorption capacity was achieved.

Future studies could test other industrial grade pesticides containing bifenthrin for its adsorption capacity and compare all brands to one another. This information could help consumers choose the more adsorbable bifenthrin brand if they are planning to use activated carbon adsorption to treat runoff water leaving their site. Alternatively, more research could be done to find other pyrethroids with similar effectiveness to bifenthrin and carry out adsorption experiments on those. If it turns out those industrial stocks display much greater adsorption while only slightly compromising performance as an insecticide, they could be considered as a more environmentally friendly alternative to bifenthrin altogether.

The extraction process for pyrethroid samples could potentially be optimized further. Due to access to limited resources, liquid-liquid extractions in this study were all carried out at room temperature (23 ± 1 °C). If another researcher were to have access to a temperature-controlled laboratory, or different rooms such as a walk-in fridge as low as 5 ºC or a sauna as high as 80 ºC, then the ideal temperature for extractions could be tested and perhaps result in a better recovery than at room temperature (77-85%). Additionally, an ideal salting agent could be tested for extractions. In this study, only sodium chloride was used. However, dozens of other salting agents for liquid-liquid extractions have been determined and compared (Hyde et al., 2017). The chemical properties of each salt could be investigated along with the chemical properties of the target pyrethroid to narrow down the list down to the best possible options for an experimental comparison.

Pyrethroid adsorption could also be tested further by simulating the performance of a filtration barrier to be installed in a drainage system. Rapid small-scale column testing could help determine the effective contact time for sufficient pyrethroid removal from water, leading to construction of a barrier to be installed in the field. Pyrethroid solutions could then be made to the manufacturer suggested ratios and applied to storm drains before being collected downstream for analysis. This would result in a comprehensive analysis for pyrethroid adsorption, considering both the proprietary industrial stock recipes and the uncertainty of real storm drain systems.

Additionally, various feedstocks and pyrolysis temperatures for the creation of activated carbon could be tested to determine which specific feedstocks result in the best pyrethroid adsorption rates, like the study conducted by Pochampally et al. (2023). This approach could help individual agricultural sites choose the best feedstock from their available biowaste for creation of their own activated carbon to use for runoff treatment.

Natural Organic Matter (NOM) is another constituent of agricultural runoff water and is a larger molecule than fertilizer nutrients or sulfate. Therefore, adsorption experiments could be conducted in the presence of varying types of NOM to assess the potential interference of NOM on adsorption rate and capacity for various pyrethroid insecticides.

The crushing and sieving process resulted in some activated carbon granules that were sheared with smooth surfaces, and some that had jagged irregular surfaces. This adds irregularities to the activated carbon batch due to the difference in granule type. In a future study, the granules could be separated by surface type and adsorption experiments could then be performed on the different granule types. It is possible that a certain type of surface is better at adsorbing certain types of pyrethroids.

Desorption studies could also be conducted using activated carbon that has already been fully saturated with pyrethroids. Once the activated carbon in a storm drain filter becomes fully saturated, it is possible that pyrethroids will leach out of the activated carbon and begin to re-contaminate the water that is leaving the treatment barrier. Thus it is important to understand the rate of desorption to help determine the time constraints for replacing an activated carbon filter once it reaches maximum capacity.

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Bachelor of Science in Earth and Environmental Science

## Skills

AutoCAD Civil 3D, BlueBeam Revu, Microsoft Office, GC-EDC, UV-vis spectrophotometry, LISST, experimental research, technical report & grant writing, bilingual (English and Spanish)

## Work Experience

### Engineer I | AtkinsRealis | Las Vegas, NV | June 2023 - Present

- Assisted with design of site plans using AutoCAD Civil 3D and BlueBeam Revu
- Prepared cost estimates and cost book exhibits
- Prepared air quality and storm water pollution prevention exhibits

### Graduate Research Assistant | University of Nevada, Las Vegas | Aug 2021 – June 2023

- Led a multidisciplinary research project focusing on the efficiency of carbon-based adsorbents for removing volatile organic contaminants from groundwater
- Experiment design, SOP writing, chemical handling, sample preparation and analysis
- Prepared charts, reports, presentations, and funding and travel applications

### Bartender | Big Easy Daiquiris | New Orleans, LA | Dec 2020 – Aug 2021

- Rotated through 10 bar/daquiri shops in the French Quarter as lead bartender
- Learned various batch daquiri recipes & liquor pairings
- Developed new upselling techniques and led team in sales, trained new team members

**Bartender | WoW Café | New Orleans, LA | Dec 2018 – Mar 2020**

- Served 100+ people per day in a fast-paced environment as an upscale mixologist
- Filled in as server when needed
- Nightly restocking, cleanup, inventory check, balancing cash drawer, and lockup

**Research Assistant | University of New Orleans | Jan 2018 – Dec 2018**

- Worked in lab analyzing grain size distribution and organic content of sediment samples
- Used Laser in Situ Scattering Transmissometer, settling tubes, Mastersizer 3000, and LOI
- Quantified data, prepared charts, and presented research

## Conference Presentations

- “The fate of fine grain sediments in backbarrier basins: processes driving sediment trajectories.” - Innovate UNO 2018 (New Orleans, LA)
- “Evaluation of feedstock and Pyrolysis temperature on Biochar production for TCE and PCE removal in water” - Waste Management Symposia 2022 (Phoenix, AZ)
- “Evaluation of feedstock and Pyrolysis temperature on Biochar production for TCE and PCE removal in water” - American Chemical Society Fall 2022: Sustainability in a Changing World (Chicago, IL)
- “Leaching Kinetics of Trichloroethylene from Walnut Biochar” - Nevada Water Resources Association 2023 (Reno, NV)
- “Leaching Kinetics of Trichloroethylene from Walnut Biochar” - Waste Management Symposia 2023 (Phoenix, AZ)
- “Leaching Kinetics of Trichloroethylene from Walnut Biochar” - American Water Works Association Spring 2023 (San Diego, CA)
- “Removal of Pyrethroid Insecticides from Runoff Water using Activated Carbon” - UNLV 25th Annual Graduate & Professional Student Research Forum (Las Vegas, NV)
- “Removal of Pyrethroid Insecticides from Runoff Water using Activated Carbon” - American Chemical Society Fall 2023: Harnessing the Power of Data (San Francisco, CA)
- “Removal of Pyrethroid Insecticides from Runoff Water using Activated Carbon” - UNLV 26th Annual Graduate & Professional Student Research Forum (Las Vegas, NV)