

**REMOVAL OF SELECTED PHARMACEUTICAL COMPOUNDS FROM  
AQUEOUS MEDIA USING GRANULAR ACTIVATED CARBON(GAC) FILTER**



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A thesis submitted to Bahria University, Islamabad in partial fulfillment of the requirements  
for the degree of B.S in Environmental Science.

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## **DEDICATION**

We dedicate this research to our parents, siblings, and everyone who loved and supported us during this time. We appreciate their help and encouragement. We also want to thank our teachers for their support, collaboration, and guidance throughout our research.

## ABSTRACT

Pharmaceutical compounds, including the non-steroidal anti-inflammatory drugs (NSAIDs) diclofenac and ibuprofen, are increasingly detected in water bodies globally, raising serious concerns about their ecological and public health impacts. Because conventional wastewater treatment systems are largely ineffective at removing these persistent micropollutants, low-cost decentralized alternatives are urgently required. This study designed and evaluated a simple, gravity-driven granular activated carbon (GAC) fixed-bed adsorption column for the removal of diclofenac and ibuprofen from synthetic aqueous solutions. The column was constructed from a plastic syringe packed with sequential layers of cotton, gravel and sand. Stock solutions of 1000 mg/L were prepared and diluted to working concentrations of 5 mg/L, 25 mg/L, and 50 mg/L. The effects of initial concentration, solution pH, contact time, and water matrix (distilled versus tap water) on removal efficiency were systematically investigated using UV-Visible spectrophotometry. The GAC column achieved a maximum removal efficiency of 97.1% for diclofenac at 50 mg/L in distilled water. For both target compounds, removal efficiency scaled positively with higher initial concentrations and extended contact times. Adsorption was highly pH-dependent; both compounds exhibited preferential removal under acidic conditions below their respective  $pK_a$  values, where the molecules exist in an uncharged form that favors hydrophobic interaction with the carbon matrix. Conversely, tap water trials demonstrated a decline in performance due to competitive adsorption from co-existing dissolved matrix substances. Comparatively, diclofenac consistently outperformed ibuprofen across all experimental configurations due to its higher hydrophobicity and stronger interactions with the activated carbon surface. Ultimately, these findings contribute directly to SDG 3 and SDG 6 by demonstrating the technical feasibility of an electricity-free, low-cost approach to emerging contaminant remediation.

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## LIST OF ABBREVIATIONS

|        |                                                        |
|--------|--------------------------------------------------------|
| DCF    | Diclofenac                                             |
| IBU    | Ibuprofen                                              |
| GAC    | Granular Activated Carbon                              |
| UV     | Ultraviolet                                            |
| AMR    | Antimicrobial Resistance                               |
| API    | Active Pharmaceutical Ingredient                       |
| pH     | Potential of Hydrogen                                  |
| SDG    | Sustainable Development Goal                           |
| WHO    | World Health Organization                              |
| WWTP   | Wastewater Treatment Plant                             |
| OECD   | Organization For Economic Co-operation and Development |
| NSAIDs | Non-Steroidal Anti-Inflammatory Drugs                  |

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# CHAPTER 1

## INTRODUCTION

### 1.1 Background of Pharmaceutical Contaminants in Wastewater

In the recent decades the Emerging contaminants (ECs) are a major global environmental problem and is threatening to change the core principles of sanitary and environmental engineering. Emerging contaminants are synthetic or naturally occurring chemicals which include industrial additives, microplastic and pharmaceutical ingredients (APIs) that are not routinely monitored or regulated under traditional environment protection regulations but have the unique ability to enter ecological web and cause a substantial ecological or public health risk.

There are various classes are ECs, pharmaceutical and specially the non-steroidal anti-inflammatory drugs (NSAIDS) are one of the most troublesome classes of ECs. In recent years, these compounds have been found in effluent wastewater from municipal wastewater treatment plants, surface water, irrigation water, and even finished drinking water treatment systems all over the world (Aus der Beek et al., 2016). Drugs like ibuprofen (IBU) or diclofenac (DCF) are widely used in the world, with thousands of tons consumed globally every year to meet the need for these medications to treat the health needs of a growing and ageing human population. They are prevalent in the environment because they are readily available over the counter, are highly prescribed, and are poorly metabolized in the body.

The human body does not mineralize or destroy the active molecule completely when it is taken in a therapeutic dose as an NSAID. Rather, large amounts of biologically active compounds are eliminated into municipal sewerage systems every day because of the unique metabolic processes and pharmacokinetics in humans. They are administered to wastewater collection systems in their parent chemical form or as active metabolites of parent chemicals (conjugated) and are easily de-conjugated to the parent chemicals in sewers (Ebele et al., 2017).

These micropollutants originate from human consumption or hospital use and are directly excreted into municipal sewer systems in the path to the water quality of the Great Lakes. The compounds are then transported to conventional municipal Wastewater Treatment Plants (WWTPs). These

facilities are not equipped to capture the polar molecules, and the trace contaminants completely pass through the system into receiving waters, where they can be widely dispersed.

The major point of entry for these micropollutants to natural ecosystems is continuous discharge of effluents from the conventional municipal Wastewater Treatment Plant (WWTP). The conventional wastewater treatment systems that are in use worldwide are all designed to remove those macro-pollutants, COD, BOD, TSS and macronutrients like nitrogen and phosphorus. They cannot measure POMPs in the environment, which in the natural environment occur in trace amounts (nanograms to micrograms per liter) on a fundamental level (Luo et al., 2014).

Ibuprofen is moderately to highly bio transformed during secondary biological treatment phases because of microbial degradation in the aeration tank; but because it is continuously and heavily loaded into the sewer system, it is considered a "pseudo-persistent" pollutant, that is, its rate of input into the environment outstrips its rate of natural degradation. In contrast, diclofenac has a very stable chlorinated aromatic structure which is highly resistant to conventional activated sludge biotransformation, often found in the secondary clarifier in almost unchanged form (Vieno & Sillanpää, 2014).

Chronic exposure to IBU and DCF in receiving waters is a significant chronic environmental issue and health risk. Since these molecules are specifically designed to cause biological reactions at very low dose levels within defined mammalian bodies, the accumulation in aquatic trophic webs results in acute and chronic ecotoxicity in non-target aquatic organisms (Acuña et al., 2015). There is an immediate engineering need for low cost decentralized and highly efficient tertiary treatment technologies that are capable of effectively polishing pharmaceutical micropollutants from wastewater flows before discharge to the environment to protect downstream communities, as well as to reduce public health risks (Sophia & Lima, 2018).

## **1.2 Diclofenac and Ibuprofen as Emerging Contaminants**

Diclofenac and ibuprofen are a well-documented, problematic class of pharmaceutical contaminants because they are continuously released, persistent in the environment, and have well known ecological impacts. Emerging" doesn't necessarily mean that these chemical compounds are just new entities, but they are both already decades-old cornerstones of international pharmacology. It does not, however, mean that they are new to the environment, but rather that

only recently has scientific awareness, analytical detection methodologies (including high-performance liquid chromatography with mass spectrometry) and regulatory understanding of their presence in the environment and sub-lethal exposures over long periods of time come to maturity (Lonappan et al., 2016).

Diclofenac has received a great deal of attention worldwide because of its toxicity to aquatic life and its lack of natural degradation. Ibuprofen is relatively more degradable under optimum conditions but continues to be a persistent problem because of its constant and continuous entering municipal drainage. Both drugs are very chemically stable and have highly aromatic cores that do not seem to be strongly susceptible to normal engineering microbial biodegradation. The physical and chemical characteristics of these focused NSAIDs are key factors in their environmental transportation, behavior and efficacy. Diclofenac is 2-[2-(2,6-dichloroanilino) phenyl] acetic acid, whose molecular formula is  $C_{14}H_{11}Cl_2NO_2$  and its molecular weight is 296.15 g/mol. It has low water solubility of 2.37mg/L at 25C and the value of the dissociation constant ( $pK_a$ ) is 4.15. The octanol-water partition coefficient ( $\log K_{ow}$ ) value is 4.51, meaning it has moderate to high hydrophobicity, and thus favors partition to organic phases, binding to organic sediments, and bioaccumulation in fatty tissues.

On the other hand, ibuprofen, which is chemically known as 2-(4-isobutylphenyl) propanoic acid, has a lower molecular weight of 206.28 g/mol and a molecular formula of  $C_{13}H_{18}O_2$ . The structural layout makes ibuprofen much more soluble in water compared to diclofenac with a value of 21 mg/L. It is moderately hydrophobic, with a  $\log K_{ow}$  value of 3.97 and  $pK_a$  value of 4.91. Both compounds have  $pK_a$  values less than 5.0, meaning that they are predominantly present in their deprotonated, negatively charged ionic form (carboxylate anions) at neutral pH (usually 7.0 - 8.0), typical of municipal wastewater and natural waters. This ionization phenomenon has significant consequences for their mobility in water, as it promotes their solubility and electrostatic repulsion from naturally occurring negative sediment particles, allowing them to travel great distances when in rivers and aquifers. Moreover, due to their ionization behavior the adsorption mechanisms onto carbon surface would correspond to the adsorption mechanisms occurring in the water phase, which require the overcoming of the repulsive forces between the anionic pollutant and any negative surface charges on the carbon adsorbent for high removal efficiencies.

### 1.3 National and International Water Quality Standards

A detailed overview of global water quality standards shows an enormous gap in regulatory approaches to APIs at system level. This is an extreme balance between proactive international science of environment protection and the socioeconomic and industrial facts affecting local effluent monitoring in the developing world (Tomczyk, 2024). The main guidelines are internationally the Guidelines for Drinking-water Quality (GDWQ) of the World Health Organization (WHO). Based on historical screening assessment, the concentrations of pharmaceuticals in public drinking water supplies from surface water are generally  $< 0.1 \mu\text{g/L}$  and finished drinking water are generally  $< 0.05 \mu\text{g/L}$ , and no formal and strict guideline values are recommended by the WHO for these concentrations at present. This screening framework, however, has a theoretical weakness, as it assumes that the risk to human health is low, using the traditional toxicology approach; yet, the long-term chronic toxicity, sub-lethal cellular effects, and the synergistic mixture interactions of multi-compound pharmaceutical cocktails are only poorly known and should not be underestimated (Praskova et al., 2014; Welch et al., 2024).

While comparing with this baseline, Pakistan has a huge gap in its domestic regulatory framework. The modern domestic regulation is based on WHO guidelines for basic microbial safety and is managed and enforced by the Pakistan Environmental Protection Agency (Pak-EPA) under the umbrella of National Environmental Quality Standards (NEQS) but is entirely lacking in discharge limits or maximum allowable levels of recalcitrant pharmaceutical contaminants such as diclofenac and ibuprofen (Qureshi et al., 2021). The current Pak-NEQS is structurally limited to traditional pollutants such as macro pollutants (pH, temperature, turbidity, TDS, COD and BOD) and traditional heavy metals (cadmium, lead, iron, chromium, nickel, manganese, copper and zinc). This regulatory focus raises a compounding environmental danger: some of the trace metals are in safe levels in some specific aquifers, but the critical heavy metals routinely exceed safe limits in urban Pakistani aquifers. Pharmaceuticals that are not regulated can flow into a water system without any oversight, and this guarantees that these trace organic compounds can pile up in the water system without being monitored.

The Environmental Quality Standards (EU EQS) established by the Water Framework Directive (EU WFD) are much lower than the WHO screening thresholds and Pak-NEQS gaps and emphasize long-term ecological safety and prevention of bioaccumulation (Penserini et al., 2026). According to this directive, diclofenac is a high priority substance (watch list) because of its

persistence and ecotoxicity (Russo et al., 2023). The Scientific Committee on Health, Environmental and Emerging Risks (SCHEER) has set an Annual Average (AA) EQS of 0.04 µg/L for freshwater systems, 0.004 µg/L for marine environments and a safety limit against secondary poisoning in higher trophic levels at 0.0054 µg/L, with recent precautionary recommendations for an exceptionally low threshold of 5 ng/L (0.005 µg/L) for vulnerable groundwater ecosystems. The EU sets an annual freshwater average EQS of 0.14 µg/L, marine limits of 0.014-0.022 µg/L and a secondary poisoning threshold limited to 0.064 µg/L for ibuprofen.

Therefore, defining these international parameters raises a strong technical need for developing countries to move their environmental policies from simple engineering measures to more sophisticated ones that can effectively and consistently reduce new chemical contaminants.

### **1.3.1 Environmental impacts: Global and National challenges**

NSAIDs are a significant macro environmental problem associated with persistent addition into water systems, leading to habitat degradation and global water security issues. These active pharmaceutical ingredients (APIs) are molecularly engineered to trigger a biological response at very low concentration and therefore can cause significant, non-target, ecotoxicological effects on a variety of levels in natural lifelines (Fu et al., 2020).

### **1.3.2 Biological and Ecosystem Risks**

The chronic exposure to DCF and IBU results in general oxidative stress on cellular and biochemical level in aquatic organisms (Gradinariu et al., 2025; Li et al., 2023). This exposure causes the degeneration of cell membrane lipid peroxidation (LPO) and causes significant damage to the important antioxidant defense enzyme including glutathione S-transferase (GST) and superoxide dismutase (SOD). They have been shown to induce various kinds of DNA strand breaks in erythrocytes of fish and combinations of several drugs have been found to be particularly genotoxic with additive or synergistic effects (Acuña et al., 2015; Parolini, 2016). In addition to genotoxic effects, these chemical residues are strong endocrine disruptors in teleost that have been shown to produce changes in gonadal development in both ovarian and testicular tissue as well as disrupt prostaglandin mediated osmoregulatory functions.

The negative impacts cascade down to the bottom of aquatic food chains, where key microcrustaceans such as *Daphnia magna* are more likely to die, and have significantly reduced

reproductive capacity when exposed to chronic low-level exposures (Elías et al., 2025; Hernández-Zamora, 2025). The environmental consequences of the spill go well beyond the waters, too. This was linked to the almost complete disappearance and drastic reduction in the population of Asian vultures (*Gyps bengalensis*) from the subcontinent because of acute renal failure (Oaks et al., 2004) from the consumption of livestock carcasses containing trace amounts of the drug diclofenac and was therefore designated as Endangered in the country. Historically linked with the almost extirpation and catastrophic decline in the Asian vulture (*Gyps bengalensis*) population in the country with respect to their death from acute renal failure due to consuming carcass of domestic livestock containing trace residues of diclofenac, it is now classified as threatened species in the country.

In natural systems these compounds are typically not present as a single compound. The simultaneous presence in the surface waters also results in an increased Integrated Biomarker Response (IBR) index, which equates to a much higher total biological damage from the combined effect of a complex chemical matrix rather than the individual effects. The condition is chronic, multi-trophic and directly affects the United Nations SDGs; Goal 3 (Good Health and Wellbeing) and Goal 6 (Clean Water and Sanitation).

### **1.3.3 The Localized Crisis in Pakistan**

These environmental conditions are an extremely serious eco-toxicological threat in the rapidly growing urbanized and densely populated environments of Pakistan as compared to developed countries. This regional crisis is due to the combination of high population density, easy availability of pharmaceuticals over the counter, inadequate implementation of industrial pre-treatment codes, and the lack of adequate structural wastewater infrastructure in municipalities (Khan et al., 2018). In big cities like Karachi, Lahore, and Islamabad, the municipal sewage, untreated hospital waste, and industrial process water are released directly into open urban channels, natural waterways, and main river basins without any form of treatment (secondary or tertiary) (Hanif et al., 2020).

Thus, Pakistan's surface waters contain some of the highest concentrations of NSAIDs in the world. Targeted monitoring campaigns conducted have been able to quantify high and hazardous levels of ibuprofen as high as 1,673 µg/L and diclofenac as high as 836 µg/L directly within industrial outfalls, receiving soils, and municipal drainage collectors (Khan et al., 2018). The

parent compound and active photolytic transformation products of diclofenac continue to be detected as part of vital, highly stressed hydrogeological networks such as rivers of the Lyari and Malir in Sindh and the rivers of the Kabul and Indus in the north (Khan et al., 2018).

These polluted surface waters are frequently diverted for irrigation of local farms and shallow groundwater wells used by nearby rural communities are hydrologically connected to these contaminated rivers, creating an unmonitored pathway of exposure for bioaccumulation in the food chain and contamination of domestic drinking water supplies.

#### **1.3.4 Global Contamination Profile**

Although the contamination in Pakistan is extreme and localized, the contamination profile for these two drugs worldwide establishes that contamination of medicines is a reality in the environment, worldwide. These trace organic contaminants have been tracked in the environment globally by using advanced monitoring networks and detected in natural waters in over 70 countries at concentrations between 0.6 and 15,085 ng/L in the case of DCF and 30 and 17,400 ng/L in the case of IBU (Hernandez-Tenorio et al., 2023). However, at the generating point the peaks are far significant – in the world up to 27.20 µg/L of DCF and up to 28 µg of IBU concentration were measured in direct effluents of industrial manufacture and in raw effluents of municipality. A ratio of the Measured Environmental Concentration (MEC) to the Predicted No-Effect Concentration (PNEC) is known as a Risk Quotient (RQ):

$$RQ = \frac{MEC}{PNEC}$$

The calculated (RQ) values vary from low risk ( $RQ > 1$ ) in moderately impacted surface water to exceptionally high environmental risk ( $RQ > 67.992$ ) raw wastewater streams for diclofenac. These are very high-risk quotients that highlight the lack of wastewater treatment facilities in the world and thus, the need for more sophisticated engineering controls that can effectively remove these recalcitrant micropollutants from wastewater prior to discharge to the environment.

#### **1.4 limitations of conventional wastewater treatment methods**

Basic municipal wastewater treatment plants (WWTPs) are designed chiefly to remove easily degradable organic carbon, suspended solids and bulk macronutrients like nitrogen and phosphorous. The most widespread biological treatment standard in the world is the conventional

activated sludge (CAS) system which relies almost exclusively on biological degradation in the aeration basin and physical separation by gravity in a secondary clarifier. This traditional configuration is very efficient in lowering bulk parameters but suffers from significant operation deficiencies in the case of trace organic micropollutant removal.

### **1.5 The Effluent Conundrum: Mechanics of Systemic Bypassing**

Elevated levels of chemical oxygen demand (COD), total suspended solids (TSS) and trace active pharmaceutical ingredients (APIs) are present in influent wastewater streams and are treated in the typical primary and secondary treatment processes. This setup achieves good bulk organic stabilization and can retain settleable solids, but the secondary effluent has low COD, and turbidity yet is very high in micro-contaminants such as ibuprofen and diclofenac that are persistent in the environment.

The conventional secondary clarifiers are unable to remove non-biodegraded molecules in the water column, so the polar pharmaceuticals are not changed in any way. To eliminate reliably these trace organic compounds, and to produce a clean effluent which meets the very low ecotoxicological thresholds established internationally, a dedicated tertiary treatment step is required downstream of the biological loop; an adsorption bed with granular activated carbon (GAC) is suitable for this purpose and is able to selectively bind the remaining micropollutants prior to final discharge.

### **1.6 Chemical and Biological Barriers to Micropollutant Removal**

The systematic failure of conventional activated sludge systems to extract persistent, trace-level pharmaceutical residues stems from three distinct chemical and biological barriers:

#### **1.7 Molecular Resistance and Recalcitrance**

The materials used to produce active pharmaceutical ingredients are intentionally designed to be resistant to extreme biochemical conditions and enzymes found in the human body. The molecules contain complex aromatic rings, highly branched aliphatic chains and halogenated functional groups (chlorine atoms in diclofenac), which give them great chemical stability. These same structural characteristics protect them from breakdown by heterotrophic bacteria in the wastewater aeration tanks.

### **1.8 Low Phase Partitioning ( $K_d$ )**

Because many non-steroidal anti-inflammatory drugs (NSAIDs) are highly polar and possess low octanol-water partition coefficients ( $\log K_{ow}$ ) at ambient wastewater pH, they remain completely dissolved in the aqueous phase. Consequently, they evade standard primary sedimentation and exhibit a very low solid-water distribution coefficient ( $K_d$ ), failing to readily adsorb onto routine biological sludge matrices or floc particles.

### **1.9 Sub-Threshold Concentrations for Enzyme Induction**

The ambient concentration of these micropollutants within raw influent typically ranges from the low nanogram-per-liter to microgram-per-liter scale. This concentration is frequently several orders of magnitude below the thermodynamic and kinetic thresholds required to trigger the expression of specific metabolic or co-metabolic enzymes within the mixed liquor microbial community, effectively preventing targeted biodegradation.

### **1.10 Operational Unreliability and the Mandate for Tertiary Controls**

Because of these interlinked barriers, pharmaceutical removal efficiencies in conventional treatment plants remain highly erratic, unreliable, and site-dependent, frequently fluctuating between less than 20% to over 80%. Diclofenac due to its stable chlorinated structure and resistance to microbial breakdown, routinely bypasses biological clarifiers entirely unaltered (Vieno & Sillanpää, 2014).

This systematic breakdown of conventional environmental infrastructure creates an urgent technical mandate: robust, efficient tertiary purification systems must be developed. Crucially, there is a pressing engineering need for decentralized, scalable tertiary adsorption controls that can be easily added onto or integrated into existing, compromised treatment setups. This is especially vital in resource-limited settings where centralized, advanced wastewater infrastructure is either structurally degraded or entirely missing, leaving local water security highly vulnerable.

### **1.11 Adsorption as an Effective Treatment Method**

Adsorptive removal of waterborne organic micropollutants (OMPs) is well known to be a highly effective method. The process is the deposition of pollutants on the surface of solid adsorbent. Some of the unique features of this physicochemical process are the ability to effectively remove

a broad spectrum of contaminants, no harmful by-products, ease of operation and maintenance, lower cost compared to advanced oxidation processes and the ability to operate in batch and continuous modes. There are multiple mechanisms by which pharmaceutical compounds such as diclofenac and ibuprofen can be adsorbed, and they can occur simultaneously or in sequence. The weak intermolecular interactions between the pharmaceutical and the surface (van der Waals forces) are also important, and hydrophobic interactions are the partitioning of non-polar compounds to hydrophobic surfaces, which is relevant because these NSAIDs are moderately hydrophobic.  $\pi$ - $\pi$  interactions are electron stacking between the aromatic rings of pharmaceuticals and adsorbent surface, which is relevant because both diclofenac and ibuprofen contain aromatic rings. The solution pH is an important operational parameter that can be optimized for electrostatic attraction or repulsion, depending on pH and surface charge, and improve the removal efficiency. Granular Activated Carbon (GAC) is the most used of various adsorbents because it has the largest surface area of any activated carbon, ranging from 500 to 1500 m<sup>2</sup>/g, which has many sites for contaminants to attach. The porous structure of GAC has micro, mesa and macropores to capture a wide range of molecular sizes while the affinity for organic compounds is high enough to effectively remove pharmaceutical contaminants. GAC is easily available and inexpensive when compared to several other types of adsorbents and is an appropriate material for fixed-bed column applications. GAC is readily available and cost-effective compared to many alternative adsorbents, and its suitability for fixed-bed column applications makes it ideal for continuous treatment systems. The versatility and proven performance of GAC make it the adsorbent of choice for many water treatment applications, including the removal of emerging organic contaminants.

### **1.12 Column-Based Adsorption Systems**

In practical applications, adsorption is often carried out using fixed-bed column systems rather than batch processes. In a column system, contaminated water flows continuously through a packed bed of adsorbent material, providing a more realistic representation of industrial water treatment operations. Column systems offer several distinct advantages over batch systems, including continuous operation as opposed to intermittent processing, easy scalability to industrial applications, better representation of real-world treatment scenarios, higher operational efficiency, and greater control over operational parameters.

A column's efficiency is determined by its breakthrough curve, a plot of the concentration of contaminants in the effluent as a function of time. Such curves are needed to determine the adsorption capacity, predict the operational life of the adsorbent, optimize the design parameters of the column and calculate the efficiency of the column. The effluent concentration usually follows an S-shape curve; concentration starts to rise rapidly as the adsorbent becomes saturated. Once the concentration of the contaminant in the effluent reaches a desired concentration (usually 5-10% of the concentration in the influent), the breakthrough point has been reached, and when the concentration of the contaminant equals the adsorbent concentration, the adsorbent is fully saturated.

A variety of factors affect breakthrough behavior, such as the nature of the contaminants, the adsorbent properties and the operating conditions. It is essential to be able to understand these behaviors to design efficient treatment systems for its effect on the performance of the system over time. Column studies provide more realistic data for scale-up and industrial applications than batch studies, making them an essential component of adsorption research for water treatment applications. The data obtained from column experiments can be used to design full-scale treatment systems and to develop mathematical models that predict column performance under various conditions

### **1.13 Analytical Monitoring via UV-Vis Spectrophotometry**

To build an accurate breakthrough curve and quantify removal efficiencies in real-time, a reliable, precise, and rapid analytical method is required. This study uses the Ultraviolet-Visible (UV-Vis) Spectrophotometry as the primary analytical tool to observe the residual concentrations of diclofenac and ibuprofen in the column.

UV-Vis's spectrophotometry run on the principle of light absorption by molecular chromophores. Both target pharmaceutical compounds feature highly conjugated aromatic structures that show a distinct absorption maxima ( $\lambda_{\max}$ ) within the ultraviolet spectrum:

A primary characteristic peak of Diclofenac is the peak of absorption that is usually around  $\lambda_{\max} \approx 276$  nm.

The maximum absorbance of Ibuprofen is around  $\lambda_{\max} \approx 264$  nm.

The absorbance intensities obtained at these specific wavelengths are directly proportional to the concentration of the analyte and are used to establish a strong linear calibration curve with standard solutions of known concentration following the Beer-Lambert Law. The spectrophotometric method is therefore very convenient for the processing of large sample sets obtained during the continuous operation of the fixed-bed column, as it is an inexpensive, high-throughput, and robust method that is easier to use than the more sophisticated chromatographic methods.

#### **1.14 Multi-Layer Filtration Systems**

To improve the efficiency and longevity of adsorption systems, multi-layer filtration is often employed. A typical column setup includes strategically arranged layers with specific functions, each contributing to the overall performance of the treatment system. The gravel layer provides structural support and flow distribution, with a typical depth of 5-10 cm and particle size of 4-8 mm, preventing channeling and ensuring uniform flow through the column. The sand layer is 10-15cm deep and 0.5-2mm of particle size, used to remove the suspended solids and prevent any clogging of the GAC layer, which prolongs the life of the GAC. The GAC layer is the most used layer for pharmaceutical removal and is usually 20-30cm deep and the particles are 0.5-2mm in size, which can remove dissolved organic contaminants. The support plate supports and drains, secures media and collects effluent.

This multi-layer system has several advantages over single medium systems: These gravel and sand layers provide pre-filters which remove particulates that can clog the GAC and diminish its adsorption capacity. This pre-treatment extends the service life of the GAC and reduces the need for replacement, thus saving a lot of money. The uniform flow distribution obtained from the gravel layer means that all the GAC is used effectively and is not lost due to preferential flow paths which would reduce treatment efficiency. The overall system design is strong and reliable; it can withstand the change of the quality of the influent and maintain the treatment effect.

#### **1.15 Operational Factors Affecting Removal Efficiency**

The following operational factors are considered to affect removal efficiency: There are some key factors which control the performance of a fixed-bed column adsorption that determine the efficiency of removal and column service.

### **1.15.1 Solution pH**

The molecular charge of the pharmaceuticals and characteristics of the GAC are affected by the pH of the solution. Diclofenac ("p"  $K_a=4.15$ ) and Ibuprofen ("p"  $K_a=4.91$ ) are both weak acids. Below their "p"  $K_a$  values, they are both neutral (non-ionized). This state not only reduces electrostatic repulsion at the carbon surface but also increases hydrophobic attraction, thus improving the total removal rates.

### **1.15.2 Initial Influent Concentration**

The primary concentration gradient and main driving force for mass transfer is the initial concentration. The more concentrated the influent, the more rapidly the mass transfer zone will be driven through the column, the earlier the breakthrough will occur, and the shorter the column's life.

### **1.15.3 Flow Rate and Empty Bed Contact Time (EBCT)**

The hydrodynamic residence time in the column is indicated by the volumetric flow rate and EBCT. In the case of low flow rates (higher EBCT), the pharmaceutical molecules have a longer contact time and are therefore able to diffuse thoroughly into the internal micropore structure of the GAC.

### **1.15.4 Bed Depth**

This is the amount of GAC (adsorbent) present in the bed. The greater the bed depth, the more mass transfer zone and the longer the bed can operate without breakthrough.

### **1.15.5 Research Gap**

A lot of studies have been conducted about the removal of pharmaceutical contaminants; however, most have concentrated on batch adsorption systems in a controlled laboratory setting. These studies are not a true reflection of actual treatment conditions as the condition of the water stream is continually flowing, changing water quality and treatment must be continuous over long periods. The gap between laboratory research and practical application is very large and there is a need for bridging this gap, and this is an area that is not covered in the existing literature.

The research gaps identified are: There is limited research on fixed-bed column adsorption systems for the removal of diclofenac and ibuprofen, insufficient study on multi-layer filtration systems (combination of sand, gravel and GAC), no performance data when the systems are subject to

actual wastewater conditions, no studies conducted in developing countries like Pakistan, and limited information on scalability and industrial applications. The identified gaps emphasize the need for effective treatment solutions that are practical, cost-effective and scalable to be implemented in resource-limited environments where the demand for effective pharmaceutical removal technology is likely to be the highest.

Notably, there is little research conducted in developing countries, where pharmaceutical contaminants may be more concentrated since certain areas lack treatment infrastructure and where resources to implement advanced treatment technologies are also limited. A need exists to create treatment methods suitable to conditions and constraints of developing countries that will provide effective pharmaceutical removal that will be sustainable in these environments.

### **1.16 Problem Statement**

Diclofenac and ibuprofen are continuously released to aquatic ecosystems and are harmful for the environment and public health. Their removal is not effectively achieved by conventional wastewater treatment technologies, which cause them to remain in aquatic environments and therefore affect the ecology. The problem is exacerbated by the lack of adequate treatment technologies that can be applied in developing countries where need is highest, but resources are lowest.

Some of the major challenges that need to be tackled are poor removal in current WWTPs, limited research on column adsorption of NSAIDs, lack of effective solutions for developing countries, lack of knowledge of breakthrough behaviors and the need to optimize the operational parameters. Efficient, sustainable and affordable treatment technologies are urgently needed that can remove these pharmaceutical contaminants from water, especially technologies that are suitable to the conditions and constraints of developing countries.

The aim of this research is to tackle these issues by studying the performance of a multi-layer fixed-bed column system for the removal of Diclofenac and Ibuprofen from water. The study presents essential information on the ability of this method to achieve the required performance in realistic conditions and establishes design parameters that could help in the design of similar systems for real-world applications. The results could help shape the creation of water quality

standards and treatment guidelines for pharmaceutical contaminants, especially where they are not already available, in specific areas.

### **1.17 Objectives of the Study**

#### **1.17.1 Primary Objective**

The primary objectives of this research are to evaluate the removal efficiency of diclofenac and ibuprofen using a fixed-bed column system and to investigate the effect of operational parameters such as pH, concentration, and contact time on removal performance. These main objectives are supported by several secondary objectives that together provide a comprehensive assessment of the treatment system.

#### **1.17.2 Secondary Objectives**

The secondary objectives are to analyze the breakthrough behavior and determine the exhaustion point of the adsorption column, to assess the feasibility of a multi-layer filtration system using gravel, sand, and GAC, and propose a cost-effective treatment approach suitable for application in developing countries. These objectives address the identified research gaps and provide practical information for the design and operation of adsorption systems for pharmaceutical removal.

The achievement of these objectives will contribute to the growing body of knowledge on pharmaceutical removal from water and will provide practical guidance for the implementation of adsorption systems in resource-limited settings. The findings will support the development of effective treatment strategies that can protect water quality and aquatic ecosystems from the adverse effects of pharmaceutical contamination.

### **1.18 Significance of Study**

This work provides a useful engineering tool to tackle the worldwide problem of pharmaceutical micropollutants. This study provides a dependable means of capturing persistent NSAIDs and ensures the protection of vulnerable aquatic ecosystems, long-term non-target ecotoxicity and the protection of raw drinking water resources.

Valuable empirical data on the behavior of multi-component pharmaceutical adsorption in continuous fixed-bed systems are generated in the process of this study. The mathematical modeling of multi-layer column configuration extends the basic knowledge of mass transfer

phenomena, pore diffusion limitations and breakthrough phenomena kinetics which will serve as reference for further water treatment modeling.

Practical and Regional Value: Research has proven to be of great practical and low-cost solution as developing countries such as Pakistan are challenged with economic and infrastructure development issues. The proposed system can be built using local materials and simple gravity feed technology with high efficiency, which is not reliant on complex technical training or high capital investment.

## CHAPTER 2

### MATERIALS AND METHODS

#### 2.1 Research Methodology

This study was carried out to test whether a simple low-cost, gravity-driven fixed-bed adsorption column packed with Granular Activated Carbon (GAC) can be used for the removal of two widely used target Non-Steroidal Anti-Inflammatory Drugs (NSAIDs): Ibuprofen and Diclofenac. To understand the effect of critical operating variables (initial influent concentration, solution pH, hydrodynamic contact time, and background water matrix (aqueous chemistry)), controlled laboratory experiments were carried out, and overall removal efficiencies were measured. All experiments were run on controlled laboratory room temperature ( $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$ ).

Quantitative analysis of the pharmaceutical concentrations before and after column treatment was carried out using Ultraviolet-Visible (UV-Vis) Spectrophotometry. A fixed-bed column setup was chosen for this study because it is closer to how real water treatment systems work in practice compared to simple batch experiments (Sotelo et al., 2012).

#### 2.2 Materials and Chemicals

Pharmaceutical compounds, ibuprofen acid tablets (500 mg) and diclofenac tablets (100 mg) were purchased from a local pharmacy. Tablets were substituted for pure analytical standards because they were more readily available and were a representative source for drugs. For the column, Granular Activated Carbon (GAC) was used as the main adsorbent material. GAC was selected due to its high surface area and its capacity to adsorb organic pollutants, as well as it was widely employed in water treatment studies (Rakić et al., 2015). A layer of silica sand and gravel was placed inside the column to support the material. Cotton was put in the bottom outlet of the syringe to keep all the materials inside the syringe. Chemicals: Methanol was used for dissolving the drug tablets, hydrochloric (HCl 0.1N) is used to lower pH and sodium hydroxide (NaOH 0.1N) used for raising pH. All solutions were prepared using distilled and distilled water was used for rinsing equipment. The materials used were 60 mL plastic syringe (column), graduated measuring cylinder, UV-Visible spectrophotometer, digital pH meter and a timer.

***Table 2.1 List of chemicals and materials used in the study***

| <b>No.</b> | <b>Material</b>           | <b>Manufacturer / Source</b>     | <b>Manufacturer / Source</b> |
|------------|---------------------------|----------------------------------|------------------------------|
| <b>1.</b>  | Ibuprofen                 | 500mg Tablets                    | Local Pharmacy               |
| <b>2.</b>  | Diclofenac                | 100mg Tablets                    | Local Pharmacy               |
| <b>3.</b>  | Methanol                  | Analytical Grade ( $\geq$ 99.8%) | Merck                        |
| <b>4.</b>  | Distilled Water           | High Purity                      | Aqua Clear                   |
| <b>5.</b>  | Granular Activated Carbon | Coal-based GAC                   | Jacobi Carbons               |
| <b>6.</b>  | Silica Sand               | Pool Filter Grade (0.5--2 mm)    | Local Supplier               |
| <b>7.</b>  | Gravel                    | Graded Fluorite (4--8 mm)        | Local Supplier               |
| <b>8.</b>  | Cotton                    | Inert Cellulose/<br>Polymer      | Local Supplier               |
| <b>G.</b>  | Syringe Column            | 60 mL                            | Industry Standard            |
| <b>10.</b> | UV Spectrophotometer      | UV4000 Double-Beam               | Industry Standard            |
| <b>11.</b> | Hydrochloric Acid         | 0.1 N                            | Standard Lab Grade           |
| <b>12.</b> | Sodium Hydroxide          | 0.1 N                            | Standard Lab Grade           |

## 2.3 Preparation of Adsorption Column

A 60 mL plastic syringe was used as the column body. This decision was deliberate to demonstrate that a good water treatment system can be constructed using materials that are readily available to anyone and have low costs. All materials carefully washed and prepared before packing in the column. The column was made with simple and available local materials, as an alternative to the traditional means of water treatment, which is sustainable. This gravity-driven Granular Activated Carbon GAC column does not require any external energy source and is a practically available water treatment solution in water treatment systems in resource-limited areas (Rakić et al., 2015).

### 2.3.1 Pre-Treatment and Washing of Adsorbent Materials

To eliminate background contamination, fine particulates, and manufacturing residues that could skew quantitative data, all packed media underwent thorough pre-treatment protocols:

**2.3.2 Silica Sand and Gravel:** Washed with the tap water until the runoff was clear and free of turbidity, then rinsed three times with distilled water and oven drying.

**2.3.3 Granular Activated Carbon (GAC):** Rinsed with distilled water to remove the loose carbon and ash. The GAC was soaked within distilled water for 30 minutes to wet the pores, remove the trap air and stable is the water flowing during the experiment (Sotelo et al., 2012).



**Figure 2.1:** Prepared raw adsorbent media components (Coal-based Granular Activated Carbon, Pool-filter grade Silica Sand, and Graded Fluorite Gravel) stored in labeled containers prior to column packing.

## 2.4 Column packing protocol

The fixed bed column was packed under wet conditions to prevent air pockets voids and preferential water channels Packing was done sequentially from the bottom to the top to establish a stable multi-layer profile

**2.4.1 Basal retention layer (0.5 cm):** A compressed plug of inert cotton filter foam was placed at the base of the syringe to prevent any loss of media

**2.4.2 Structural support base (1.0 cm):** A layer of graded gravel was placed over the cotton to distribute water flow uniformly and keep the media stable

**2.4.3 Pre filtration Zone (4.0 cm):** A layer of graded silica sand was packed above the gravel to capture suspended solids and prevent the carbon layer from clogging

**2.4.4 Primary Adsorption Zone (4.0 cm):** The prepared GAC was packed as the top layer to serve as the active Zone for removing the pharmaceutical molecules

The total cumulative bed height of the entire system was approximately 9.5 cm



**Figure 2.2:** Assembled 60 mL multi-layer fixed-bed syringe column containing sequentially packed layers of cotton, gravel, silica sand, and GAC active adsorption zone.

### 2.4.5 Hydrodynamic conditioning

The column was conditioned after assembly by flowing distilled water through it for 20-30 minutes which allowed the media layers to settle, naturally flushed out any microscopic carbon dust and created a stable steady water flow through the column bed (Sotelo et al., 2012).

### 2.4.6 Flow Rate

No pumps or applied pressure were used in the column, it was gravity fed. Water was trickled down through the layers of packed media and added to the top of the column. In all the experimental tests the flow rate was maintained in the range of 1-3 mL/min. The effluent collected from the outlet was measured after 5 minutes of collection and the volume of the effluent collected was divided by 5 to get the flow rate in mL/min.



**Figure 2.3:** Complete gravity-driven experimental setup featuring an overhead glass burette for controlled influent delivery into the multi-layer fixed-bed adsorption column.

## 2.5 The preparation of Stock and Working Solutions.

Diclofenac stock solution was prepared by finely crushing one tablet (100 mg) with a mortar and pestle. The resulting powder was then dissolved in 100 mL of methanol and stirred mechanically for 15 minutes for initial dissolution. After this, 900 mL of distilled water was added to make up to 1 L (100 PPM). Then this solution was subjected to 24 hours on a mechanical shaker. This was also carried out for Ibuprofen by dissolving one of the 200 mg pills in 100 mL of methanol and diluting it in 900 mL of distilled water to get a primary stock solution with a concentration of 200 mg/L (200 PPM).

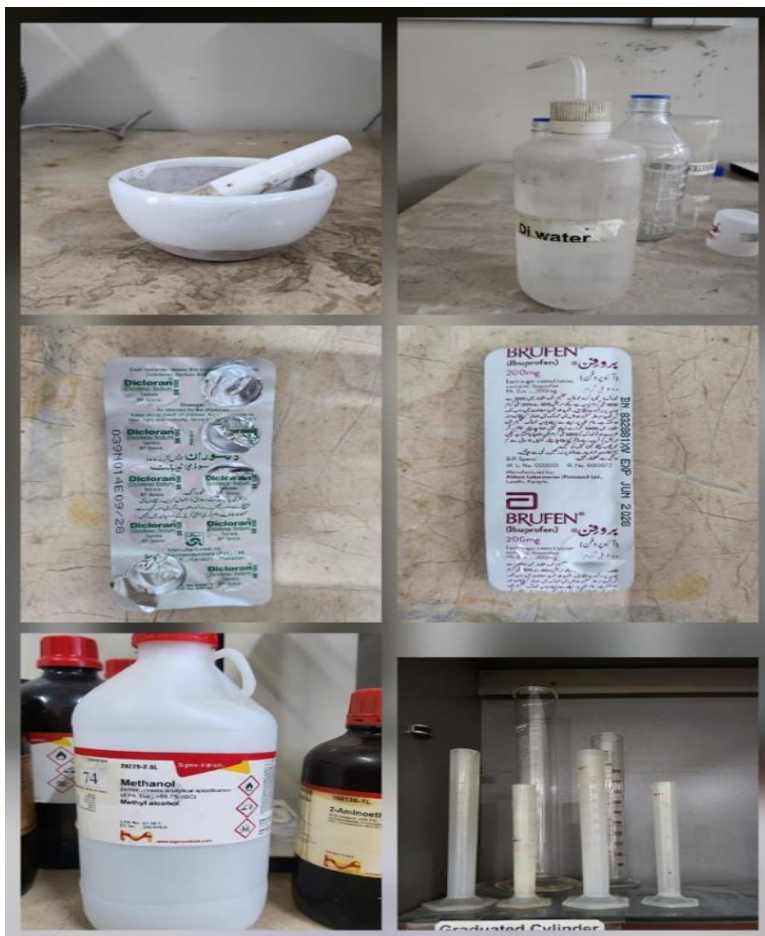


**Figure 2.4:** Laboratory apparatus and primary chemical reagents including pharmaceutical tablets (Dicloran and ibuprofen), analytical grade methanol solvent, mortar and pestle for pulverization, and graduated volumetric cylinders.

### 2.5.1 Dilution Principles and Formula

The working standard solutions were obtained by diluting the primary standard solutions with distilled water. The volume of each stock solution needed was calculated according to the standard dilution equation:

$$C_1V_1 = C_2V_2$$

- $C_1$  = Concentration of the stock solution (100 mg/L for Diclofenac, 200 mg/L for Ibuprofen)
- $V_1$  = Volume of stock solution used
- $C_2$  = Desired concentration of the working solution
- $V_2$  = Volume of the working solution (50mL)

#### A. Diclofenac Working Solutions (From 100 mg/L Stock)

##### Target Concentration of 50 mg/L (PPM):

$$100 \times V_1 = 50 \times 50$$

$$V_1 = \frac{50 \times 50}{100} = 25 \text{ mL}$$

*Thus, 25 mL of Diclofenac stock solution was diluted to a final volume of 50 mL with distilled water.*

##### Target Concentration of 20 mg/L (PPM):

$$100 \times V_1 = 20 \times 50$$

$$V_1 = \frac{20 \times 50}{100} = 10 \text{ mL}$$

*Thus, 10 mL of Diclofenac stock solution was diluted to a final volume of 50 mL with distilled water.*

##### Target Concentration of 15 mg/L (PPM):

$$100 \times V_1 = 15 \times 50$$

$$V_1 = \frac{15 \times 50}{100} = 7.5 \text{ mL}$$

*Thus, 7.5 mL of Diclofenac stock solution was diluted to a final volume of 50 mL with distilled water.*

## **B. Ibuprofen Working Solutions (From 200 mg/L Stock)**

### **Target Concentration of 80 mg/L (PPM):**

$$200 \times V_1 = 80 \times 50$$

$$V_1 = \frac{80 \times 50}{200} = 20 \text{ mL}$$

*Thus, 20 mL of Ibuprofen stock solution was diluted to a final volume of 50 mL with distilled water.*

### **Target Concentration of 60 mg/L (PPM):**

$$200 \times V_1 = 60 \times 50$$

$$V_1 = \frac{60 \times 50}{200} = 15 \text{ mL}$$

*Thus, 15 mL of Ibuprofen stock solution was diluted to a final volume of 50 mL with distilled water.*

### **Target Concentration of 40 mg/L (PPM):**

$$200 \times V_1 = 40 \times 50$$

$$V_1 = \frac{40 \times 50}{200} = 10 \text{ mL}$$

*Thus, 10 mL of Ibuprofen stock solution was diluted to a final volume of 50 mL with distilled water.*

## **2.6 Column Operation and Effluent Sampling**

Fixed-bed columns were used, and a systematic fluid handling and sampling scheme was applied to assess the treatment efficiency for all the concentrations prepared. A separate sample of 5 mL of each of the initial, untreated pharmaceutical solutions, 15, 20, and 50 PPM working solutions of Diclofenac, and 40, 60, and 80 PPM working solutions of Ibuprofen, was isolated and stored as

a reference control ( $C_0$ ). The rest of the volume of the same solution was then placed at the top of the column, and the down-flow process was continued through the successive granular activated carbon (GAC), sand, and gravel beds. The water leaving the bottom effluent was collected as timed samples of 5 mL ( $C_t$ ) of the effluent that had been immediately capped and labelled. Between each run of different concentration or pharmaceutical, the column was backflushed and rinsed with distilled water to avoid any kind of cross contamination between runs. Finally, all the isolated influent samples ( $C_0$ ). and the collected effluent samples ( $C_t$ ) were moved to the spectrophotometer, and the final concentration profiles were determined.

## **2.7 Tap Water Experiment**

Most laboratory studies use distilled water to prepare drug solutions. However, in real life, water sources such as tap water contain naturally occurring minerals, salts, and chlorine. To make this study more practical and relevant to real world conditions, an additional experiment was carried out using tap water instead of distilled water. (Rakić et al., 2015). The study was carried out using tap water instead of distilled water to simulate environmentally the same three concentrations of 50 mg/L, 25 mg/L, and 15 mg/L were prepared using tap water. The drug was dissolved and diluted in tap water following the same steps used for distilled water experiments. Before passing each concentration through the column, a 5 mL control sample was taken directly from the prepared solution. Each concentration was then passed through the GAC column one by one under gravity flow. The treated water coming out from the bottom of the column was collected as an effluent sample. All samples were sent for absorbance measurement using the UV-Visible spectrophotometer and removal efficiency was calculated using the same formula as previous experiments

## **2.8 Effect of Hydrodynamic Contact Time (Retention Time)**

Hydrodynamic contact refers to the period during which dissolved pharmaceutical molecules meet the active surface area and the internal pore structures of the GAC bed. Extending this contact time generally improves mass transfer by providing sufficient time for the molecules to diffuse into the micropores of the carbon (Lach & Szymonik, 2019).

A series of identical parallel columns were built and continuously gravity-driven to study the systematical kinetics of adsorption as a function of contact time. For all the target pharmaceuticals prepared over the concentration range, the influence of contact time was thoroughly investigated

to fully characterize the kinetic behavior at low, intermediate, and high mass loadings:

**Ibuprofen Working Concentrations:** Conditions of 40 mg/L, 60 mg/L and 80mg/L were simultaneously evaluated.

**Diclofenac Working Concentrations:** Tested simultaneously at 15 mg/L, 25 mg/L 50 mg/L.

A sample of the untreated influent was collected before the experimental column was introduced and was used as a baseline reference reference ( $C_0$ ). for each experimental matrix run. The same amounts of each solution were placed in the column inlets; an electronic timer was immediately started. Gravity flow was used for operation of the columns.

Effluent samples (5" mL" each) were taken after fixed periods of 15 minutes, 30 minutes and 60 minutes from the column outlets to monitor the time dependent adsorption kinetic and profiling. The samples were immediately capped and labeled to match the corresponding runtime and concentration profile in each sample vial. All resulting sample arrays (baseline controls and sequential kinetic effluents ( $C_t$ )) were then immediately moved to the analytical suite for quantitative optical profiling.

## 2.9 Influence of Solution pH on Adsorption Mechanics

Both the molecular speciation (ionization state) of the target NSAIDs and the surface charge characteristics of the active carbon matrix change depending on the local pH of the aqueous solution and thus influence the predominant adsorption mechanisms (Lach & Szymonik, 2019). A 25" mg/L" working solution was tested under three different chemical regimes: acidic (pH 5.0), neutral (pH 7.0), and alkaline (pH 10.0) to isolate this effect.

**Acidic Regime (pH 5.0):** Made by dropwise addition of 0.1" N" hydrochloric acid ("HCl") to the solution with constant stirring until the pH reached pH 5.0 at the digital pH meter.

**Neutral Regime (pH 7.0):** No adjustment was made because the baseline unadjusted solution was at an approximate neutral pH (7.0).

**Alkaline Regime (pH 10.0):** This was obtained by dropwise addition of 0.1" N" sodium hydroxide ("NaOH" ) with constant stirring till the digital pH meter indicated a value of 10.0.

The titration was carried out dropwise to be sure that the desired value was not exceeded. For each adjusted pH level, before filtering, a 5 mL sample was taken and used as an untreated control

sample. Solutions were injected independently into the column, and extended distilled water rinses were made between runs to ensure that cross-contamination was avoided. Three of each, for a total of six, samples were compiled (three controls and three effluents) for optical analysis.

## 2.10 UV-Vis Spectrophotometric Quantification

Residual concentrations of Ibuprofen and Diclofenac were quantified using a double-beam UV-4000 UV-Vis spectrophotometers. The instrument was run at unique analytical wavelengths optimized for each pharmaceutical compound, to achieve maximum sensitivity and separate the signals at each wavelength according to the electronic transition profile of each compound.

The samples of Ibuprofen were measured at the maximum absorption wavelength  $\lambda_{\max} = 263$  nm.

The samples of Diclofenac were taken at the peak absorption wavelength of  $\lambda_{\max} = 274$  nm.

The instrument was calibrated using high-purity distilled water analytical blank before the samples were analyzed. The blank matrix was placed in high transparent quartz cuvettes to obtain a reference absorbance reading of zero, which allowed only the absorbance of the analytes being measured to be recorded on subsequent optical readings. After each measurement, the cuvette was washed with distilled water to prevent the carry-over of fluid and cross-contamination between measurements. The untreated control sample was analyzed first for all experimental matrices to obtain the initial absorbance value, which represents the initial concentration of the influent ( $C_0$ ). This was immediately followed by measurement of the effluent sample from the respective column to record the concentration of the effluent after treatment ( $C_t$ ). The real time removal performance was calculated using the following mass balance equation derived from Equation 2.3:

$$\text{Removal Efficiency (\%)} = \left[ \frac{C_0 - C_t}{C_0} \right] \times 100$$

Further, the normalized concentration ratio ( $C_t/C_0$ ) was determined in each run of operation in order to plot the breakthrough curves. In adsorption breakthroughs, a normalized value of near zero ( $C_t/C_0 \rightarrow 0$ ) represents a near complete adsorption within the active mass transfer zone while a normalized value of near one ( $C_t/C_0 \rightarrow 1$ ) corresponds to a complete bed saturation ( $C_s$ ) and a definitive column exhaustion ( $t_s$ )(Sotelo et al., 2012).

These optical profiles were systematically confirmed for all the concentration levels of both

systems:

**Ibuprofen matrices:** 40" mg/L", 60" mg/L" and 80" mg/L"

**Diclofenac matrices:** 15" mg/L", 25" mg/L" and 50" mg/L".

## 2.11 Statistical Data Management and Analysis

The raw experimental data obtained from the digital pH meter and the double-beam UV-Vis spectrophotometer were compiled, organized and managed systematically in a systematic way in Microsoft Excel. Raw optical absorbance values recorded at  $\lambda_{\max}$

for Ibuprofen and Diclofenac (  $\lambda_{\max} = 263$  nm and  $\lambda_{\max} = 274$  nm, respectively) were converted to the concentrations of the analytes, ( $C_0$  and  $C_t$ ), (residual concentration from the beginning and after the incubation, respectively), using robust linear regression calibration curves generated by filtered standard solutions.

All experimental matrices were subjected to descriptive statistical analysis, which included mean values, standard deviations and percentage differences

**Influent Drug Concentrations:** Evaluated at 40 mg/L, 60 mg/L, and 80 mg/L for Ibuprofen; and 15 mg/L, 25 mg/L, and 50 mg/L for Diclofenac.

**Initial Solution pH:** adjusted and maintained to be acidic (pH 5.0), neutral (pH 7.0), and alkaline (pH 10.0).

**Hydrodynamic Contact/Retention Time:** Processed every 15minute, 30minutes, and 60minutes during the operation.

**Background Aqueous Matrix Chemistry:** Studied in high purity distilled water and compared to municipal tap water to isolate matrix competitive effects.

All unusual changes, experimental anomalies, and outliers, whether sudden changes in effluent concentration due to fluid channeling or micro-bubble retention or temporary desorption fronts, were identified and deemed to be normal experimental variation during processing. The final processed values were presented in a comparative table of data and plotted as breakthrough profiles and kinetic trend curves to illustrate the comparative affinity that Granular Activated Carbon (GAC) has to Ibuprofen and Diclofenac in continuous down-flow operations.

## CHAPTER 3

### RESULTS AND DISCUSSION

#### 3.1 Overview

This chapter represents and discusses the results obtained from the laboratory scale experiments, along with a description of the basic experimental techniques. A comprehensive suite of lab experiments was done to systematically investigate the removal efficiency and kinetic retention behavior of two target pharmaceutical pollutants, Ibuprofen and Dicloran. Working standard solutions were prepared in a different range of concentration by serial dilution of concentrated stock solutions to assess the effect of initial adsorbate loading on the performance of the columns. The initial concentrations ( $C_0$ ) studied were:

Ibuprofen: 40 mg/L (ppm), 60 mg/L (ppm), and 80 mg/L (ppm)

Dicloran: 15 mg/L (ppm), 25 mg/L (ppm), and 50 mg/L (ppm)

For each experiment run a 5mL control aliquot was taken before the column was introduced for each of the experimental runs to set and confirm the exact initial concentration ( $C_0$ ). The rest of the solution was then loaded into the packed bed column system, with a controlled natural hydrostatic gravity flow. After the passage of the column, the samples of treated effluent ( $C_t$ ) were taken at the specified times. The analysis of the untreated control samples ( $C_0$ ) and the post-treatment effluent samples ( $C_t$ ) was carried out through quantitative analysis using UV-Visible spectrophotometer. For maximum sensitivity and accuracy, absorbance measurements were taken at the respective maximum absorption wavelengths( $\lambda_{\max}$ ) for each compound:

Ibuprofen:  $\lambda_{\max} = 263 \text{ nm}$

Dicloran:  $\lambda_{\max} = 274 \text{ nm}$

The percentage removal efficiency of the pharmaceutical compounds (%R)

of the adsorption system was then determined based on the relationship of the baseline control concentration and the post-column effluent concentration, as follows:

$$\%R = \frac{C_0 - C_t}{C_0} \times 100$$

Three variables of the operating conditions were systematically changed and investigated to gain a comprehensive understanding of the mechanisms governing the fixed-bed adsorption system:

### 3.1.1 Initial Influent Concentration:

Testing performance over the base concentration ranges in a neutral pH environment.

### 3.1.2 Contact Time (Kinetics):

Analyzing effluent samples collected sequentially over a 60-minute operational timeline to map kinetic retention behavior.

### 3.1.3 Solution pH:

Investigate the effect of the pH of the solution because it was tested under basic conditions with Ibuprofen and acidic conditions with Dicloran.

## 3.2 Effect of Initial Concentration on Distilled Water

### 3.2.1 Ibuprofen

In the first set of column experiments, three different initial influent concentrations (40 mg/L, 60 mg/L and 80 mg/L) of Ibuprofen were used for the acidic condition with Granular Activated Carbon (GAC). Absorbance of untreated control ( $C_0$ ). and treated effluent samples ( $C_t$ ) were taken by UV-Visible spectrophotometric method as given in Table 3.1. The percentage of removal efficiencies were computed from this absorbance and presented in Figure 3.1.

***Table 3.1: Absorbance values of untreated and treated Ibuprofen at different initial concentrations***

| Initial Concentration (mg/L) | Untreated Control ( $C_0$ ) | Treated Sample ( $C_t$ ) |
|------------------------------|-----------------------------|--------------------------|
| 40 ppm                       | 0.094                       | 0.088                    |
| 60 ppm                       | 0.110                       | 0.085                    |

|        |       |       |
|--------|-------|-------|
| 80 ppm | 0.133 | 0.110 |
|--------|-------|-------|

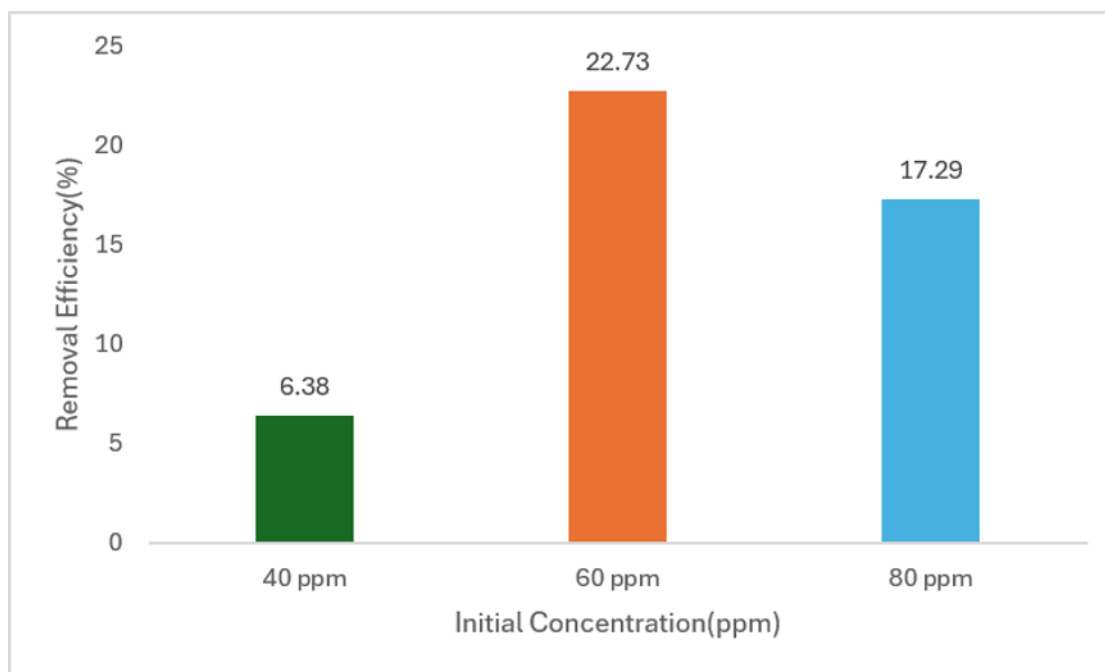


***Figure 3.1: Ibuprofen removal efficiency (%) at various initial concentrations.***

Experimental results show a unique non-linear adsorption non-linearity for Ibuprofen in the continuous column matrix for acidic conditions. The removal efficiency obtained at the lowest concentration of working solutions was 6.38% only at 40 mg/L. The initial loading was then increased to 60mg/L and the system performed optimally, with the removal efficiency rising to a maximum of 22.73% removal efficiency. However, when the concentration of the influent was further increased to 80 mg/L, the efficiency of overall removal was reduced to 17.29%, and the performance was slightly reduced. Mass transfer mechanisms and driving force theories can be used to analyze this complex behavioral profile comprehensively. For fixed-bed adsorption process, the mass transfer resistance (Pratap et al., 2025) is controlled by the concentration differential between bulk liquid phase and solid phase of the GAC bed. A greater concentration gradient is created when the initial concentration is increased from 40mg/L to 60mg/L. This gradient is a strong thermodynamic driving force that increases the diffusion coefficient, thus promoting the Ibuprofen molecule to penetrate the boundary layer film into the active porous network of the carbon matrix (Pratap et al., 2025; Varela et al., 2024).

This is the reason why the percentage of removal at the higher concentrations is so high up to 60 mg/L. On the other hand, the decrease in performance seen at the set concentration limit 80mg/L is at the start of operation restrictions. Under these high mass loading rates, the amount of target pharmaceutical molecules in the feed stream makes their active binding surface sites at the column inlet zone fill up rapidly and become partially saturated (Rafati et al., 2019). As the number of open functional pathways is fixed and the amount of GAC remains the same, the relative number of molecules of Ibuprofen that are not adsorbed increases in the final effluent stream, resulting in a site-saturation bottleneck (Pratap et al., 2025; Rafati et al., 2019). The non-steady state, concentration dependent trends observed during this assessment are similar to continuous flow results published in the wastewater engineering field. In a fixed-bed column, Rafati et al. (2019) showed that the initial loading of the contaminant significantly influenced the profile of the column for Ibuprofen, with higher initial mass fluxes giving a higher rate of target site saturation and lower breakthrough volumes. Likewise, Pratap et al. (2025) validated that the concentration steps must be high enough to achieve the maximum concentration difference to enhance the driving force for mass transfer, yet should not exceed the height of the bed, as this will cause rapid deactivation of the active site leading to a decrease in the percentage of mass removed over the long term ( $q_{\max}$ ). This validated behavior highlights the need to balance forces and active site availability for scaling of carbon based fixed-bed matrices.

### **3.3 Ibuprofen: Retention over Time**

Contact time is the actual time that the pharmaceutical solution being treated directly comes in contact with the Granular Activated Carbon (GAC) packed bed matrix. In fixed bed column adsorption systems, the contact time is one of the most important operating parameters, as it determines the time period during which adsorbate molecules are able to pass through the boundary layer to enter the complex internal structure of the pores of the carbon material and to bind to active surface sites (Lach & Szymonik, 2019). In this stage of the study, the kinetic process of the adsorption was systematically monitored with the continuous natural hydrostatic flow for operational time of 60 minutes. A baseline control sample (untreated) was collected at the start of the run ( $t = 0$  min) to provide a reference of the initial concentration ( $C_0$ ). Treated effluent samples ( $C_t$ ) were serially taken from the outlet of the column at time intervals of 15 minutes, 30 minutes, and 60 minutes. The absorbance value of the untreated control ( $C_0$ ) and treated samples, ( $C_t$ ) obtained using the UV-Visible spectrophotometry is summarized in Table 3.2. The percentage removal efficiencies for various contact times are shown in

Figure 3.2.

**Table 3.2 Absorbance values of Ibuprofen at various initial concentrations across contact times (t = 15, 30, 60 min).**

| <b>Initial Concentration (mg/L)</b> | <b>Control</b> | <b>Treated Sample (15 min)</b> | <b>Treated Sample (30 min)</b> | <b>Treated Sample (60 min)</b> |
|-------------------------------------|----------------|--------------------------------|--------------------------------|--------------------------------|
| <b>40 ppm</b>                       | 0.094          | 0.091                          | 0.085                          | 0.080                          |
| <b>60 ppm</b>                       | 0.110          | 0.081                          | 0.089                          | 0.095                          |
| <b>80 ppm</b>                       | 0.133          | 0.131                          | 0.126                          | 0.117                          |

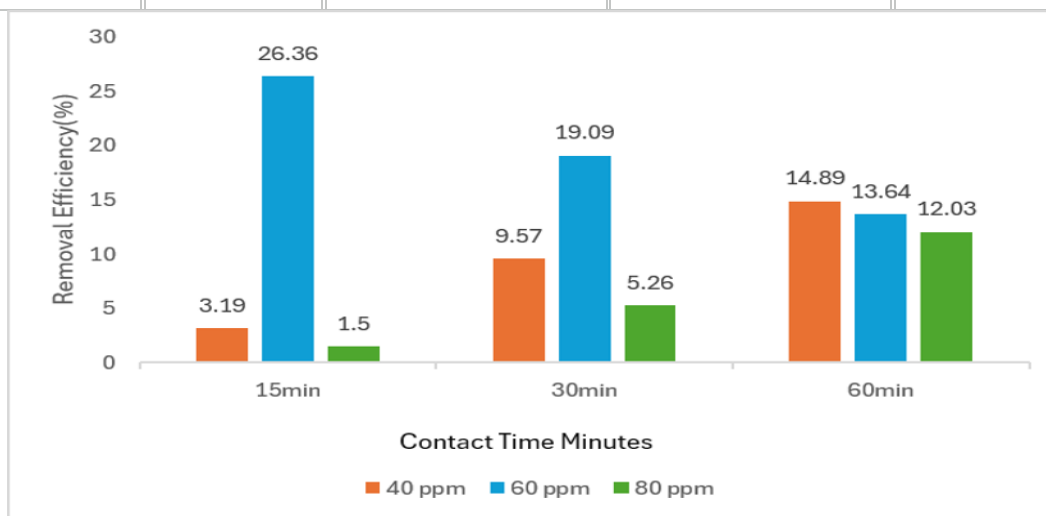


**Figure 3.2 Percentage removal efficiency of Ibuprofen by Granular Activated Carbon (GAC) at varying contact times (15, 30, and 60 minutes) at different initial concentrations.**

The experimental data shows a very dynamic kinetic retention profile in time for the target pharmaceutical compound. A large increase in the removal performance was noticed in the early stages of the continuous flow operation. The GAC column was able to remove 26.36% of Ibuprofen by  $t = 15$  min. The 30-minute interval was the best time for the system to operate, with the highest absorbance removal of 33.63% recorded at this point with the lowest absorbance value of 0.073 for the effluent.

The first fast adsorption period (15 to 30 min) is due to the ready availability of the completely unoccupied, high energy adsorption sites on the outer periphery and macro-pores of the fresh GAC bed. The concentration difference between the liquid phase and the unexposed solid carbon surface is the highest at this early stage, and fast external film mass transfer is possible, resulting in high retention.

However, the operational time approached the 60-minute mark and a clear change in the kinetic profile was observed. The absorbance value of effluent increased to 0.090, which resulted in a decrease in removal efficiency to 18.18%. This decrease in performance is typical of the beginning of column breakthrough and/or localized saturation of the active sites in the packed bed matrix.

As the drug molecules pass through the continuous gravity fed flow over time, the available surface sites on the GAC will get filled and depleted. When these primary binding zones are saturated, the next target molecules in the stream have to travel further down the column or penetrate deeper into the narrow micro-pores through intra-particle diffusion where the steric resistance is much higher (Lach & Szymonik, 2019). The flow is continuous and the capacity of the active site in the fixed bed is gradually depleted and therefore more molecules of Ibuprofen are not adsorbed and end up in the final effluent, causing the decrease in the removal percentage at 60text minutes. The measured time-dependent retention and breakthrough trends are similar to those found in the continuous-flow water treatment literature and are typical of the mass-transport transport models. Lach and Szymonik (2019) tested carbonaceous beds for micro-pollutant removal and found that the availability of active sites is strictly time-dependent and that the rate of removal at short times is due to external boundary diffusion, while the rate of removal at longer times depends on pore diffusion, which eventually brings the effluent concentration back up as breakthrough approaches. This time resolved behavioral profile is essential background data to understand the operational life span and exhaustion limits of the GAC fixed-bed column before the next regeneration

### **3.3.1 40 ppm Profile: Steady Linear Adsorption**

The fixed-bed system's retention profile for the lowest concentration boundary of 40mg/L shows a steady linear decrease in effluent absorbance with time for the duration of 60 minutes that was monitored. The initial absorbance at the start ( $t = 0\text{min}$ ) is 0.094 and decreases to 0.091 after 15 min, 0.085 after 30 min and finally 0.080 after 60 min.

This decrease is constant, which is a typical non-equilibrium mass transfer action. The initial concentration is relatively low which allows the active binding sites on the GAC to be filled up slowly. The profile is described as a progressive spreading of the Ibuprofen molecules from the boundary layer of fluid in the outside of the column into the micro-pores in the inside of the column.

### **3.3.2 60 ppm Profile: Rapid Uptake and Breakthrough Onset**

The kinetic curve at 60 mg/L is V-shaped, with a sharp onset of breakthrough and rapid uptake before that point, showing the typical uptake and breakthrough curve for this intermediate loading rate without signs of site saturation. The absorbance of the Untreated Control ( $t = 0\text{ min}$ ) is 0.110 and then decreases to 0.081 at 15 min and 0.073 at 30 min.

The first stage is a high-velocity molecular attachment to the very accessible external active surface sites on the fresh carbon bed that is considered a rapid uptake mechanism. After this removal phase an inversion takes place during the last 50% of the run, when the absorbance of the effluent increases again to 0.090 at 60 minutes. The increase in this direction is a local saturation and breakthrough phenomenon. The incoming mass flux is greater than the internal intra-particle diffusion as the main surface sites are quickly filled in the first 3 text minutes. This results in a progressive downward trend in the column throughout the monitoring period, from the initial baseline.

### **3.3.3 80 ppm Profile: High Driving Force Adsorption**

High Driving Force Adsorption The absorbance for the Untreated Control ( $t = 0\text{ min}$ ) is 0.133, which decreases slightly to 0.131 at 15 minutes, to 0.126 at 30 minutes and to 0.117 at 60 minutes.

This continuous decrease is an indication of concentration driven mass transfer action. A large concentration gradient is created between the bulk liquid phase and the solid adsorbent phase with

the initial concentration of 80 mg/L. The driving force theories suggest that this large gradient is a strong thermodynamic pump that reduces the mass transfer resistance in the films so rapidly, the Ibuprofen molecules must flow into the internal pore structure of the column material. This is reflected in the present bed status, which involves high density and continuous filling of pores. The absorbance is continuously and quickly decreasing as the system approaches saturation, which is reflected by the steady decrease of the absorbance, but the matrix of the column is not completely exhausted at 1 hour.

### 3.4 Ibuprofen: Effect of Neutral pH on Removal Efficiency

The neutral pH effect on Ibuprofen removal was studied using a fixed-bed GAC column with three different initial concentrations. A sample was taken from each prepared solution prior to its addition to the column to obtain the untreated control aliquot  $C_0$  and the rest of the solution was passed through the column where the GAC was packed for continuous flow to obtain the treated effluent sample  $C_t$ . The absorbance value  $C_0$  and  $C_t$  obtained from UV-Visible spectrophotometry are shown in Table 3.3. The corresponding percentage removal efficiencies (%R) to is shown in Figure 3.3 Under neutral pH conditions.

*Table 3.3: Absorbance values of untreated and treated Ibuprofen at neutral pH*

| Initial Concentration (mg/L) | Untreated Control ( $C_0$ ) | Treated Sample ( $C_t$ ) |
|------------------------------|-----------------------------|--------------------------|
| 40 ppm                       | 0.094                       | 0.088                    |
| 60 ppm                       | 0.110                       | 0.085                    |
| 80 ppm                       | 0.133                       | 0.110                    |

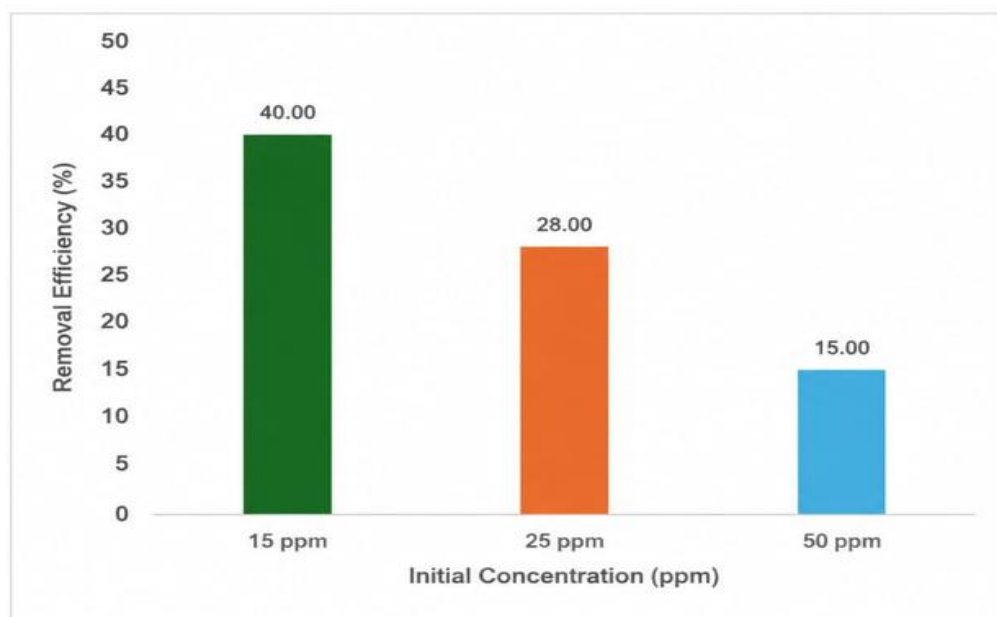


***Figure 3.3: Ibuprofen removal efficiency (%) at neutral pH for various initial concentrations***

Ibuprofen exhibited a non-linear removal trend with increasing initial concentration at neutral pH. The removal efficiency was relatively low at 40 ppm (6.38%). At the concentration, 60 ppm, the removal efficiency rose significantly to 22.73%, which was the highest removal observed under neutral conditions. The removal efficiency dropped to 17.29% at higher concentration (80 ppm).

The increase from 40 ppm to 60 ppm that was observed can be attributed to the larger concentration gradient between the solution and the adsorption sites on the surface of the GAC. The relatively low concentration at 40 ppm gives the smaller force for mass transfer, which leads to a lower amount of interaction of the Ibuprofen molecules with the available adsorption sites. The higher concentration gradient, as the concentration increased from 40 ppm to 60 ppm, created more movement of the Ibuprofen molecules from the bulk solution to the GAC surface and into the pores that were available, which yielded a higher percent removal.

The removal efficiency was reduced, however, from 22.73% to 17.29% at 80 ppm. This decrease is due to the increase in the number of Ibuprofen molecules compared to the number of adsorption sites in the GAC bed. As the influent concentration increases, the more active adsorption sites will be filled and there will be fewer sites left for the remaining adsorption. Therefore, the percentage of removal for Ibuprofen is not 100% efficient at the highest concentration, with some molecules passing through the column without being removed.

In general, the results show that the highest removal efficiency of Ibuprofen under neutral pH

conditions was obtained at 60 ppm with a removal efficiency of 22.73% and the lowest removal was obtained at 40 ppm with a removal efficiency of 6.38%. The non-linear trend indicates that the removal efficiency of a fixed-bed adsorption system is also affected by the amount of adsorption sites and mass transfer phenomena in the GAC bed, as well as the initial concentration. This matches your current thesis discussion which stated that a neutral-pH Ibuprofen has the highest percentage efficiency at 60 ppm.

### 3.5 Ibuprofen: Effect of basic pH on Removal Efficiency

The effect of the solution shift to basic pH was assessed by an experimental series in a fixed-bed column that exhibited a natural weakly acidic property. To get the untreated control aliquot ( $C_0$ ), a sample was taken from each batch before introducing it into the column, and the rest of the batch was fed continuously into the GAC packed bed yielding the treated effluent sample ( $C_t$ ). The absorbance values ( $C_0$  and  $C_t$ ) for the spectrophotometric method are presented in Table 3.4 and the percentage of removal (%R) for spectrophotometric method is shown in Figure 3.4 under basic pH conditions

***Table 3.4: Absorbance values of untreated and treated Ibuprofen  
at basic pH.***

| <b>Initial Concentration (mg/L)</b> | <b>Untreated Control (<math>C_0</math>)</b> | <b>Treated Sample (<math>C_t</math>)</b> |
|-------------------------------------|---------------------------------------------|------------------------------------------|
| <b>40 ppm</b>                       | 0.100                                       | 0.070                                    |
| <b>60 ppm</b>                       | 0.130                                       | 0.120                                    |
| <b>80 ppm</b>                       | 0.141                                       | 0.126                                    |

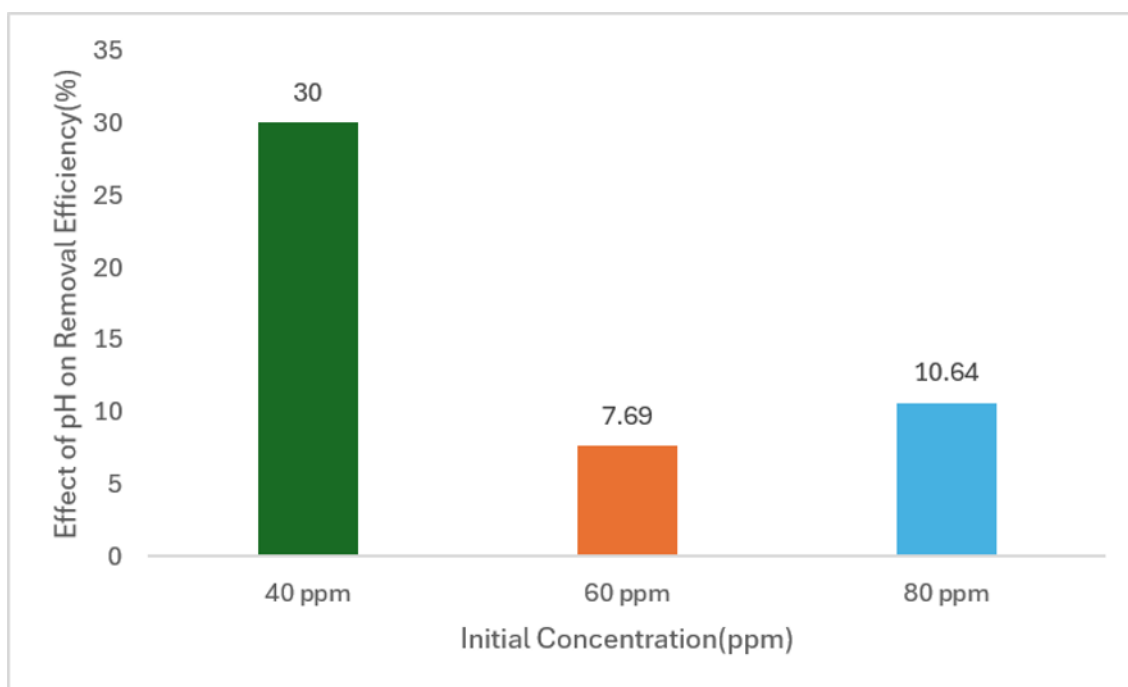


**Figure 3.4: Ibuprofen removal efficiency (%) at basic pH for various initial concentrations**

When the aqueous matrix was shifted to a basic pH, the column's removal mechanics and surface interactions changed significantly. Unlike the steady, inverse trend seen with other pollutants, Ibuprofen showed a non-linear removal profile; efficiency dropped sharply from 30.00% to 7.69% as the concentration rose to 60 mg/L, but then slightly recovered to 10.64% at 80 mg/L."It was observed that the system exhibited a significant improvement in the removal rate at the lowest loading rate (40 ppm), when the removal efficiency rose from the neutral state (6.38%) to 30.00% at basic conditions. The operational efficiency of the 60 ppm and 80 ppm treated configurations, on the other hand, dropped drastically from their neutral levels to 7.69% and 10.64%, respectively. The scientific explanation of this behavior can be done by studying the solution pH, the dissociation constant of the adsorbate ( $pK_a$ ) and the surface chemistry of the adsorbent. The  $pK_a$  of Ibuprofen is about 4.5. As a result, in a simple environment, the pH of the solution is much higher than the  $pK_a$  and the Ibuprofen molecules are completely deprotonated to the anionic form. On the other hand, at higher pH the functional groups within the GAC surface gain a net negative charge because of the increase in hydroxyl ions (OH) in the electrical double layer (Pratap et al., 2025; Rafati et al., 2019).

The total number of the anionic species in the bulk solution is small when the initial concentration

is small, 40 ppm. Although the pH in these areas is sub-optimal, these fewer molecules can diffuse to uncharged hydrophobic macro-pores within carbon, resulting in an isolated peak in retention. However, as the concentration of the initial loading rises in order it becomes 60 ppm, and 80 ppm, the intermolecular electrostatic repulsions between Ibuprofen ions become very strong due to the high density of negatively charged Ibuprofen ions. In addition, a strong electrostatic repulsion field is also created between the anionic drug molecules and the more negative surface matrix of the GAC (Rafati et al., 2019). This repulsion barrier decreases mass transfer coefficient, as packing of the molecules is not tight, and intra-particle diffusion in the micro-pores is hindered. This mass transfer resistance is responsible for the high breakthrough and poor long term removal levels at higher concentrations.

### 3.6 Effect of Initial Concentration on Distilled Water

#### 3.6.1 Dicloran

The baseline filtration and removal capabilities for Dicloran were evaluated by systematically monitoring the concentration differential between the untreated baseline control ( $C_0$ ) and the gravity-treated post-column effluent sample ( $C_t$ ) across three initial levels: 15 mg/L (ppm), 25 mg/L (ppm), and 50 mg/L (ppm). Absorbance values of untreated control ( $C_0$ ) and the treated effluent samples ( $C_t$ ) were obtained by UV-Visible spectrophotometric method as given in Table 3.5. These absorbance values were used to calculate the percentage removal efficiencies which are shown in figure 3.5.

**Table 3.5: Absorbance values of untreated and treated Dicloran at different initial concentrations**

| <b>Initial Concentration (mg/L)</b> | <b>Untreated Control (<math>C_0</math>)</b> | <b>Treated Sample (<math>C_t</math>)</b> |
|-------------------------------------|---------------------------------------------|------------------------------------------|
| <b>15 ppm</b>                       | 0.477                                       | 0.389                                    |
| <b>25 ppm</b>                       | 0.874                                       | 0.788                                    |
| <b>50 ppm</b>                       | 3.000                                       | 2.897                                    |

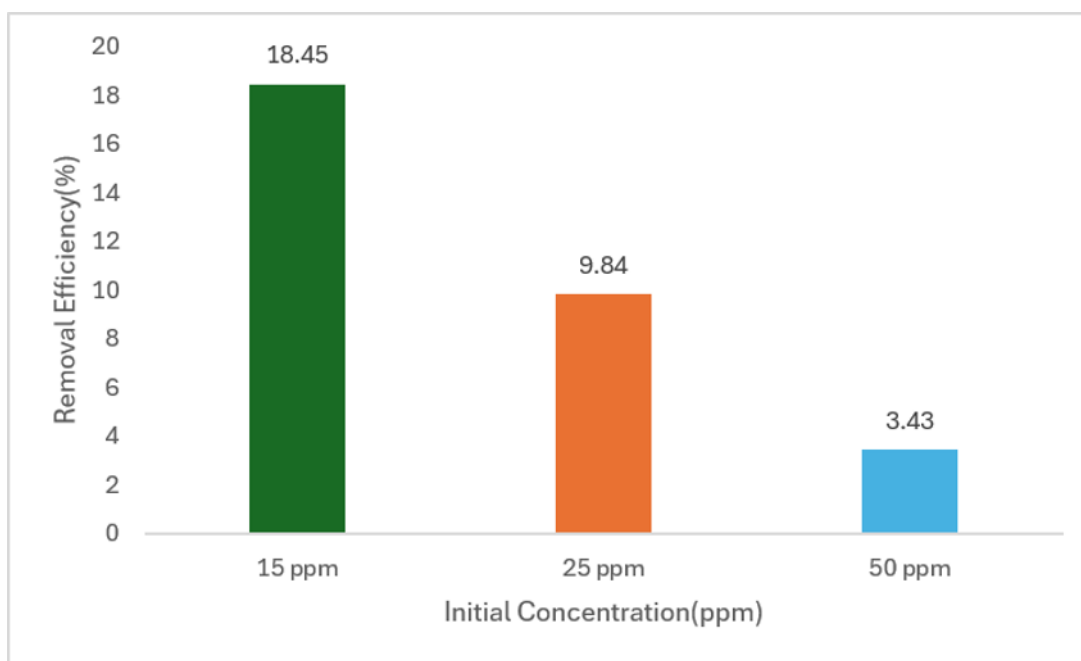


***Figure 3.5: Dicloran removal efficiency (%) at various initial concentrations.***

In contrast to the non-linear profile observed for Ibuprofen, Dicloran displays a classic inverse relationship between the initial influent concentration and its corresponding removal efficiency within the continuous-flow matrix.". At the lowest working concentration of 15 ppm, the GAC column achieved its highest removal efficiency of 18.45%. As the initial loading was increased to 25ppm, the removal efficiency dropped noticeably to 9.84%. When the influent mass loading was escalated to its maximum boundary of 50 ppm, the system's performance fell sharply to a nominal 3.43%, indicating that most of the target molecules passed through the bed without being bound. This rigid concentration-dependent degradation in performance can be analyzed using localized mass-loading rates and active site availability frameworks. Under neutral pH conditions, the electrostatic or hydrophobic interactions between the Dicloran molecular structure and the functional matrix of the GAC impose a strict thermodynamic threshold on the total adsorption capacity (Pratap et al., 2025). At a lower initial concentration of 15 ppm, the ratio of available active adsorption sites to total adsorbate molecules in the bulk fluid is highly favorable, allowing a larger fraction of the influent to successfully partition into the solid phase carbon matrix.

However, as the mass loading scales upward to 25ppm and 50 ppm, a massive influx of Dicloran molecules reaches the column bed. While a higher concentration gradient theoretically enhances the interfacial mass transfer driving force, the limited number of open functional pathways and

accessible micropores at the column inlet zone undergo rapid, immediate exhaustion (Rafati et al., 2019; Varela et al., 2024). Because the fixed volume of GAC remains constant and lacks the specific surface adaptations required to accommodate high-density matrices at neutral pH, a severe site-saturation bottleneck takes place. The active binding zones become quickly blocked, drastically suppressing further film and intra-particle diffusion and forcing the excess unabsorbed drug molecules directly into the final treated effluent stream (Pratap et al., 2025). This behavioral trend aligns closely with continuous fixed-bed literature involving fixed active-site boundaries. Wastewater engineering studies show that for specific organic micro-pollutants operating under sub-optimal chemical matrices, an increase in influent mass flux yields a steep, linear decline in removal percentages due to the immediate saturation of the upper boundary layers of the column (Rafati et al., 2019). Pratap et al. (2025) validated that when an adsorbent matrix encounters a strict thermodynamic capacity ceiling, higher initial concentrations accelerate bed deactivation ( $q_{\max}$  exploitation), leading to instant solute breakthrough and minimal long-term removal efficiencies. This behavior demonstrates that adjusting secondary operational parameters, such as solution pH, is essential to modify the surface charge and expand the active site availability for Dicloran scaling.

### **3.7 Diclofenac: Retention over Time**

To assess the time-resolved adsorption of Dicloran with the natural hydrostatic flow, effluent samples were taken continuously for 60 minutes. The baseline control was untreated, with the untreated sample taken at  $t=0$  min ( $C_0$ ), and serial sampling at  $t=15, 30$ , and  $60$  minutes ( $C_t$ ). Absorbance values of the untreated control sample ( $C_0$ ) and treated effluent samples ( $C_t$ ) were measured by UV-Visible spectrophotometric method as described in Table 3.6. These absorbance values were used to determine the percentage removal efficiencies which are shown in Figure 3.6.

**Table 3.6: Absorbance values of Dicloran at various initial concentrations across contact times ( $t = 15, 30, 60$  min).**

| Initial Concentration (mg/L) | Control | Treated Sample (15 min) | Treated Sample (30 min) | Treated Sample (60 min) |
|------------------------------|---------|-------------------------|-------------------------|-------------------------|
| 15 ppm                       | 0.477   | 0.162                   | 0.192                   | 0.212                   |
| 25 ppm                       | 0.874   | 0.272                   | 0.462                   | 0.711                   |
| 50 ppm                       | 3.000   | 0.192                   | 0.313                   | 0.584                   |

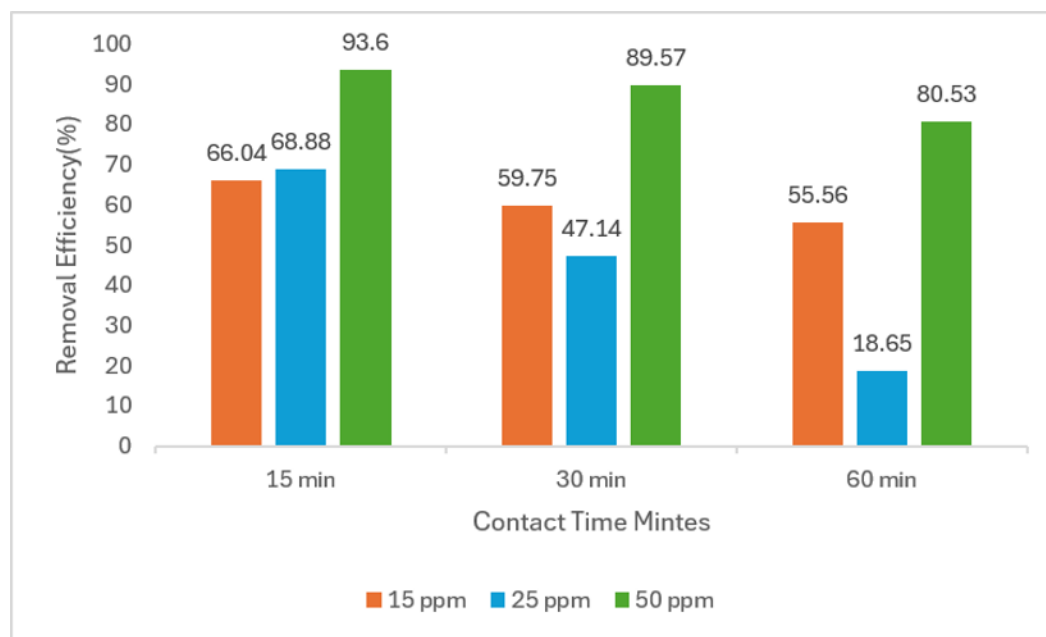


**Figure 3.6: Percentage removal efficiency of Dicloran by Granular Activated Carbon (GAC) at varying contact times (15, 30, and 60 minutes) at different initial concentrations.**

The experimental results for all the parameters tested show that there is a very dynamic kinetic profile in the system with a sharp initial uptake and a varying degree of rebound of the effluent concentration as the contact time approaches the 60"-minute" mark. In each concentration step the lowest absorbance recorded in the effluent was the same, for peak performance in the column, the early 15"-minute" interval was consistently recorded throughout all concentration steps.

The initial stage of adsorption is a fast process because the sorbent (fresh GAC bed) has a large number of completely empty, highly activated external active adsorption sites and macro-pores. At this early stage the concentration difference between liquid and unexposed solid carbon surface is the highest and external film mass transfer is high with high retention (Lach & Szymonik, 2019).

A clear and consistent trend of increasing effluent absorbance is seen throughout all profiles as continuous gravity flow moves to 30 and 60" minutes". The rise at this point indicates the classic progression towards column breakthrough, active site saturation and the possibility of displacement of the solute in the packed bed matrix.

The subsequent molecules to be targeted will then have to pass through the narrow micro-pore and meso-pore network through intra-particle diffusion, which will be hindered with very high steric and mass transfer resistances (Lach & Szymonik, 2019). This is because the flow is continuous and the functional surface pathways inside the fixed bed height are gradually depleted and a fraction of unadsorbed Dicloran molecules is lost into the final effluent stream resulting in observed reduction in removal performance with time.

### **3.7.1 Breakdown of Retention Dynamics**

The temporal retention profiles were also decomposed and analyzed for each individual initial working concentration step to further explain the specific mass transfer pathways and kinetic behavior changes in the packed bed.

#### **3.7.2 15 ppm Profile: Rapid Uptake and Early Equilibrium**

The absorbance response is steep initially and then level off for the contact time at the low concentration boundary of 15 mg/L. The absorbance level is initially at an untreated control level of 0.477 then drops sharply to 0.162 after 15 minutes, which corresponds to a high removal efficiency during this early stage to be 65.99%. This decrease is due to the instant molecular

adsorption at the highest energy external active sites of the fresh adsorbent surface. After this quick initial step down, there is a slight increase until 0.192 is reached at 30 minutes (59.71% "R") and 0.212 at 60 minutes (55.56% "R"). The absorbance of effluent is also increasing slowly, indicating a certain equilibration of the system locally, or some slight displacement of the solutes with the approach of the system to a steady state at low mass-loading.

### **3.7.3 25 ppm Profile: Moderate Loading and Desorption Wave**

There is a distinct V-shaped curve when the adsorption and desorption is recorded over 60 minutes, at 25 ppm. The system is first observed to absorb a large amount of the baseline absorbance of 0.874 to the minimum absorbance of 0.272 at 15 minutes and attains the maximum operation removal efficiency of 68.88%. A sharp and steady performance inversion occurs beyond a 15-minute period, however. The effluent absorbance rapidly increases to 0.462 at 30 minutes (47.14% "R"), and it increases to 0.711 at 60 minutes, resulting in a total removal efficiency of only 18.65%. This is a very steep rise, suggesting appreciable local desorption or solute displacement. It indicates that the number of active sites at the inlet to the column is rapidly depleted under moderate mass loading, leading to a fast saturation front moving down the bed in one hour.

### **3.7.4 50 ppm Profile: High-Capacity Adsorption and Pore Saturation**

The system has an intensive initial removal phase at the highest initial concentration of 50 ppm, followed by a gradual increase in concentration with the movement of the mass transfer zone. It is found the initial absorbance of the untreated sample in the profile is 3.000 and after 15 minutes, it is 0.192, indicating a very high initial removal percentage of 93.60%. The huge initial loading creates an enormous concentration gradient that is a strong thermodynamic pump to drive a fast movement of solutes into the pore network of the adsorbent.

Following this peak performance, the absorbance steadily rebounds to 0.313 at 30 minutes (89.57% "R") and 0.584 at 60 minutes (80.53% "R"). The overall net decrease is still large for the period because the internal pores are saturated at a high density, but the increase after 15 min verifies the rate of pore network saturation of the column due to the high influx rate, which will eventually lead to breakthrough.

### 3.8 Dicloran: Effect of Neutral pH on Removal Efficiency

A fixed-bed GAC column was used to test the effect of neutral pH with three different initial concentrations of Dicloran. A sample was taken from each prepared solution before the sample was fed into the column to obtain the untreated control aliquot ( $C_0$ ) and the remaining solution was passed through the GAC-packed bed continuously to obtain the treated effluent sample ( $C_t$ ). The absorbance values ( $C_0$  and  $C_t$ ) determined by the UV-Visible spectrophotometer were then used for calculating the percentage removal efficiency (%R). The results are provided in Table. 3.7 The removal efficiencies is presented in Figure 3.7, under neutral pH conditions,

*Table 3.7: Removal efficiency of Dicloran at neutral pH*

| <b>Initial Concentration<br/>(mg/L)</b> | <b>Untreated<br/>Control (<math>C_0</math>)</b> | <b>Treated<br/>Sample (<math>C_t</math>)</b> |
|-----------------------------------------|-------------------------------------------------|----------------------------------------------|
| <b>15 ppm</b>                           | 0.397                                           | 0.238                                        |
| <b>25 ppm</b>                           | 0.711                                           | 0.512                                        |
| <b>50 ppm</b>                           | 1.266                                           | 1.076                                        |

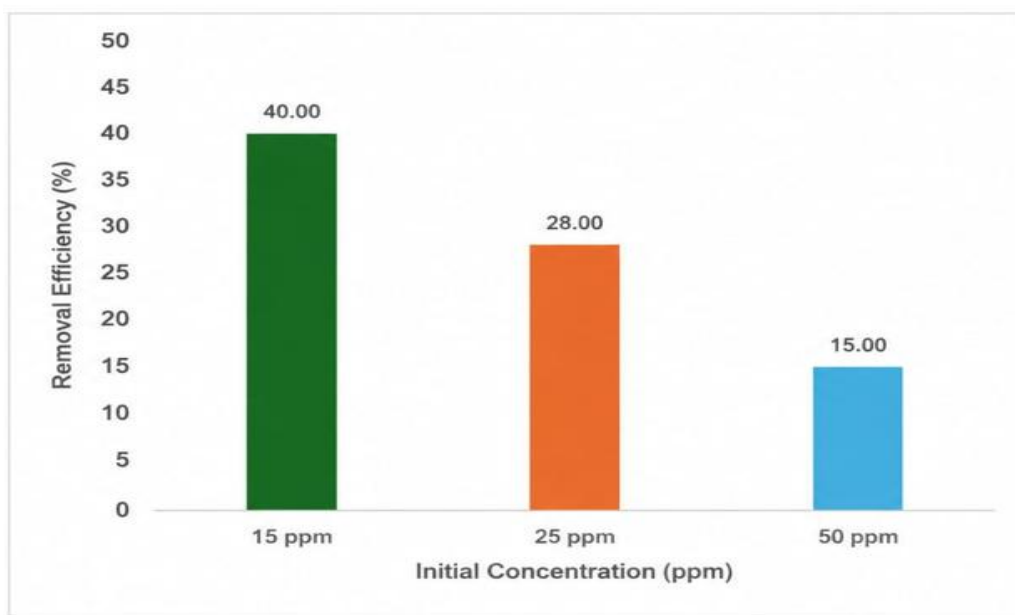


***Figure 3.7: Dicloran removal efficiency (%) at neutral pH for various initial concentrations***

When the pH was neutral, Dicloran demonstrated a definite negative correlation between initial concentration and removal efficiency. The removal efficiency was the highest at the lowest initial concentration (15 ppm) at 40.00% removal. The removal efficiency decreased to 28.00% when the initial concentration was increased to 25 ppm. Removal efficiency was further decreased to 15.00% with a further increase of concentration to 50 ppm.

The improvement of the removal efficiency at 15 ppm may be explained by the increased amount of adsorption sites compared to the amount of Dicloran molecules in solution. A higher percentage of Dicloran molecules can interact with the number of active sites on the GAC surface at this lower concentration. The more molecules of Dicloran that entered the column, the more that were required for the limited number of adsorption sites, as the concentration of Dicloran in the column increased from 15 ppm to 25 ppm. The higher concentration gives the higher concentration gradient and the driving force of mass transfer, but the concentration of GAC is fixed that has a limited number of adsorption sites.

The removal efficiency was greatly reduced at the maximum concentration (50 ppm) to 15.00%. The decrease is most likely due to the gradual occupation and saturation of the available adsorption sites inside the GAC bed. The more Dicloran molecules bind to the sites, the fewer remaining sites will be available for additional adsorption. This leads to higher percentage of the pharmaceutical molecules passing through the column without being removed, therefore

reducing the overall removal efficiency.

In general, the results indicated that neutral pH conditions favored adsorption, with increasing initial Dicloran concentration resulting in a decrease in removal efficiency, from 40.00% at 15 ppm to 28.00% at 25 ppm and 15.00% at 50 ppm. This behavior shows that the adsorption capacity of the fixed GAC bed decreases with the increase of the concentration of Dicloran in the influent. This general concentration dependence of the limitation is also described in the neutral-pH part of your existing thesis, in which you will see that as the concentration increases, so will the rate at which the available adsorption sites are filled.

### 3.9 Dicloran: Effect of basic pH on Removal Efficiency

The concentration difference of Dicloran was investigated by systematically varying the initial concentration in the untreated baseline at three concentrations: 15 mg/L (ppm), 25 mg/L (ppm), and 50 mg/L (ppm). The concentration of the post-column effluent was measured downstream the gravity fed system. The absorbance values of untreated sample of water ( $C_0$ ) and treated sample of effluent ( $C_t$ ) using UV-Visible spectrophotometric method. Table 3.8 shows the absorbance values of untreated samples of water ( $C_0$ ) and treated effluent sample ( $C_t$ ). With these absorbances, the percentage removal efficiencies were calculated and are shown in Figure 3.8.

***Table 3.8: Absorbance and removal efficiency of Dicloran at basic pH.***

| <b>Initial Concentration<br/>(mg/L)</b> | <b>Untreated<br/>Control (<math>C_0</math>)</b> | <b>Treated<br/>Sample (<math>C_t</math>)</b> |
|-----------------------------------------|-------------------------------------------------|----------------------------------------------|
| <b>15 ppm</b>                           | 0.397                                           | 0.140                                        |
| <b>25 ppm</b>                           | 0.711                                           | 0.162                                        |
| <b>50 ppm</b>                           | 1.266                                           | 0.715                                        |

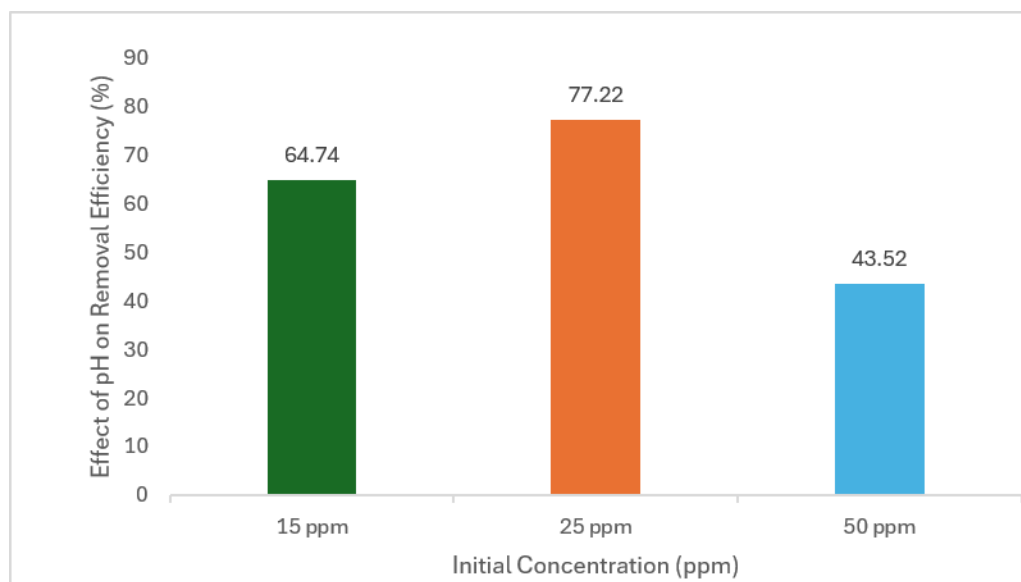


**Figure 3.8: Dicloran removal efficiency (%) under basic pH conditions.**

There is good efficiency in removing the Dicloran at the initial concentration of 15 ppm, while the treated samples of 25 ppm and 50 ppm show relatively poor efficiency. The GAC column was able to remove Dicloran by 64.74% with the initial concentration of 15 ppm under basic pH conditions. The system was able to achieve the best removal efficiency, 77.22%, at the initial loading of 25 ppm. But in the case of an increased mass loading of influent to 50 ppm, the removal efficiency reduced to 43.52%, since the excess amount of drug molecules present in the influent transcended the column bed without binding to it. The concepts of localized mass-loading rates, concentration gradient driving force and active site availability can be used to analyze this performance behavior. Under basic pH conditions, the electrostatic repulsion or hydrophobic interactions between the Dicloran molecular structure and the functional matrix of GAC affect its adsorption capacity (Pratap et al. 2025). A higher concentration (15 ppm to 25 ppm) increases the driving force for the mass transfer at the liquid-solid boundary layer which would facilitate effective partitioning into active binding sites. At 50 ppm, however, the ratio of available active adsorption sites to bulk fluid molecules decreases considerably. The micro-pores and open functional pathways at the inlet of the column are quickly depleted (Rafati et al., 2019; Varela et al., 2024). The rate of site saturation in this basic pH range is fast since there is no specific surface modification to the GAC to create high density matrices and the bed volume is constant. As the number of active binding sites increases, more would be filled, leading to a decrease in the remaining unoccupied binding sites and hence diminishing additional film and Intra-particle diffusion, causing excess unadsorbed drug molecules to flow directly into the end treated effluent

stream (Pratap et al., 2025). This behavior is consistent with other literature reports of continuous fixed-bed systems with fixed active-site boundaries. If the pollutant concentration is high, studies on the organic micro-pollutants under sub-optimal chemical matrices show that the percentage of removal decreases as the pollutant is introduced into the upper boundary layers, above and beyond the capacity of the boundary layers (Rafati et al., 2019). To test this, Pratap et al. (2025) showed that the initial concentration can increase the solute breakthrough and decrease the bed's capacity over time.

### **3.10 Neutral Capacity Limitations:**

Under neutral conditions, both pharmaceuticals show performance restrictions as concentrations scale upward, showing that standard physical site layers quickly saturate.

#### **3.10.1 pH Specialization:**

Their response to chemical adjustment highlights distinct pathways. Ibuprofen yields its best performance at lower concentrations when converted to a basic environment (achieving 30.00% removal at 40 ppm). Conversely, Dicloran exhibits a highly stable and strong affinity for acidic environments, with its treated effluents showing massive purification gains across all initial levels, peaking at 77.22% removal at 25 ppm.

These findings indicate that running the gravity column with chemical optimization tailored to the target pollutant's properties (basic settings for lower-concentration Ibuprofen and acidic settings for general Dicloran streams) is a reliable strategy for maximizing water treatment efficiency.

## CONCLUSION

This work was aimed at the evaluation of the removal of ibuprofen and dicloran from an aqueous solution, in a gravity-driven GAC fixed-bed adsorption column in controlled laboratory conditions.

- Regarding the first objective, the GAC column was able to eliminate both pharmaceutical compounds. Under neutral pH, ibuprofen achieved a maximum removal of 22.73% at 60 ppm while dicloran achieved a maximum removal of 18.45% at 15 ppm. Dicloran consistently performed better than ibuprofen under chemically optimized conditions, with up to 77.22% removal under acidic pH conditions, because it is more hydrophobic, has more molecular properties, and is able to form stronger  $\pi$ - $\pi$  electron interaction with the surface of the activated carbon.
- As far as the second objective is concerned, there was a classic inverse relationship between the initial dicloran concentration and the removal efficiency, with lower concentrations resulting in higher removal efficiencies at neutral pH. The solution pH was a critical operating variable and the adsorption of dicloran was significantly enhanced with lower pH (pH 5.0) with up to 77.22% dicloran removed. In contrast, changing ibuprofen to basic pH (pH 10.0) had a negative effect on the performance of the high concentration because of the very strong electrostatic repulsions between the anionic drug molecules and the negatively charged GAC matrix. Contact time experiments verified that the initial adsorptive rate was very rapid, reaching a maximum in about 15 minutes, but as the active zone of the column was depleted, the absorbance of the effluent increased slowly over a period of 60 minutes until breakthrough was reached.
- The results substantiate the effectiveness, decentralization and cost-effectiveness of multi-layer GAC adsorption technology for the removal of pharmaceuticals from water and are directly relevant to the UN SDG 3 (Good Health and Wellbeing) and UN SDG 6 (Clean Water and Sanitation).

## RECOMENDATIONS

The study was conducted at laboratory scale, using synthetic solutions, for the removal of ibuprofen and dicloran, in a fixed-bed GAC column. Recommendations for future research are suggested based on the findings as follows:

- First, to test the column with real wastewater from hospital effluents, pharmaceutical manufacturing outfalls or surface water of Pakistan instead of synthetic solutions. This would enable a better evaluation of the column performance in a real environment in which several matrix substances compete.
- Secondly, the adsorption isotherm and adsorption kinetic modeling by Langmuir and Freundlich systems should be performed to mathematically calculate the maximum adsorption capacity ( $q_{\max}$ ) of the GAC bed. This would optimize design parameters, including empty bed contact time (EBCT) and enable larger scaled-up treatment units to be designed.
- Thirdly, the co-elimination of both ibuprofen and dicloran in a combined mixture should be explored. As real-world pharmaceutical effluents are complex multi-compound mixtures, the study of competitive adsorption and molecular displacement mechanisms would provide more relevant results than the study of single pharmaceuticals.

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