PHARMACEUTICAL WASTEWATER TREATMENT USING

GRAPHENE OXIDE DERIVATIVES

by

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Acknowledgement

Dedication

To my parents and ammi ji

Abstract

The rising problem of pharmaceutical contamination in different water bodies calls for a swift action in the treatment and removal of these emerging pollutants from water using advanced methods. Adsorption is employed as a primary treatment method for treating water containing Diclofenac sodium, Aspirin and Paracetamol (Acetaminophen). Two graphene oxide-based adsorbents namely, reduced graphene oxide magnetite (RGOM) and graphene oxide nickel ferrite (GONF) were used for the adsorption process. Batch experiments were conducted to find the optimum conditions such as contact time, adsorption dosage, pH of the solution, temperature and initial concentration. These optimum values were then used to perform a number of experiments in order to fit isotherm models such as Langmuir, Freundlich and Temkin model. Pseudo-first and pseudo-second order kinetic models were also used to fit the kinetic data. Thermodynamic properties such as change in Gibbs free energy, enthalpy and entropy were then calculated to get further insight of the adsorption process. RGOM showed better results with the removal efficiency of more than 90% for the above-mentioned pharmaceuticals. The removal efficiency of GONF to remove Diclofenac sodium, Aspirin and Paracetamol was around 20%, 40% and 65% respectively. Reusability of both RGOM and GONF was studied for economic aspects of their applicability. Based on its better performance, RGOM was also used to study continuous fixed-bed adsorption of all three pharmaceuticals and the effect of flow rate of contaminated water and the bed depth of adsorbent in the column was studied. The adsorption data was fitted using different continuous adsorption models to obtain adsorption parameters.

Keywords: *Pharmaceutical, Adsorption, wastewater treatment, graphene oxide, nanocomposites*

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List of Abbreviations

AC   Activated carbon

AOP   Advance oxidation processes

API   Active pharmaceutical ingredients

ASP   Aspirin

ATC   Anatomical Therapeutic Chemical Classification System

BET   Brunauer Emmett Teller analysis

DCS   Diclofenac sodium

EDC   Endocrine disrupting chemicals

EDS   Energy dispersive X-ray spectroscopy

FTIR   Fourier Transform Infrared spectroscopy

GO   Graphene Oxide

GONF   Graphene oxide nickel ferrite

MBR   Membrane bio-reactors

MTD   Minimum therapeutic dosage

NSAID   Non-steroidal anti-inflammatory drugs

PAR   Paracetamol (Acetaminophen)

PFO   Pseudo-first order kinetic model

PPCPs   Pharmaceuticals and personal care products

PSO   Pseudo-second order kinetic model

RGOM   Reduced graphene oxide magnetite

SEM   Scanning Electron Microscopy

WWTP   Wastewater treatment plants

Chapter 1. Introduction

This chapter provides a short introduction about the arising issue of water scarcity and the importance of wastewater treatment. Details on pharmaceuticals and personal care products (PPCPs) as emerging contaminants and the need for their removal before entering water bodies is presented. Thesis objectives and the contribution of this research is also presented. Finally, a brief overview of the thesis organization is offered.

1.1. Overview

Water is considered the most important constituent for the survival of any living being. Although abundant in quantity, the quality of water available for different purposes is being seriously adulterated. Hence, the difference between the demand and supply of usable water is increasing day by day. This has led to an overwhelming concern about wastewater treatment and its reuse to overcome this significant issue. With an estimated global production of millions of tons, and still increasing due to their high demand for both human and veterinary usage, PPCPs are one of the most consumed products worldwide [1]. Contrary to the other chemical industries, the consumption of water in pharmaceutical industries is not very high but the wastewater generated by these industries is highly polluted and unsafe to the environment due to the presence of stable, persistent and biologically active organic components [2, 3]. Moreover, other direct or indirect sources such as hospital waste, treatment plant effluents and improper manufacturer's disposal have the potential to contaminate different water bodies. The presence of these pharmaceuticals in wastewater has led to a serious concern over their effect on human and animals because of their bioaccumulation in the food chain [4]. Therefore, serious efforts are being made in the recent years to remove these contaminations from wastewater in order to reduce their effect on environment.

1.2. Thesis Objectives

The main objective of the proposed work is to investigate and analyse the efficiency of graphene oxide derivatives for the removal of pharmaceutical compounds from wastewater. The aim is to use adsorption as a primary treatment method to treat process water generated from pharmaceutical industries. Optimum conditions such as

adsorption dosage, contact time, pH, temperature and concentration will be evaluated. Different isotherm and kinetics models will be fitted to describe the adsorption process. Reusability study was also be performed using the recycled adsorbent for three cycles in order to get an insight from an economic point of view. Continuous fixed-bed column study will be conducted in the end with the adsorbent with better efficiency.

1.3. Research Contribution

This research work contributes in the following ways:

- This work will help understanding the importance of removing emerging contaminants from different water reservoirs.
- This work provides optimum conditions for individual removal of most frequently found pharmaceuticals from water.
- The study also provides conditions and data related to adsorption of pharmaceuticals in a continuous fixed-bed adsorption column.
- This study covers the topics such as effect of flow rate and bed depth in a fized-bed column for the applicability of process on industrial scale.

1.4. Thesis Organization

The rest of the thesis is organized as follows: Chapter 2 provides background about the rising issue of the presence of pharmaceuticals in water bodies. The sources, effects and regulations are discussed. Different removal techniques are described for comparative reasons. A detailed view of adsorption process, isotherms, kinetics, mechanism and thermodynamics along with an overview of adsorbents used in this study is presented. Chapter 3 comprises of the materials and methods used in this study. Chapter 4 discusses the results found in the research work. Finally, Chapter 5 concludes the studies and recommends any further studies.

Chapter 2. Background and Literature Review

2.1. Pharmaceuticals Wastewater Sources, Effects and Regulations

Many pharmaceuticals compounds, sometimes with a concentration as high as in mg/L, is detected in water generated by pharmaceutical manufacturing sites making them the main source of pharmaceutical contamination in water bodies. This water is eventually discharged into the environment causing pollution [5]. Maintenance and cleaning procedure in these industries also produces large amount of wastewater [6]. Sewage effluent also play a role in contaminating wastewater with pharmaceuticals. Hospital waste discharge, excrements from humans and animals using these drugs are different routes for the presence of these contaminations in sewage water [7, 8]. The conventional treatment technologies have been found to be inefficient in the removal of PPCPs [6, 9]. This is attributed to the biological persistence and bioaccumulation of the active pharmaceutical ingredients (APIs) present in the aquatic environment. The difference in structure, properties and concentration of pharmaceutical compounds in wastewater discharged from the different industries also make it difficult to efficiently remove them from water[9]. Hence, the partially treated water finds its way to the aquatic environment posing serious threats to different ecological species.

Generally, three main toxicological effects are attributed to the presence of pharmaceuticals in wastewater including chronic toxicity, carcinogenicity and reproductive, developmental and neurotoxicity [10]. Serious concern is arising worldwide, due to inadequate toxicological information and the potential effect of long term exposure to pharmaceutical and personal care products [11]. Studies are being conducted in order to find whether the presence of these contaminations pose a threat to human health. Analysis in different regions like United Kingdom, United States of America and Australia have shown that the presence of these contaminants is very low, sometimes 1000 folds less than the minimum therapeutic dose (MTD) [12]. Endocrine disrupting compounds (EDCs) in water has shown a potential threat due to their disruptive activity on human endocrine system [9, 13]. However, the effects of these contaminants on other aquatic organisms are adverse. Many studies have shown that long term exposure to low concentration of these pharmaceutical compounds have led to drastic effects in aquatic and marine life, such as acute and chronic damages [14, 15],

behavioural changes [16], changes in sexual orientation of fish [17] and alligators [18, 19], tissue accumulation [20], decrease in reproductive efficiency [21], reduction in fecundity in fish [22], and changes in migratory patterns of salmon [23]. As an example, the cause of extinction of vultures in the subcontinent region was found to be a common drug called diclofenac [24]. An overview of the sources and effects of pharmaceuticals in water is presented in Figure 1 [25].
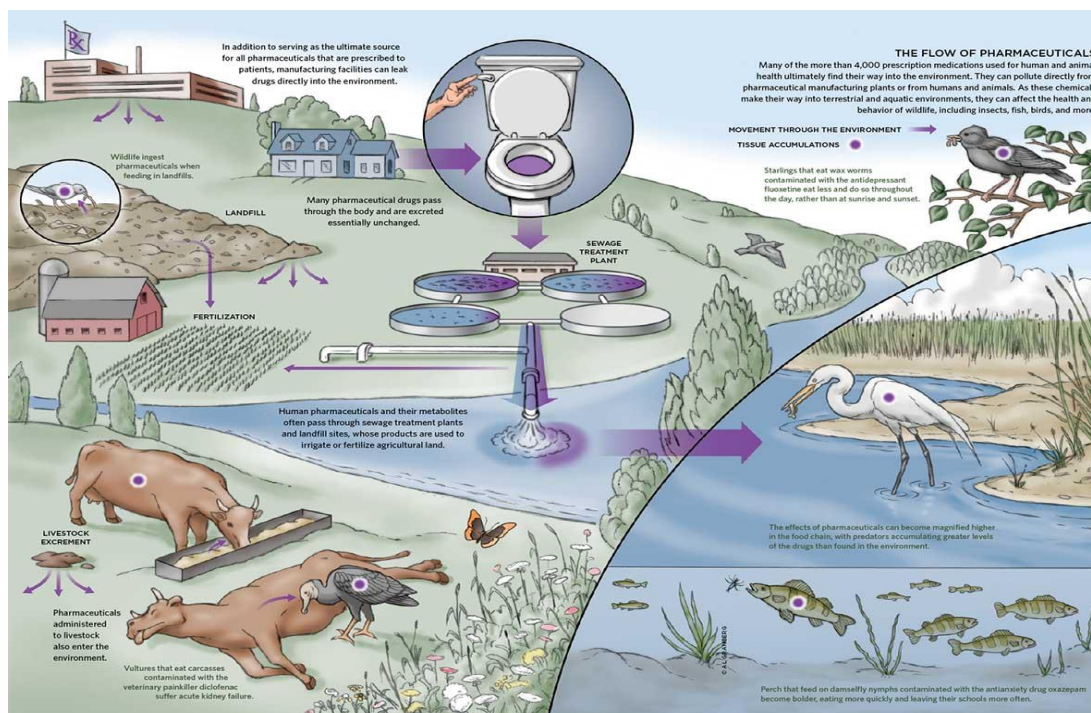
Figure 1. Sources and Effects of presence of pharmaceutical compounds in wastewater [25].

To this day, no regulations exist to check and control the levels of pharmaceuticals in waster, either waste or drinking, according to the United States Environmental Protection Agency (EPA). Although EPA considers eight pharmaceuticals as hazardous waste, only four have been added to the pharmaceutical contaminant candidate list [26].

Many countries in the European Union such as Norway and Germany are urging the legislative authorities to introduce more strict rules and regulation in order to tackle the effect of pharmaceutical contaminants at both state and union level [27].

China and India, two of the largest producers of pharmaceuticals and personal care products, do not have any regulations for the assessment of pharmaceuticals in wastewater [28] nor are there any specific guidelines [29] which reflects the need to

introduce more protocols and procedures to overcome the issue of PPCPs in environment.

2.2. Classification of Pharmaceuticals

So far more than 3000 PPCPs have been developed as human and veterinary medication [30]. These pharmaceuticals are categorized in various groups depending upon their certain properties and functions e.g. chemical or physical properties, mode of action, pharmacological activity, effects and ecological effect [31]. The World Health Organization (WHO) established a global standard for drugs classification known as Anatomical Therapeutic Chemical (ATC) Classification System. This system classifies each drug in five different levels [32]. Another important classification is the World Health Organization (WHO) model list of essential medicines. This classification includes 30 major classes and more than 70 subclasses containing most important and effective medicines in health system [33].

Some of the most widely used and most frequently detected pharmaceuticals families are antibiotics, analgesics, cardiovascular drugs. These are discussed briefly here. A few important representative members of these families and their properties are listed in Table 1 while the structures are given in Figure 2.

2.2.1. Antibiotics. Antibiotics are the type of antimicrobial drugs which are used to cure bacterial infections by either killing harmful bacteria or inhibiting its growth [34]. More than 30% increase in the global consumption have been observed in the last decade [35]. Due to continuous introduction in environment, antibiotics are regarded as pseudo-persistent compounds.

These compounds are especially designed to kill the microorganisms or inhibit their growth. The presence of several antibiotics has been detected in wastewater. Since about 90% of antibiotics are excreted from human bodies, it raises a lot of concern on their occurrence and persistence in the environment [36].

2.2.2. Analgesics and anti-inflammatory drugs. Analgesics and anti-inflammatory drugs are used for pain relief and in the treatment of inflammation. Consumption of these drugs are also high in both developed and developing countries.

This class is further divided into subclasses such as pain relievers (analgesics), fever reducing (antipyretic) and anti-inflammation (NSAIDs) [37]. Drugs such as

acetaminophen (Paracetamol), ibuprofen and diclofenac are regarded as serious pollutants since they are persistent in both ground and surface water [38].

2.2.3. Antihypertensives and cardiovascular drugs. Antihypertensive and cardiovascular drugs are a very wide range of drugs used for heart and blood circulation related problems. These are among the most prescribed drugs in United Sates of America. Depending on their mode of action, these drugs are categorized into various subclasses such as beta-blockers, antilipemic and anticoagulants [39]. Just like the other two important classes, these drugs are also frequently found in wastewater and hence the removal of these compounds is necessary [31].

(a) Amoxicillin

(b) Aspirin

(c) Atenolol

(d) Atorvastatin

(e) Ciprofloxacin

(f) Diclofenac

(g) Enalapril

(h) Ibuprofen

(i) Levofloxacin

(j) Acetaminophen

(k) Sulfamethoxazole
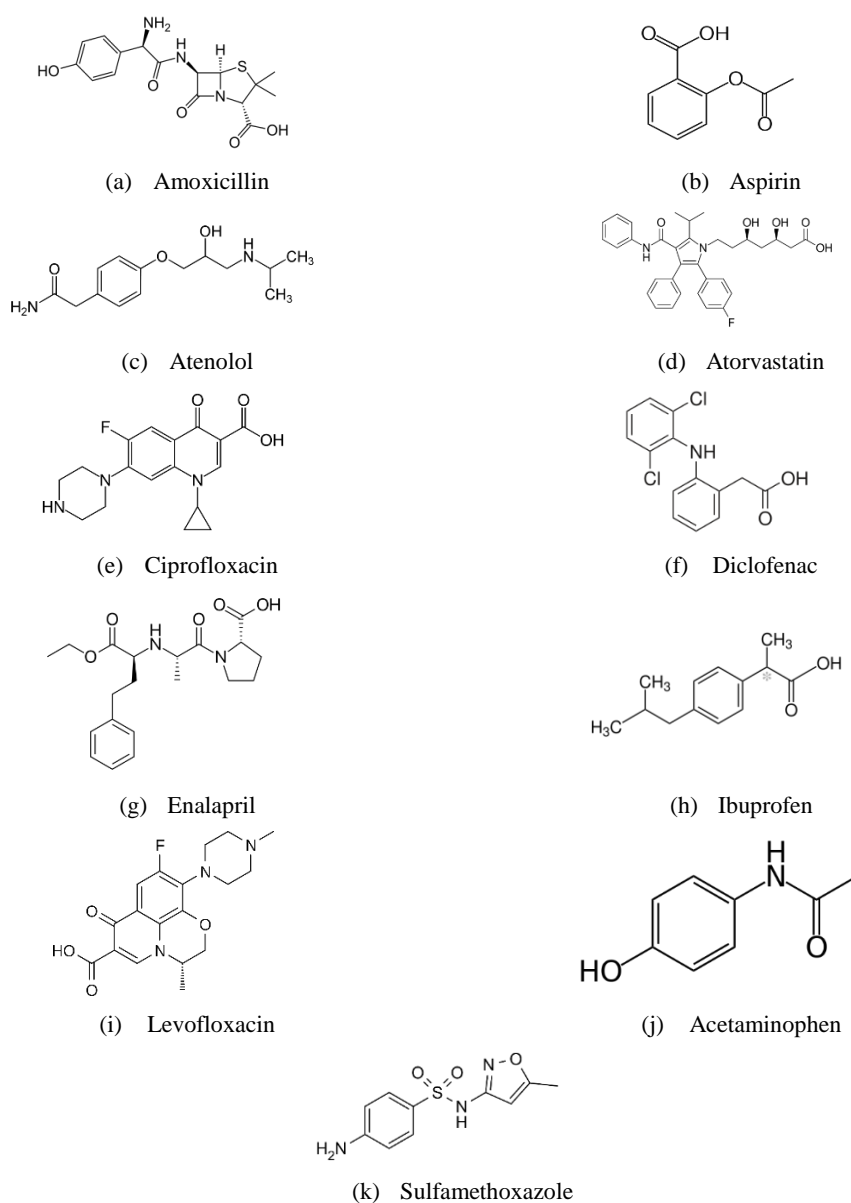
Figure 2. Structure of Pharmaceutical Drugs.

Table 1. Representative compounds of some important pharmaceuticals

Pharmaceuticals	Representative Compounds	Molecular Weight	pKa Value
Antibiotics			
	Sulfamethoxazole	253.3	1.6
	Amoxicillin	365.4	3.2
	Levofloxacin	361.4	6.24
	Ciprofloxacin	331.3	6.09
Nonsteroidal Anti-Inflammatory Drugs			
	Ibuprofen	206.3	4.91
	Diclofenac Sodium	318.1	4.35
	Acetaminophen	151.2	9.38
	Aspirin	180.2	3.49
Cardiovascular Drugs			
	Atenolol	266.3	9.6
	Atorvastatin	558.6	4.3
	Enalapril	376.4	2.97

2.3. Removal Techniques

A wide variety of these compounds are generated by the pharmaceutical industry; therefore, the choice of removal techniques is different for each product and manufacturing process. Several factors e.g. production amount, environmental regulations, materials and methods play an important role in choosing the right removal technique. Hence it is an arduous task to specify a certain treatment system to such a complex and diversified industry. The removal methods for PPCPs in wastewater is generally classified into three main categories i.e. physical, biological and chemical treatments. The fourth class is a combined biological and chemical processes in a same process simultaneously [1]. These methods will be discussed briefly.

2.3.1. Biological treatment. One of the most important and extensively used method for the treatment of pharmaceuticals in wastewater is the biological treatment method. This is mainly due to the benefits of having mild operational conditions, harmless sludge disposal and low cost [9, 39].

Two types of processes are used in the biological treatment i.e. the conventional activated sludge process and the membrane bioreactor (MBR). Wastewater treatment plants (WWTP) employ Activated sludge process extensively in the treatment of wastewater. However, presence in low quantity reduces the removal efficiency of pollutants using WWTP [36].

The main mechanism of removal in this process is biodegradation and adsorption along with minimal contribution from volatilization [40-42]. Samaras et al. [43] studied the removal mechanism of different pharmaceutical compounds in WWTP and found biodegradation to be the main mechanism. Jelic et al. [44] concluded in another study that a number of pharmaceuticals were removed due to adsorption in sludge. Hence both biodegradation and adsorption play an important role in the pharmaceutical removal in conventional WWTP. However, the low efficiency can be attributed to low abundance and concentration of degraders and short Sludge Retention Time (SRT) [1, 36].

Membrane Bioreactor (MBR) Technology annex a low-pressure membrane with the conventional activated sludge process which can contain the microorganism due to a physical hindrance. It is considered more efficient in the removal of micro-pollutants than the former process [36]. This is due to several factors e.g. low suspended solids, high pathogen removal, high quality effluent and low sludge production [45].

MBRs are used commonly in the hospital wastewater treatment and found to be more efficient in the removal of many pharmaceuticals such as sulfamethoxazole, acetaminophen and caffeine. However, some of the pharmaceuticals like carbamazepine and gemfibrozil remain untreated [38, 46].

The MBR technology can prove to be very successful and economical for pharmaceutical wastewater due to its low sludge production and high removal percentage. Still a couple of factors including membrane fouling and laborious washing restricts the usage of MBR on large scales [36].

2.3.2. Chemical treatment. It is clear from the discussion above that a conventional wastewater treatment process is inefficient in removing the PPCPs completely. Therefore, there is a strong need for implementing other processes to deal with this wastewater. Chemical treatment is another approach for this purpose. Ozone and other oxidizing agents employed commonly in oxidation processes have found to be effective in the removal of persistent PPCPs from wastewater with very high efficiency [47]. Few commonly used methods are Ozonation, Fenton oxidation, and UV/Hydrogen Peroxide treatment.

Wastewater treatment process use ozone commonly as a disinfectant. It can also be utilized in the removal of certain organic compounds from water through degradation. Through its strong oxidizing ability, it can easily react with water to generate hydroxyl radicals. The mechanism of ozonation in water is controlled by these hydroxyls. Many organic substances such as phenolic compounds, amines, and aliphatic hydrocarbons react with hydroxyl ions to give variety of products [48].

The rate of ozonation is directly proportional to the concentration of these hydroxyl radicals. Ozonation have been successively applied to remove PPCPs from wastewater. Various pharmaceuticals such as sulfamethoxazole and carbamazepine [49], bezafibrate [48], antibiotics [50], paracetamol [51] and steroids [46] have been effectively removed using the ozonation process. Typical studies showed that the ozone tend to remove PPCPs with an efficiency of up to 90% [37]. One of the back draws of ozonation is the generation of toxic by-products [1].

Another significant and recent process used for the removal of different types of contaminations is Fenton oxidation. Hydrogen peroxide and iron salts are used in the presence of metal-based catalysts to generate hydroxyl radicals at acidic conditions. Hence this process is also reliant on the oxidizing capabilities of hydroxyl ions. Several PPCPs from antibiotics and Nonsteroidal anti-inflammatory drugs (NSAID) have been removed using Fenton and Fenton-like processes [52, 53]. This process can also lead to the generation of toxic by-products hence limiting its utilization [1]. Another method employed to get remove PPCPS from water is referred as "photolysis" in which photo-degradation using Ultraviolet (UV) treatment occurs [54]. Breaking the chemical bonding of the contaminants through the use of direct UV exposure is the main idea of the process. Diclofenac [55] and triclosan [56] have been removed using UV photolysis.

However, high efficiency is not observed for the PPCPs removal using this method. Therefore, combining UV light with hydrogen peroxide was suggested in one of the studies which was found to be more efficient [57]. This process is very similar to the above-mentioned processes in terms of mechanism i.e. the generation of hydroxyl radicals from H_2O_2 through UV absorption. On the other hand, UV treatment requires a relatively large dose hence limiting its use [37].

2.3.3. Combined chemical and biological treatment. The production of oxidation resistant intermediates, long time requirements and high costs in chemical treatment and persistency and toxicity of contaminations to microorganisms in biological treatment have led to the combination of advanced oxidation processes (AOP) and biological methods [58].

Various studies have been carried out to find the efficiency and effectiveness of this hybrid method in order to get rid of pharmaceutical contaminants such as tetracycline, cefalexin, carbamazepine and diclofenac [59-61]. Although, better efficiency in removing PPCPs and the intermediates formed during the AOP were observed in this hybrid method, more study is still required to obtain an optimum combination of different parameters governing the process including retention time, temperature, reactor and operating conditions needs [1].

2.3.4. Physical treatment. Advanced physical treatment processes are used as either pre-treatment step to enhance the efficiency of the process [9, 37] or as a tertiary treatment method for the removal of micro-pollutants in order to enhance the effluent quality coming from secondary treatment methods [37]. Membrane technology and adsorption are commonly discussed in this method.

It has been observed that the usage of low pressure membranes are an efficient method for the removal of various PPCPs such as diclofenac and ibuprofen [62]. Yoon et al. [63] used Nano filtration and ultrafiltration membranes to remove pharmaceutical compounds. The Nano filtration was more efficient in retaining PPCPs than the ultrafiltration membranes since the retention is depending upon membrane pore size. Another study [64] showed that the process of Nano filtration and reverse osmosis (RO) with pressure-driven membranes have higher tendency to remove PPCPs from wastewater. Despite showing good results in removal efficiency using reverse osmosis

and nano-filtration, the concentrate disposal is a concerning problem effecting economy [9, 31]. An overview of efficiency of different techniques in the removal of pharmaceuticals is given in Table 2.

Table 2. Comparison of removal efficiency of pharmaceuticals using different techniques

Drug	Technique	% Removal	Remarks	Ref.
Diclofenac	Biological	80	Bardenpho Process	[65]
	Combined	10-60	Bio/UV disinfection	[66]
	Biological	20	Sludge digestion	[67]
	Physical	40	Adsorption	[68]
	Physical	80	Adsorption	[69]
	Chemical	100	Ozonation	[70]
	Chemical	100	Ozonation	[71]
	Chemical	20	Fenton	[72]
Paracetamol	Biological	99	Bardenpho Process	[65]
	Physical	46	Adsorption	[73]
	Physical	70	Adsorption	[68]
	Chemical	53	Ozonation	[74]
	Chemical	90	UV	[75]
Aspirin	Biological	92	Bardenpho Process	[65]
	Biological	81	Conventional WWTP	[53]
	Physical	98	Adsorption	[76]
	Chemical	~80	Electrochemical	[77]

Small concentrations of organic pollutants are also removed from wastewater using one of the most common process called adsorption. Activated Carbon (AC) have

been found to be capable of removing PPCPs especially the endocrine disruptive compounds. Liu et al. gave an extensive review on the removal of pharmaceuticals compounds using AC as an adsorbent [78]. Though the removal efficiency vary from compound to compound, two common issues occurring in the use of AC for adsorption is the decrease in adsorption capacity and deformation of AC in complex [1]. Hence a search for new adsorbents is always on track. Other adsorbent including bio-sorbents, graphene, graphene oxide, carbon nanotubes (CNT) and activated carbon fibres are also used extensively [1]. A detail account on adsorption and adsorbents is given in the next section of this chapter.

2.4. Adsorption

Adsorption is a widely used process applied for many decades in removal of unwanted substances from fluids. In this phenomenon, molecules are transferred from one phase to the surface of another phase, usually solid, forming a distinct layer. Every separation process requires a driving force which is mainly the difference in the property of the substance which need to be separated.

In adsorption, the extent of mass transfer depends on the ability of one component being more readily adsorbed than the other one. The phenomena of adsorption occur when the molecules of adsorbate present in the fluid phase are attracted by the forces present on the adjacent solid surface. These forces are present in all surfaces but mainly depend on total surface per unit mass. This is the reason that some substances in highly porous form exhibit high internal surfaces and hence labelled as "adsorbents".

The selection of suitable adsorbent is the most important and challenging task. A good adsorbent must have large internal surface area, pore size should be large and selective in nature, easy regeneration, long life and good mechanical strength [79].

When a molecule is attached to a surface, it can bind itself either with chemical interaction or physical attraction. The adsorption resulting due to van der Waals forces are referred as physical adsorption while the adsorption which involves electron sharing or exchange are referred as chemical adsorption or chemisorption. A comparison of chemical and physical adsorption is given in Table 3. Adsorption normally occurs in three steps. At first, there is a movement of adsorbate molecules towards the external

surface of the adsorbent. This step is called film diffusion. Secondly, the adsorbate molecules diffuse inside the pores of adsorbent. This step is known as particle diffusion. And lastly, the adsorption takes place on the adsorbent surface [79, 80].

Adsorption process is a major industrial technique and find its use in many applications such as drying of gases, removal of HCl from hydrogen, recovery and purification of steroids and amino acids, removal of organic pigments, colour removal from syrups and gases and separation of olefins and aromatics from paraffin [79]. Adsorption is extensively used for the removal of pharmaceutical compounds from wastewater as well.

Activated Carbon (AC) has been employed for the removal of certain compounds such as sulfamethoxazole, bezafibrate and paracetamol. Graphene and Graphene oxide (GO) are another important adsorbent usually employed for the removal of PPCPs from wastewater [81, 82]. Due to its limitation in capacity and difficult regeneration, adsorption was not very frequently used in early industrial processes. But the increase in number of adsorbent and recent research and development, the situation is changed, and it is now regarded as one of the most efficient ways for wastewater treatment [79].

Table 3. Comparison of chemical and physical adsorption

	Chemical Adsorption	Physical Adsorption
Mechanism	Electron exchange or sharing	Polarization
Type of bonds	Chemical bond	Van der Waals attractions
Strength of bonds	strong	weak
Bonding Energies	≥ 100 KJ/mol	≤ 30 KJ/mol

2.4.1. Adsorption isotherms. Adsorption equilibrium is achieved when enough time has been given to the phase containing adsorbate to remain in contact with the adsorbent so that the adsorption and desorption phases become equal. Usually the capacity of an adsorbent to attach any adsorbate on its surface is governed by two factors, temperature ans the concentration of adsorbate. The concentration here refers to both in solid phase and liquid phase

Adsorption isotherms are developed by keeping the temperature constant and studying the distribution of adsorbate in two phases. These isotherms play a vital role in determining the adsorption performance, analysis and operations. Several different two-parameter models have been developed to study the behaviour of isotherms [79, 83]. Some of the important ones are discussed here.

Langmuir isotherm model. Langmuir Isotherm model was first developed by Langmuir in 1916 to study the adsorption of gas on a solid phase (activated carbon). The governing mathematical expression is given in Eq. 1 [84].

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

(1)

Whereas the linear form of this equation is as follows

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

(2)

where Q_e is the quantity of adsorbate adsorbed at equilibrium (mg/g), Q_m is the maximum adsorption capacity of the adsorbent (mg/g), C_e is the concentration of adsorbate at equilibrium (mg/L) and K_L is the Langmuir Isotherm Constant (L/mg). If the adsorption is governed by Langmuir isotherm, a plot of C_e/Q_e along C_e will give a straight line with $1/Q_m K_L$ as an intercept and $1/Q_m$ as slope.

It is important that Langmuir isotherm is based on the assumption that adsorption is occurring in single layer. It also assumes that there are fixed number of active sites for the adsorbate to get itself attached with adsorbent, no interaction and steric hindrance between the adsorbed molecules and adsorbent surface, no phase transitions, homogenous distribution of energy on the surface and the achievement of equilibrium and reversibility [85].

Freundlich isotherm model. Freundlich isotherm is not restricted to monolayer adsorption only but also considers multilayer adsorption. A linearized form of this model is represented in Eq. 3.

$$logQ_e = logK_F + \frac{1}{n}logC_e \tag{3}$$

where K_F and n are Freundlich constants describing adsorption capacity and adsorption intensity respectively. While Q_e and C_e are the adsorbate quantity adsorbed and equilibrium concentration in mg/g and mg/L respectively.

Adsorption is represented by Freundlich isotherm if the graph between log Q_e and log C_e gives straight line with slope $1/n$ and intercept log K_F [84].

Temkin isotherm model. Unlike Freundlich model, Temkin isotherm model revolves around the assumption that the decrease in heat of adsorption is not logarithmic but linear and ignores very low or very high concentrations. A linear form of Temkin model is given in Eq. 4.

$$Q_e = BlnK_T + BlnC_e \tag{4}$$

where K_T is the Temkin Isotherm equilibrium binding constant (L/g), B is Temkin constant and T is the absolute temperature (K) [69, 70].

2.4.2. Adsorption kinetics. The study of adsorption kinetics is important in understanding the adsorption rate and, mechanism and effectiveness. Kinetics of adsorption also play an important role in the designing of adsorption system [86]. Several different models have been developed so far to study the adsorption kinetics. Common models such as pseudo first order and pseudo second order are described here.

Pseudo first order model. The pseudo first order kinetic model was given by Lagergren and Svenska in 1898. Pseudo-first order kinetics model (PFO) assumes that while the adsorption reaction is taking place, the concentration of one of the reactants remains almost constant. In other words, one of the reactants is in abundant amount and hence the overall change on its concentration is negligible.

The linear form is given in Eq. 5.

$$\ln(Q_e - Q_t) = -K_1t + lnQ_e \tag{5}$$

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where Q_t is the amount adsorbed at any time t (mg/g), k_1 is the rate constant for pseudo first order sorption (min^{-1}). The constant k_1 can be obtained by plotting (Q_e - Q_t) against time t [84].

Pseudo second order model. Linearized form of pseudo second order kinetic model [87] is given in Eq. 6.

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{K_2 Q_e^2} \tag{6}$$

where k_2 is the rate constant for pseudo second order kinetics in (g mg^{-1}min^{-1}) and is calculated by plotting t/Q_t vs time t [70].

2.4.3. Adsorption thermodynamics. The adsorption process cannot be transformed into practical use without the calculations of some important thermodynamic properties such as change in Gibbs free energy (ΔG), change in entropy (ΔS) and change in enthalpy (ΔH).

To calculate the thermodynamic properties, Sip's equation [88] is used which is given in Eq. 7

$$Q_e = Q_e^{th} \frac{K_{eq} C_e^{n_s}}{1 + K_{eq} C_e^{n_s}} \tag{7}$$

where Q_e^{th} (mg/g) is the maximum theoretical capacity and n_s is the Sips constant. Eq.8 is used to estimate the equilibrium constant, K_{eq} as a function of temperature. Once the value of Q_e^{th}, n_s and K_{eq} is determined through regression analysis, the Van't Hoff plot is obtained. The change in Gibbs free energy is then calculated using Eq. 8 given by Yu et. al [89].

$$\Delta G = -RT ln K_{eq} \tag{8}$$

where R is the general gas constant (J/mol K) and T is temperature (K). Change in enthalpy and entropy of the system can be then calculated by plotting a graph between $1/T$ and K_{eq}. Equation 9 can be then utilized for the calculation of ΔH and ΔS.

$$ln K_{eq} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{9}$$

The sign of entropy gives an idea about the degree of freedom for adsorbate, the sign of enthalpy change determines whether the adsorption is endothermic or

exothermic, while the sign of Gibbs free energy provides information about the spontaneous nature of process [90]. The graph between 1/T and K_{eq} is usually linear meaning that the enthalpy and entropy change remains constant over the range of temperature. However, sometimes, the system does not fit linearly, and polynomial fitting is utilized [91]. In this case, equations 10-12 are used for the calculation of ΔH and ΔS.

$$ln K_{eq} = a + \frac{b}{T} + \frac{c}{T^2} \tag{10}$$

$$\Delta H = -R(b + \frac{2c}{T}) \tag{11}$$

$$\Delta S = R(a - \frac{c}{T^2}) \tag{12}$$

2.4.4. Continuous fixed-bed column studies. Apart from batch experiments, fixed bed adsorption study is useful for the industrial applicability of water treatment through adsorption. The study was conducted in a long glass tube with a dimeter of 1 cm and length of 50 cm. The flow rate was maintained by continuous addition of contaminated water from the top. Glass wool was placed at the top and bottom of the adsorbent bed to provide mechanical support and to avoid any loss of adsorbent.

The condition in a continuous packed bed column does not remain at equilibrium and different parameters, such as flow rate, affect the adsorption process significantly [92]. Interpretation of adsorption mechanism in a packed bed column depends on several factors such as adsorption kinetics, resistance to film, diffusion mechanism and dispersions in liquid flow.

Several models for adsorption in fixed bed column are reported in literature. Thomas model, Bohart and Adams model, Clark model and Yan et. al. model [93] is applied in this study for the interpretation of data obtained from break through curves (concentration-time profile). The linearized form of these models is given from Eq. 13-16.

$$ln\left(\frac{C_o}{C_t} - 1\right) = \frac{K_{TH}q_o m}{Q} - K_{TH}C_o t \tag{13}$$

$$ln\left(\frac{C_t}{C_o}\right) = K_{AB}C_o t - K_{AB}N_o\left(\frac{Z}{U_o}\right) \tag{14}$$

$$ln\left(\left(\frac{C_o}{C_t}\right)^{n-1} - 1\right) = ln[A] - rt \tag{15}$$

$$ln\left(\frac{C_o}{C_o - C_e}\right) = a\,ln[V] - a\,ln[b] \tag{16}$$

where C_o, C_t, t and n are initial concentration of the pharmaceutical (mg/L), concentration of pharmaceutical at any time t (mg/L), time (min) and Freundlich parameter respectively. K_{TH} and K_{AB} are the rate constants for Thomas and Bohart and Adams model respectively. A and r are parameters for Clark model. V is the volume (mL) whereas a and b are the parameters for Yan et al. model. Z is the bed depth (cm), No is the saturation concentration (mg/L), U_o is the superficial velocity (cm/min), Q is the flow rate (mL/min) and q_o is the adsorption capacity (mg/g).

2.5. Adsorbents

2.5.1. Graphene and graphene oxide. Graphene is a novel member in carbon materials with one atom thick and honeycomb like structure as shown in Figure 3 [94]. The hybridized carbons in graphene are hexagonally in sp2 hybridization bonds. The history of graphene dates to mid-20th century but it was isolated in 2004 by Andre Geim and Kostya Novoselov. Graphene is the basic structural element of many carbon materials such graphite, carbon nanotubes and fullerenes [95, 96].
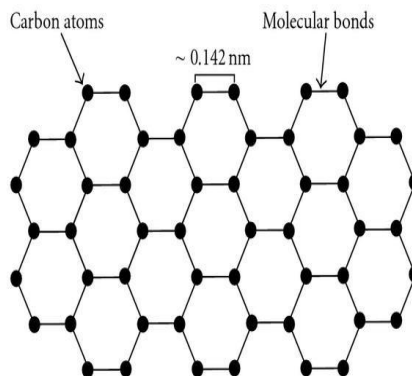
Figure 3. Atomic structure of graphene.

There are several methods used to synthesize graphene. Currently three important techniques are used which are as follows [97]:

- "Mechanical Exfoliation Method" uses scotch tape to split apart graphite into flakes and atomic surfaces. This method is low cost and easy but produce uneven films of graphene and considered to be not suitable for large scale production.
- "Liquid Film Mechanical Exfoliation Method" utilizes sonicated carbon nanotubes mixed with a surfactant to exfoliate graphene from graphite.
- "Highly Ordered Pyrolytic Graphite" is used to synthesize graphene since it is the block unit of bulk material. Naturally occurring graphite cannot be used to manufacture due to difference in in-plane and out-plane dimensions.

Graphene is one of the most popular material owing to its excellent features such as high surface area, tuneable band gap, electrical, thermal and conducting properties. This is the reason that its application area has expanded a lot. The application of graphene includes but not restricted to hydrogen storage, fuel cells, batteries, organic photo voltaic cells, superconductors and electronics [96]. Owing to its high surface area and excellent adsorptive properties, graphene is extensively used in wastewater treatment. It has shown promising performance for the removal of heavy metals, dyes, toxic chemicals and organic compounds [95]. It has also shown good results in the treatment of pharmaceutical wastewater [1].

Like graphene, graphene oxide (GO) has a layered structure but with high numbers of oxygen containing groups on carbon atoms. Hence it is also a single atom layer with carbon, hydrogen and oxygen obtained through the oxidation of graphite [96]. Oxidization of graphite, which is a 3-dimensional (3D) carbon-based material, with strong oxidizing agents produces a highly ordered chemical structure containing clusters of reactive oxygen functional groups.

Graphene oxide was first generated in 1859 using graphite and $KClO_3$ in the presence of HNO_3. Hummer and Offeman gave a better manufacturing method using $NaNO_3$, $KMnO_4$, and concentrated H_2SO_4. The original Hummer's process had the disadvantage of low production and release of toxic gases. Hence modifications have been throughout the previous years to overcome these years [98].

One of the most important property of GO is its good water dispersibility due to the oxygen functionalities present on its structure. It also shows a higher specific area than conventional activated carbon. Due to these properties GO can be used in wastewater treatment as a promising adsorbent as well as in other fields such as energy storage and electronics. Graphene oxide have also shown good results in the removal of pharmaceutical pollutants such as atenolol and propranolol [1, 96].

2.5.2. Graphene oxide based nano-composites. In the past few years, efforts have been to assimilate graphene oxide with other materials in order to have an increase the water dispersible properties of GO. Nanocomposite of Graphene oxide and magnetite has shown good results not only in preserving the original properties but also in their enhancement. These GO based nanocomposites can be very useful in different processes such as photo catalysis, advanced oxidation processes, super capacitors and wastewater treatment [98, 99].

Iron oxide or magnetite (Fe_3O_4) is used considerably in research chemistry due to its unique features. The substance has good magnetic, catalytic and electric properties. Biocompatibility and low toxicity are other factors which enhance its usage in different fields such as catalysis and wastewater treatment. However due to aggregation and formation of large particle due to strong dipolar interactions in aqueous phase, magnetite nanocomposites can lose their activity and specific properties [99]. Therefore, there is a need to immobilize the nanoparticles on certain carriers in order to prevent the loss of these properties.

Several methods have been devised to produce GO based nanocomposites. Some of the important methods are hydrothermal method, electrochemical deposition, In Situ polymerization, Sol-gel technique, Sonochemical treatment, electrospinning, microwave treatment and photo catalysis [98].

GO/Fe_3O_4 nanocomposite have shown favourable results in the removal of different pollutants such as methylene blue [100], Chrysoidine Y [101] and other organic compounds [102]. Hence it can be proposed to be used for pharmaceutical wastewater treatment as well.

Apart from ferrous composites, different metal ferrites are also combined with graphene oxide to achieve tailor made properties [103]. These metallic ferrites are

utilized in different chemical processes such as high silica bauxite digestion [104] and extraction processes for the recovery of heavy metals and precious metals [105]. In wastewater, nano-composite materials derived from metals and graphene oxide have shown good results. Their magnetic properties and chemical stability make them an effective material to be used for the removal of contaminants from water [106-109]. In this work, reduced graphene oxide magnetite (RGOM) is used as an adsorbent.

Nickel ferrite ($NiFe_2O_4$) is one such material which has shown its applications in a range of fields such as drug delivery, magnetic resonance imaging (MRI), gas-sensors, and microwave devices. Good internal surface area, magnetic properties, chemical stability, good sorption capacities, and structural characteristics make it an excellent choice for adsorption process [103, 110-112]. Graphene oxide nickel ferrite (GONF) was used as the second adsorbent in this study for the removal of pharmaceuticals.

Chapter 3. Materials and Methods

3.1. Materials

Pure samples of Diclofenac sodium (DCS), Aspirin (ASP) and Paracetamol (PAR) were provided by Julphar Gulf Pharmaceutical Industries Manufacturers (UAE). Commercial grade graphene oxide (GO) was bought from Xiamen Tmax Battery Equipment (China). Iron (III) chloride ($FeCl_3.4H_2O$), Iron (II) nitrate ($Fe (NO_3)_2.9H_2O$) and Nickel nitrate ($Ni (NO_3)_3.9H_2O$) were obtained from Sigma Aldrich Inc. (Germany). 0.1 M NaCl and 0.1 M HCl was used for pH adjustment. Reduced graphene oxide magnetite (RGOM) and graphene oxide nickel ferrite (GONF) nanocomposites were prepared in laboratory. Ammonia (28%) was obtained from Merck Millipore (Germany). Distilled water was used for all experiments.

3.2. Instrumentation

Distilled water was generated through Water Still Aquatron A4000D. The samples were shaken in temperature controlled multi stack refrigerated shaking incubator (DAIHAN Scientific, China). 0.45 µm syringe filters (MCE Membrane, Membrane Solutions) were used for filtration of treated samples. UV-VIS spectroscopy was done on Cary 50 Conc spectrophotometer (Varian, Australia). Orion 210 A+ basic pH meter was used to measure the pH. Drying of samples were carried out in fan oven (GALLENKAMP, Weiss Technik, UK). Centrifugation was carried out in (HERMLE Labortechnik) Centrifuge. FTIR Analysis was done using FTIR Spectrometer (Perkin Elmer, USA). Scanning Electron Microscope (Tescan Vega 3-Imu, USA) was used for SEM Imaging. TGA Analysis was don using TGA Analyzer (Perkin Elmer, USA). The Brunauer Emmett Teller (BET) Analysis for surface area was done using autosorb®-iQ (Quantachrome Instruments, USA).

3.3. Experimentation

3.3.1. Preparation of RGOM.
Reduced graphene oxide magnetite (RGOM) nanocomposites (mass ratio 1:20) were synthesized using a method reported earlier [100]. In a typical procedure, GO particles were dispersed in 500 mL of distilled water and then sonicated for three hours.

Ammonia solution was then added dropwise to GO suspension until the pH becomes more than 11. $FeCl_2.4H_2O$ was then added very slowly. Vigorous stirring was

carried out for three hours after which the mixture was left overnight. The solution was then filtered and washed with distilled water to remove any ammonia before drying it in a hot air oven at 60°C.

3.3.2. Preparation of GONF. Graphene oxide nickel ferrite was prepared using the procedure described by Lingamdinne et. al. [103]. 1.0 gram of graphene oxide was dispersed in approximately 700 mL of distilled water for 1 hour. 100 mL solution of Fe $(NO_3).9H_2O$ and Ni $(NO_3)_3.9H_2O$ was then prepared separately (wt. ratio 2:1). The solution was added drop-wise in GO suspension with vigorous stirring. pH of the solution was then raised to >12 using NaOH solution.

The solution was then kept at 80°C for 45 minutes keeping continuous stirring. Finally, it was allowed to cool to room temperature before washing several times with distilled water and drying at 60°C in an oven. The final solid product was then crushed to obtain a black powder.

3.3.3. Reusability study. Keeping in mind the economics of the process, reusability study was performed for both RGOM and GONF. The procedure is given below:

Reusability study for RGOM. The pharmaceutical solution (100 mg/L) was stirred with RGOM powder under optimum conditions. RGOM was then separated through filtration and mixed with 0.01 M NaOH solution. The solution was then sonicated for 2 hours and the adsorbent was washed with hot water to remove adsorbate molecules. Finally, the adsorbent was dried at 120°C in an air oven before reusing it for further cycles.

Reusability study for GONF. The pharmaceutical solution (100 mg/L) was stirred with RGOM powder under optimum conditions. After that, GONF was separated through filtration and mixed HNO_3 solution (pH=1.0). In the end, the solution was sonicated and washed with distilled water before drying it in air oven. The dried adsorbent was then further used for next cycle of experiments.

3.3.4. Characterization of adsorbent. The characterization of adsorbent is very important to gain insight of the changes taking place at it surface.

Different techniques used for characterization are briefly described here:

Energy-dispersive X-ray spectroscopy. One of the analytical techniques used in surface characterization of materials is energy-dispersive x-ray spectroscopy (EDS). EDS technique relies on the uniqueness of each element's response to X-ray excitation [113]. The analysis is used in this study to observe the changes occurring on the surface of GO, RGOM and GONF after synthesis.

Scanning electron microscope analysis. Scanning Electron Microscope (SEM) analysis is used to get information about the structure of adsorbents. SEM produces highly magnified images using a beam of high energy electrons on the surface of object under observation in order to generate signals.

Brunauer-Emmet-Teller analysis. Brunauer-Emmett-Teller (BET) method [114] is used in order to have an idea about the available surface area of adsorbents. Nitrogen is used in this analysis as an adsorbate at very low temperature (-195°C). The analysis was done using autosorb® -iQ (Quantachrome Instruments, USA).

Fourier-transform infrared spectroscopy analysis. Fourier-transform infrared spectroscopy (FTIR) analysis is a handy technique to obtain an infrared spectrum of absorption of transmittance of a substance. The analysis gives information about different functional groups present in the structure of object under observation

3.4. Preparation of Calibration Curve

Calibration curve was prepared using known samples of each drug in order to calculate the concentration of drug in water after adsorption experiment. In a typical method, several solutions were prepared at different known concentration and their absorbance was measured using UV visible spectroscopy. The wavelength at which maximum absorbance occurred was chosen and a calibration curve was formed along with trend line and R^2 value

3.5. Adsorption Experiments

Batch mode adsorption experiments were carried out based on One Factor at a Time (OFAT) method to determine the effect of different parameters such as contact time, temperature, pH, initial concentration and dosage of adsorbent. A typical solution of known concentration was prepared for each pharmaceutical drug. The pH was adjusted using 0.1 M HCl and 0.1 M NaOH solutions. This solution was then transferred to 50 mL Erlenmeyer flasks. Known mass of adsorbent was added to the solution and

was placed in a shaking incubator (175 rpm) at the required temperature and time. After that the solutions were filtered using 0.45 µm syringe filters of specific pore size. The absorbance of the solution was then measured through UV visible spectroscopy. The concentration was then calculated using calibration curve. The effect of all parameters was optimized for the removal of pharmaceutical drug from wastewater using different adsorbents.

Chapter 4. Results and Discussion

4.1. Characterization

The adsorbent selected for this study were characterized using several techniques which are discussed briefly in the previous chapter. The scanning electron microscope (SEM) images of graphene oxide, RGOM and RGOM after the adsorption of DCS, ASP and PAR is shown in Figure 4. It can be observed that the structure of graphene changed in appearance after its reduction and the addition of magnetite particles. The rigid structure of GO was converted into soft and fluffy appearance. The adsorption of pharmaceuticals showed the adsorption in SEM images as well. On the other hand, SEM images of GONF, shown in Figure 5 confirmed the attachment of nickel magnetite particles onto the stiff surface of GO. The images of GONF obtained after the adsorption of pharmaceuticals also showed the topographical changes.

The FTIR spectra are shown in Figures 6-9. The peak at around 3400 cm^{-1} signifies the presence of entrapped moisture. The emergence of new peaks at around 800 and 890 and 1720 cm^{-1} in addition to the peaks already present in the spectra of GO confirms the attachment of magnetite particles on its surface and generation of RGOM nanoparticles. The emergence and the change in intensity of peaks such as one at around 750, 1100, 1400 and 1550 cm^{-1} for DCS adsorption and at 600, 1550 cm^{-1} for ASP adsorption and 600, 1250 and 1500 cm^{-1} for PAR adsorption confirms the attachment of pharmaceutical molecules on the surface of RGOM. On the other hand, GONF also showed a change in FTIR spectra with new peaks emerging between 3500 and 4000 cm^{-1} and at around 2300 cm^{-1}. The spectra of GONF after adsorption of DCS. ASP and PAR also showed a change in intensity of different peaks such as at around 3750 and 3850 cm^{-1} and around 500 cm^{-1} hence confirming the adsorption process.

The EDS and BET analysis results of GO, RGOM and GONF surface is shown in Figure 10 and the results are summarized in Table 4. It is evident from the analysis that the weight percent of the elements present on the surface of RGOM and GONF changed from the elemental analysis of GO. GO surface was solely composed of carbon (C) and oxygen (O). While iron (Fe) was significantly present on the surface of both RGOM and GONF and nickel (Ni) was present on the surface of GONF, hence confirming the successful preparation of both composites.

The change in the surface area of GO after the addition of magnetite and nickel-magnetite particles for the preparation of RGOM and GONF respectively, also signifies that these particles increase the surface area hence allowing more active sites for the adsorption of contaminants.

(a)

(b)

(c)

(d)

(e)
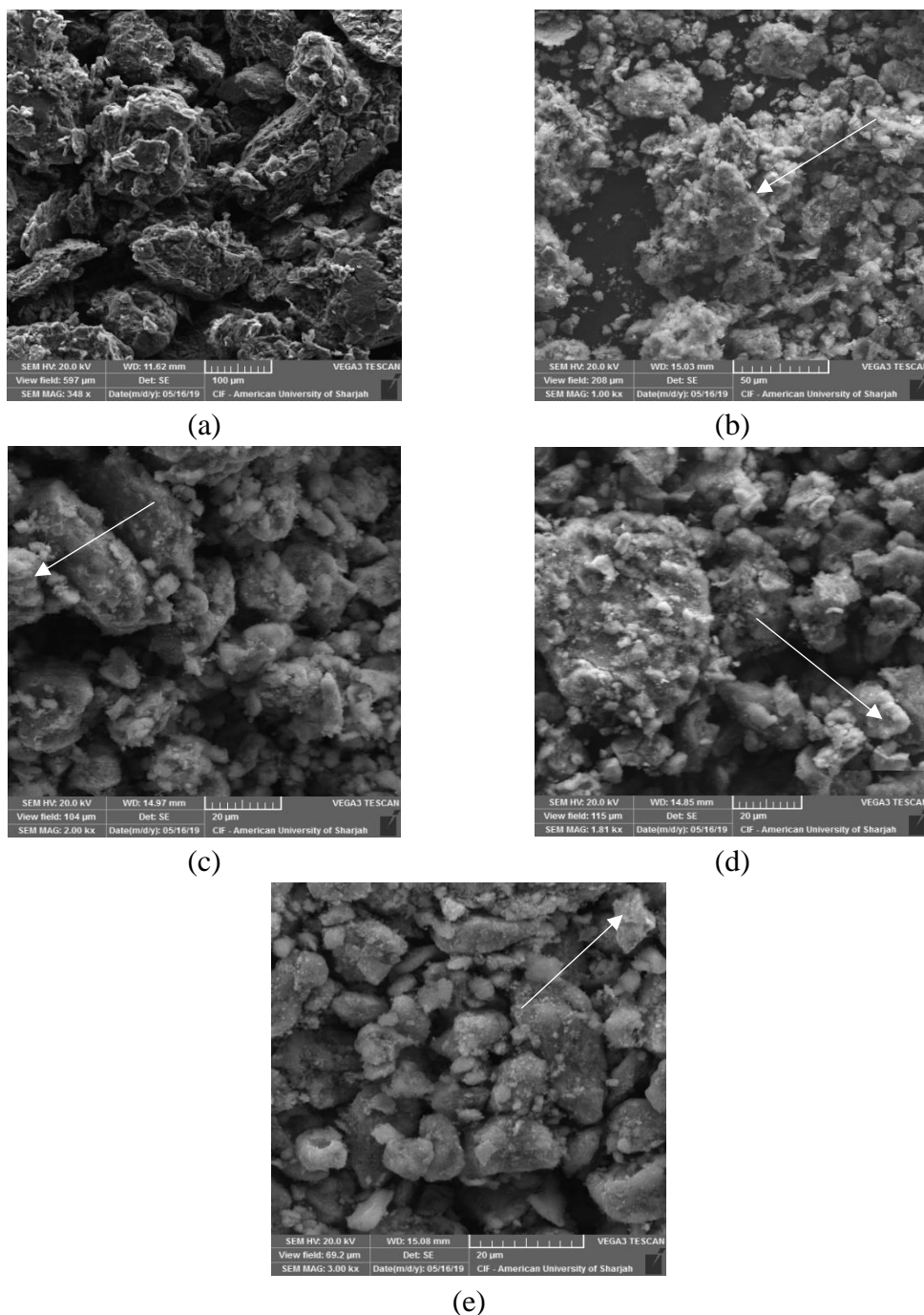
Figure 4. SEM images of (a) Graphene oxide (b) RGOM (c) RGOM after adsorption of DCS (d) RGOM after adsorption of ASP (e) RGOM after adsorption of PAR.
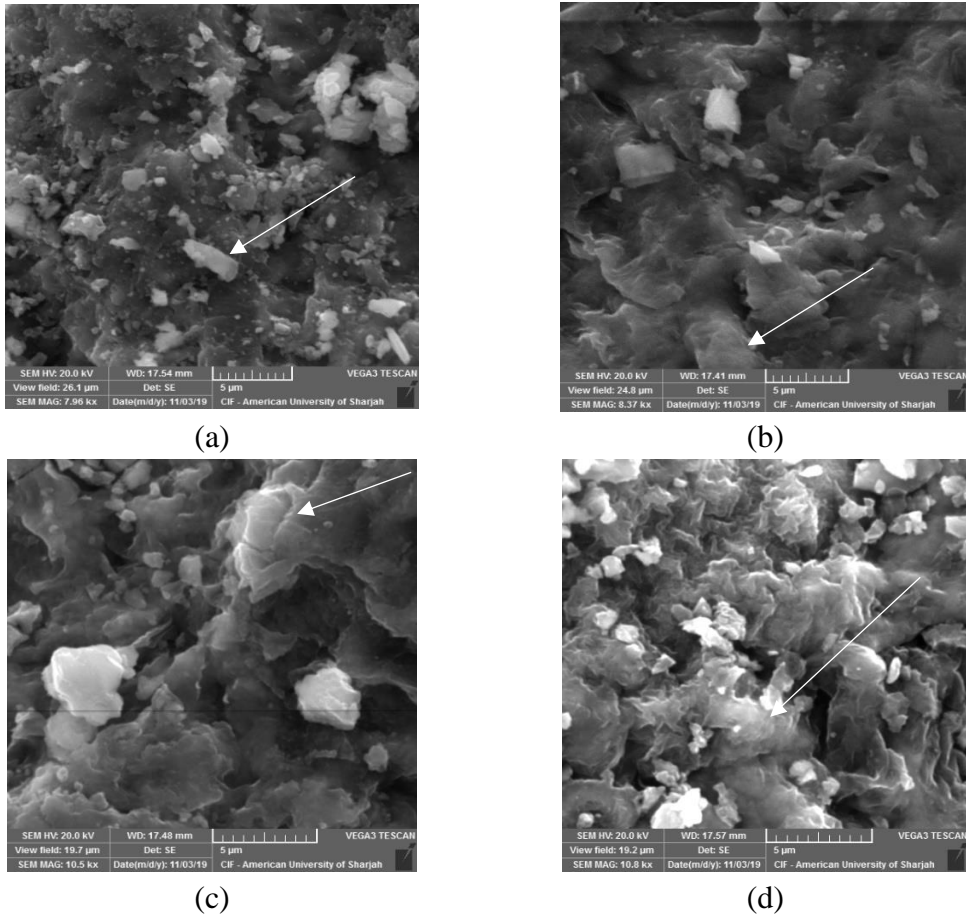
Figure 5. SEM images of (a) GONF (b) GONF after adsorption of DCS (c) GONF after adsorption of ASP (d) GONF after adsorption of PAR.
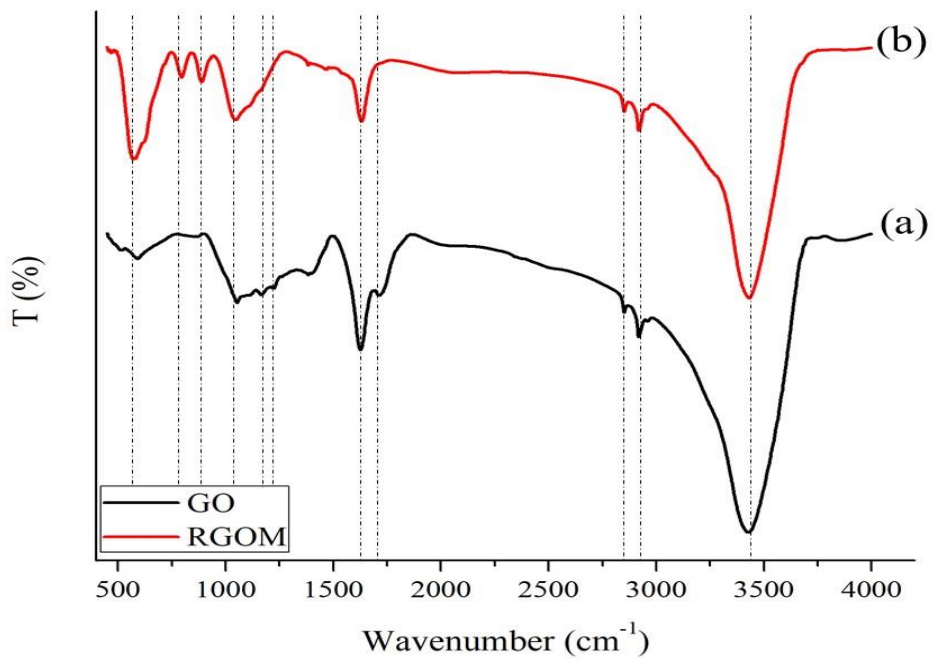
Figure 6. FTIR Spectra of (a) GO (b) RGOM.
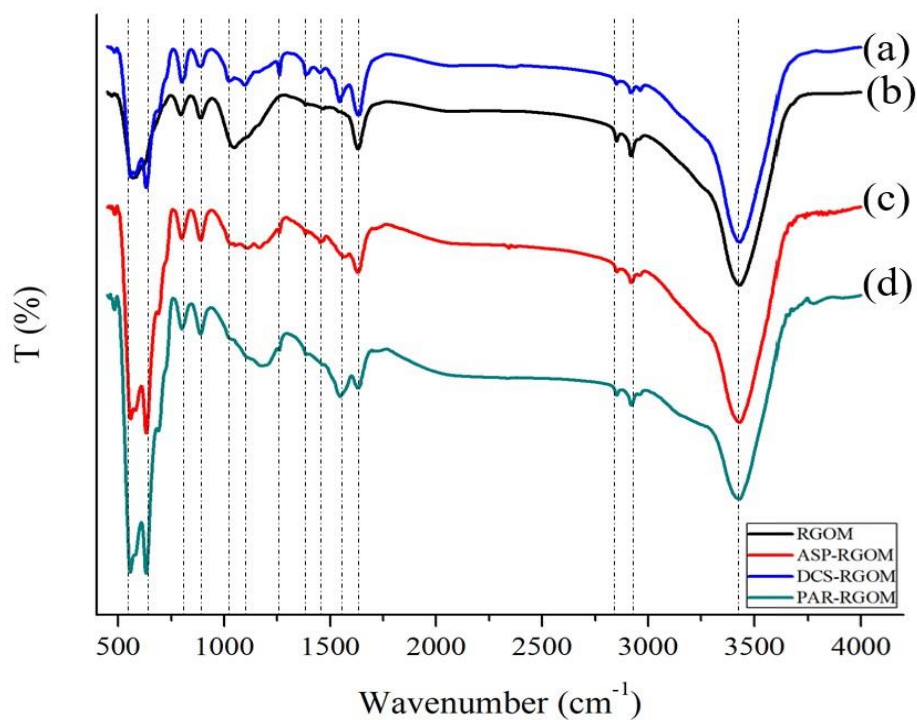
Figure 7. FTIR Spectra of (a) DCS-RGOM, (b) RGOM, (c) ASP-RGOM and (d) PAR-RGOM.
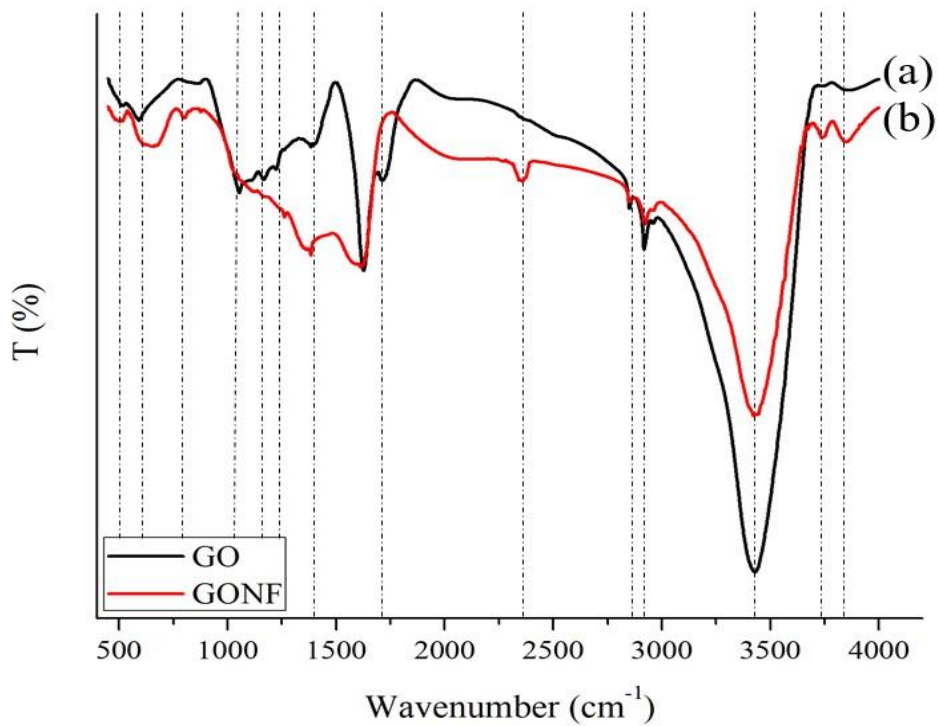
Figure 8. FTIR Spectra of (a) GO, (b) GONF.
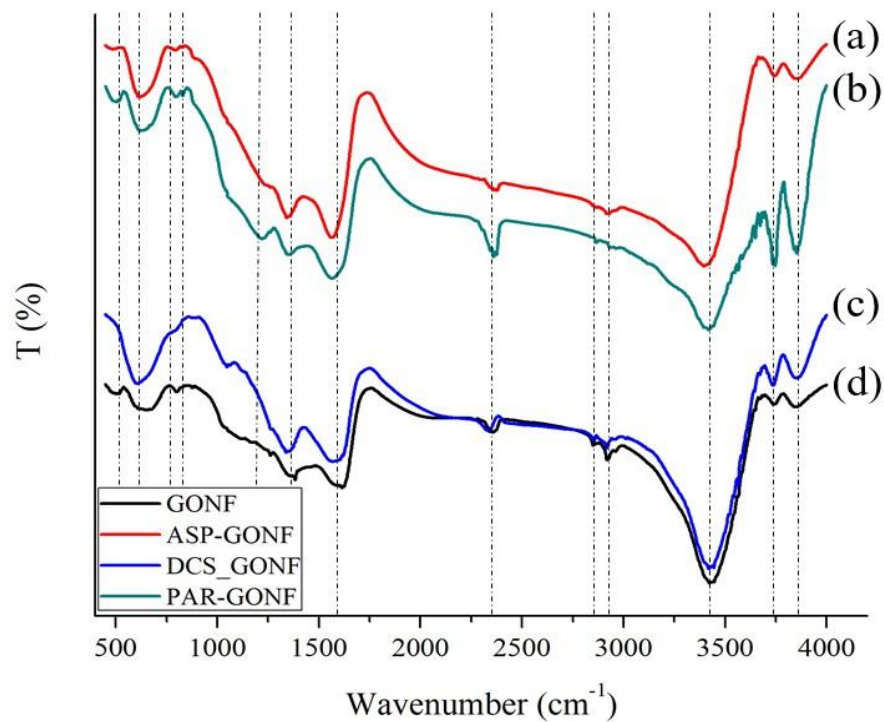
Figure 9. FTIR Spectra of (a) GO, RGOM, ASP-RGOM, DCS-RGOM and PAR-RGOM (b) GO, GONF, ASP-GONF, DCS-GONF and PAR-GONF.

Table 4. EDS analysis

Sample	C	O	Fe	Ni	BET Surface Area (m^2/g)
GO	51.1	48.88	0.01	--	114.07
RGOM	8.82	51.39	39.79	--	185.05
GONF	21.88	49.29	21.04	7.79	196.10
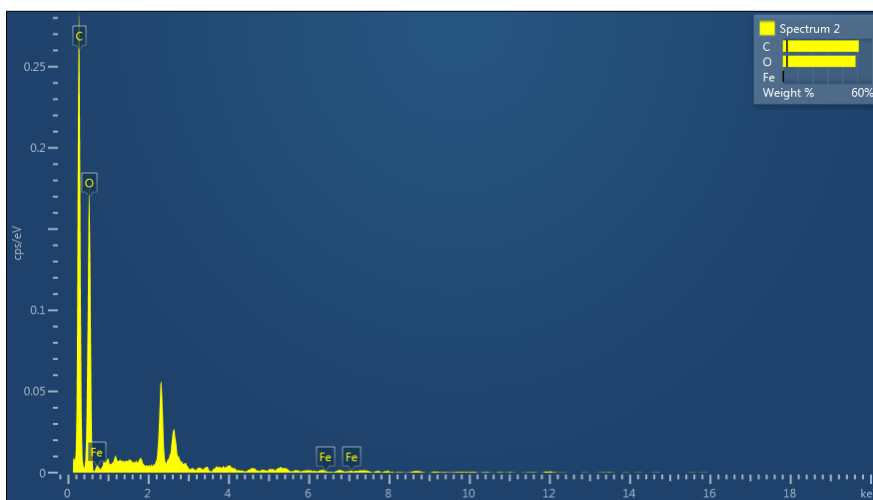
(a)
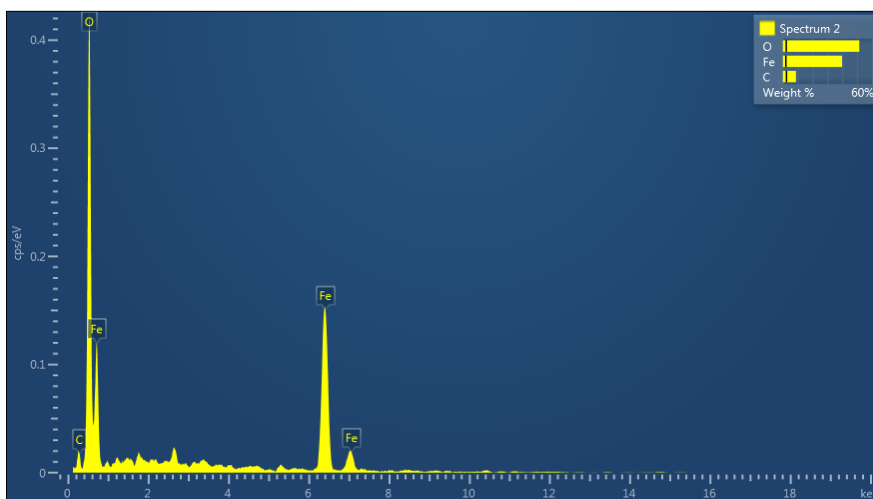
(b)
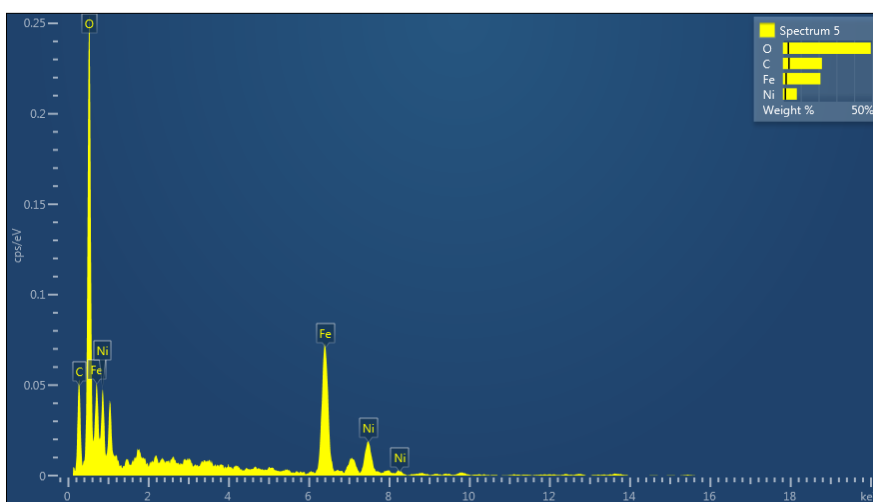
(c)

Figure 10. EDS spectra of (a) GO (b) RGOM and (c) GONF.

4.2. Adsorption Analysis

4.2.1. Preparation of calibration curve. The concentration of pharmaceuticals after treating the water with adsorbents was calculated using calibration curves. The light absorbance spectra of solutions containing different known amount of DCS, PAR and ASP were obtained from UV-Vis spectrometer. The value of λ_{max} was obtained at a wavelength showing maximum absorbance. The calibration curves for DCS, ASP and PAR were obtained at a wavelength of 276, 296 and 244 nm respectively and are shown in Figure 11.

(a)

(b)

(c)
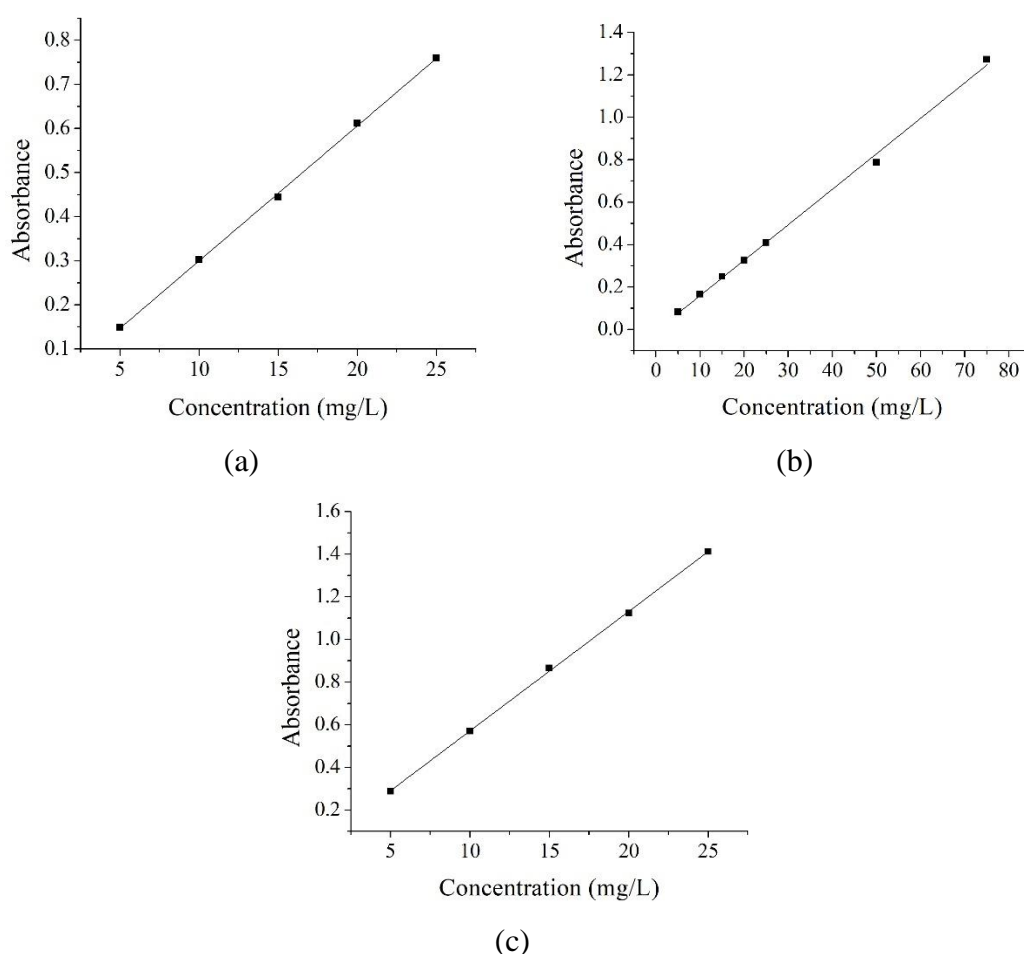
Figure 11. Calibration Curve for (a) DCS (b) ASP and (c) PAR.

4.2.2. Effect of adsorbent dosage. The amount of adsorbent required for an adsorption process is a very important parameter for its applicability in real life. Usually, an increase in the dosage of adsorbent results in an increase in removal efficiency until all the available sites are saturated.

After this point, the adsorption efficiency becomes constant due to the unavailability of driving forces under specified conditions [93]. Figure 12 shows the

removal efficiency with respect to the dosage of RGOM and GONF. The overall efficiency was higher for RGOM as compared to GONF. In case of RGOM, efficiency for all pharmaceuticals increased in an exponential form until it reaches a point where no further change was observed.

On the other hand, the increase in the removal efficiency was not that high for an increase of GONF dosage. PAR showed maximum efficiency with a removal of around 66%. DCS showed lowest removal. Based on the experiments, dosage of GONF for DCS, PAR was selected as 14 g/L and for ASP was chosen to be 12 g/L. While, for RGOM, a dosage value of 14 g/L was selected for DCS and 16 g/L for ASP and PAR removal.

(a)   (b)
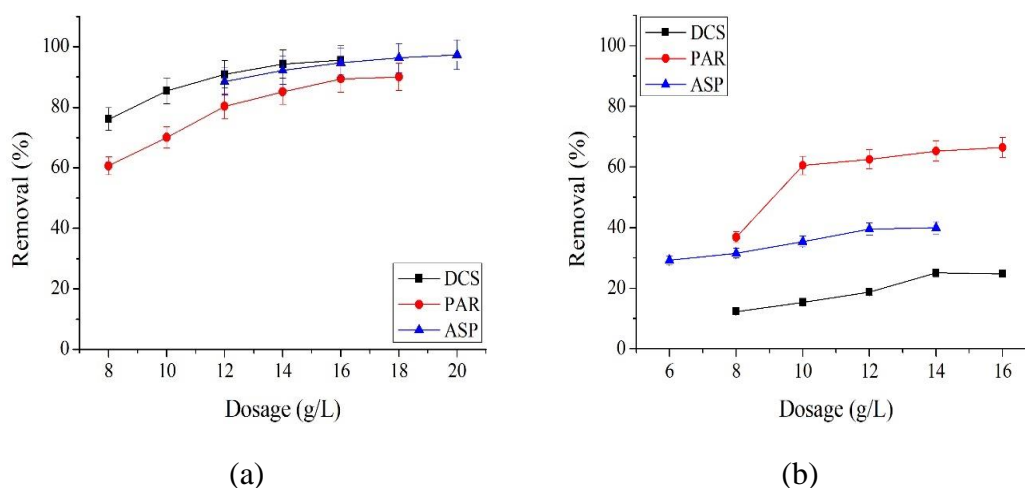
Figure 12. Effect of adsorbent dosage on the removal efficiency of DCS, PAR and ASP by (a) RGOM (b) GONF (Shaker Speed: 175 rpm; Time: 120 mins; Initial concentrations of DCS, PAR and ASP: 100 mg/L; pH: 5±0.1 for DCS and PAR and 3±0.1 for ASP; Temperature: 25°C).

4.2.3. Effect of contact time. The effect of time on the removal efficiency of the three pharmaceuticals is shown in Figure 13. The removal of drugs using RGOM showed fast kinetics with 80% removal occurring within ten minutes. Using GONF as an adsorbent showed slower kinetics and less efficiency.

The removal rate gradually slows down with respect to time due to the decrease of active sites [115]. As observed from the Figure 13, 40 minutes of contact time was selected for adsorption involving RGOM as an adsorbent. On the other hand, further adsorption experiments using GONF were provided a contact time of 60 minutes. Some additional time in these experiments was provided in order to obtain an accurate value

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of efficiency which is no longer changing significantly. The contact time between adsorbate and adsorbent also indicates the spontaneous nature of adsorption in both cases i.e. using RGOM and GONF as an adsorbent. This is also confirmed by the negative values of change in Gibbs free energy (ΔG) obtained in the calculation of thermodynamic properties later in this chapter.

(a)   (b)

Figure 13. Effect of time on the removal efficiency of DCS, PAR and ASP by (a) RGOM (b) GONF (Shaker Speed: 175 rpm; Dosage: 14 g/L for DCS and PAR and 12 g/L for ASP (RGOM), 16 g/L for PAR and ASP and 14 g/L for DCS (GONF); Initial concentrations of DCS, PAR and ASP: 100 mg/L ; pH: 5±0.1 for DCS and PAR and 3±0.1 for ASP; Temperature: 25°C).

4.2.4. Effect of pH. One of the most important factors in determining the efficiency of an adsorption process is pH. The effect of pH on the removal of three pharmaceuticals is shown in Figure 14. For RGOM, all pharmaceuticals showed high adsorption at acidic pH and changed very slightly until the value of pH 9. After that, the efficiency drops abruptly.

Adsorption was maximum for DCS and PAR at pH 5 while, for ASP, the optimum pH was 3 for both adsorbents. Tayyebi et. al. [116] showed that the surface of RGOM carries a positive charge at pH below 1.9 and remains negatively charged above this value. Hence the removal efficiency of DCS remains high when it behaves as a neutral ion i.e. when the pH is acidic. As the pH value is increased, negative charge starts accumulating the surface of DCS thus creating electric repulsions resulting in low removal. Due to the partial protonation of aspirin owing to its weak acid nature (pKa = 3.5), the surface of aspirin will exhibit negative charge at high pH thus leading to a decrease in removal efficiency. The effect of pH on the removal of PAR using RGOM

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was not that sharp. PAR has a pKa value of around 9 and thus it becomes negatively charged at a pH value of more than 9 [117]. This negative charge results in the slight decrease in the adsorbed amount of PAR onto RGOM. On the other hand, the surface of GONF becomes weakly negative after pH 5 [103]. Thus, the adsorption of DCS slightly decreases after that pH. However, the effect of pH on the adsorption of ASP onto GONF does not change significantly. The adsorption of PAR at the surface of GONF also decreases after pH 9 just like its adsorption on RGOM.

(a)   (b)
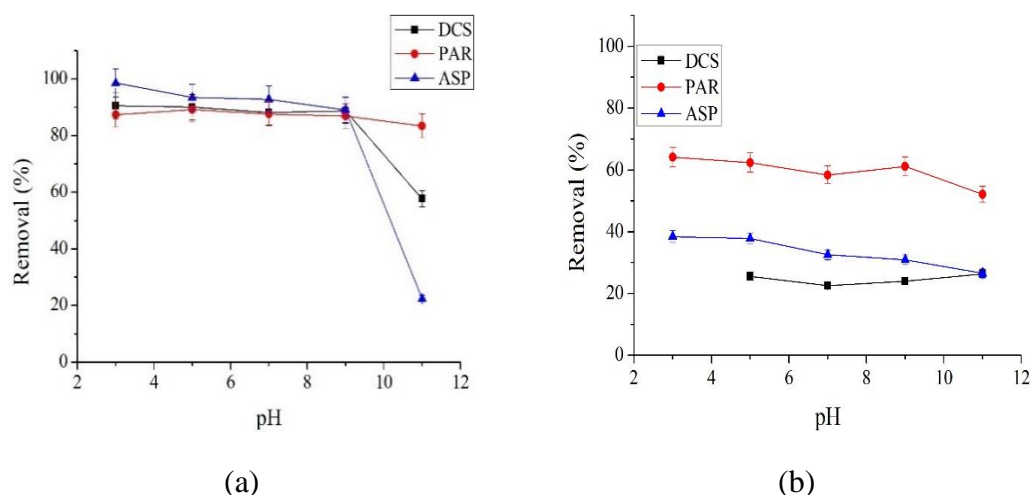
Figure 14. Effect of pH on the removal efficiency of DCS, PAR and ASP by (a) RGOM (b) GONF (Shaker Speed: 175 rpm; Dosage: Dosage: 14 g/L for DCS and PAR and 12 g/L for ASP (RGOM), 16 g/L for PAR and ASP and 14 g/L for DCS (GONF); Time: 40 mins (RGOM) and 60 mins (GONF) Initial concentrations of DCS, PAR and ASP: 100 mg/L; Temperature: 25°C).

4.2.5. Effect of concentration. The initial concentration of the pharmaceutical in industrial process varies according to the quantity produced in a batch and the water used. The wastewater generated by the manufacturing initially contains a very high concentration and hence it is useful to find the optimum concentration at which the process shows most efficiency.

The concentration of the pharmaceuticals was varied to study its possible effect on the removal efficiency using both adsorbents. Figure 15 depicts the effect of change in concentration graphically. It is evident that an increase in the initial concentration resulted in a decreased efficiency. This is due to the saturation of adsorbent sites for higher concentrations.

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| (a) | (b) |
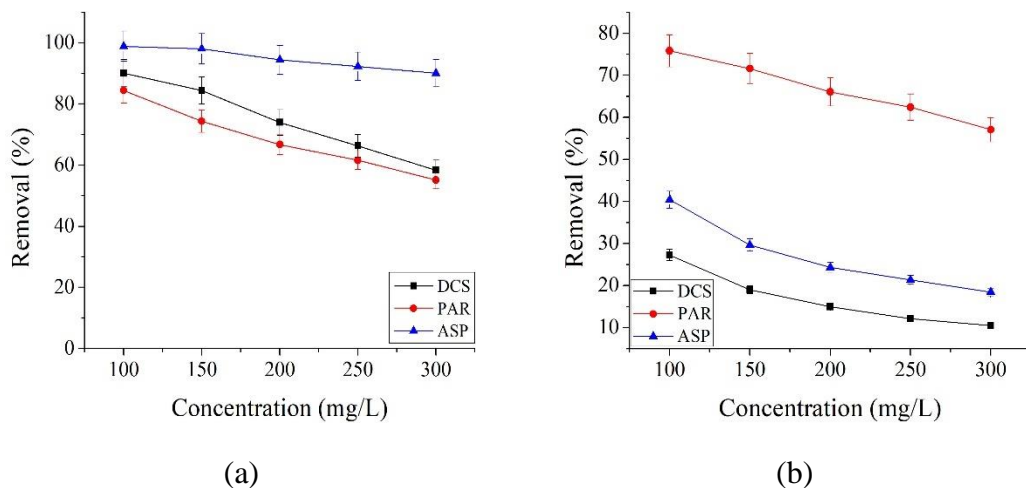
Figure 15. Effect of initial concentration on the removal efficiency of DCS, PAR and ASP by (a) RGOM (b) GONF (Shaker Speed: 175 rpm; Dosage: 14 g/L for DCS and PAR and 12 g/L for ASP (RGOM), 16 g/L for PAR and ASP and 14 g/L for DCS (GONF); Time: 40 mins (RGOM) 60 mins (GONF); pH: 5±0.1 for DCS and PAR and 3±0.1 for ASP; Temperature: 25°C).

4.2.6. Effect of temperature. The effect of temperature on the efficiency of RGOM and GONF to removal DCS, ASP and PAR is shown in Fig. 16.
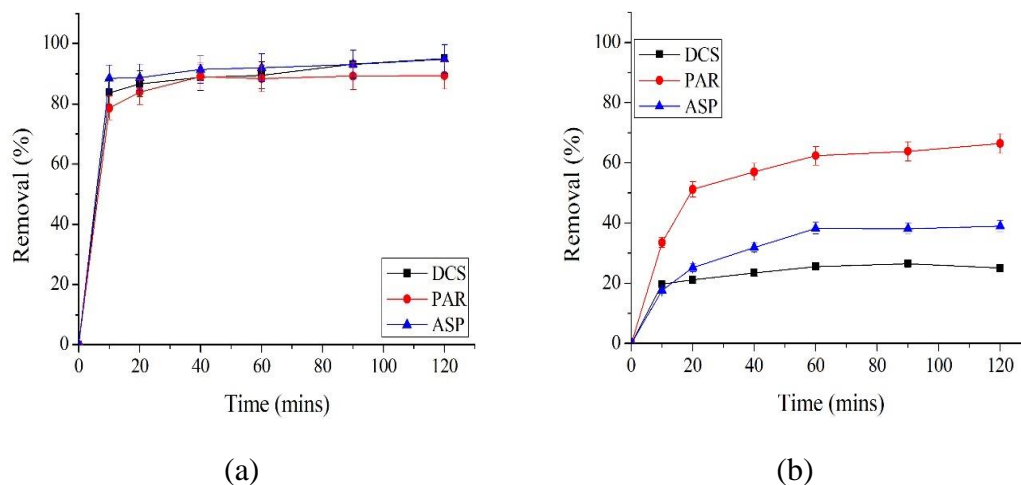

| (a) | (b) |
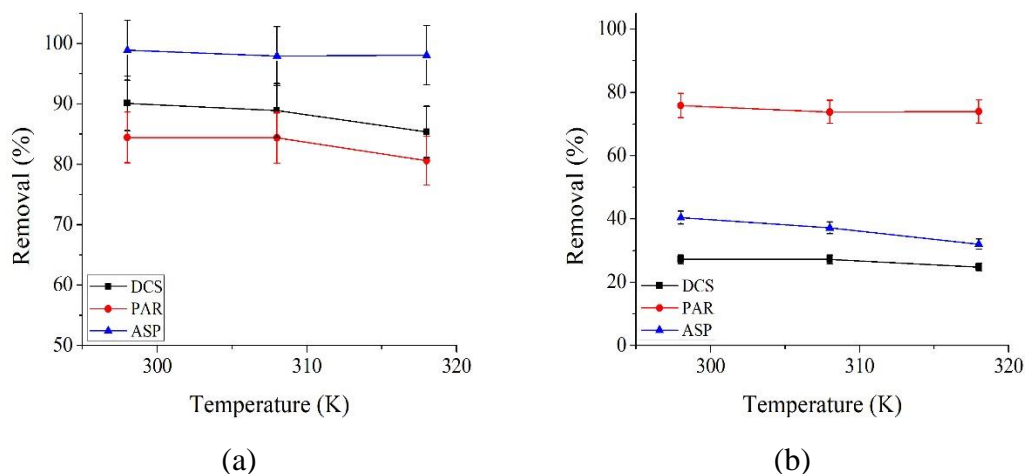
Figure 16. Effect of temperature on the removal efficiency of DCS, PAR and ASP by (a) RGOM (b) GONF (Shaker Speed: 175 rpm; Dosage: Dosage: 14 g/L for DCS and PAR and 12 g/L for ASP (RGOM), 16 g/L for PAR and ASP and 14 g/L for DCS (GONF); Time: 40 mins (RGOM) and 60 mins (GONF) Initial concentrations of DCS, PAR and ASP: 100 mg/L; pH: 5±0.1 for DCS and PAR and 3±0.1 for ASP).

The adsorption of DCS and PAR on the surface of RGOM and DCS and ASP on the surface of GONF decreased slightly with the increase in temperature keeping

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other conditions optimum. On the other hand, ASP removal using RGOM and PAR removal using GONF remained almost constant. The thermodynamic nature of adsorption is further confirmed later in this chapter.

4.3. Adsorption Isotherms

Adsorption isotherms are defined by the correlation of mass of adsorbate per unit mass of adsorbent keeping the surrounding conditions optimum. Three isotherm models namely, Langmuir isotherm model, Freundlich isotherm model and Temkin isotherm model were used to fit the data obtained from experiments conducted at specified conditions. Initial concentration of the drugs was varied keeping the temperature constant to obtain the data. The comparison of the isotherms is discussed here.

4.3.1. Langmuir isotherms. Figure 17 shows the Langmuir isotherm model fit for RGOM and GONF respectively. The maximum adsorption capacity of RGOM was 12.85 mg/g ($R^2 = 0.999$), 13.60 mg/g ($R^2 = 0.988$) and 21.41 mg/g ($R^2 = 0.985$) for DCS, PAR and ASP respectively. While, GONF showed an adsorption capacity of 2.35 mg/g ($R^2 = 0.999$), 19.57 mg/g ($R^2 = 0.996$) and 5.31 mg/g ($R^2 = 0.997$) for DCS, PAR and ASP respectively. It is obvious that the adsorption capacity of GONF was very low for DCS and ASP as compared to RGOM but showed better capacity than RGOM for the adsorption of PAR.

(a)   (b)
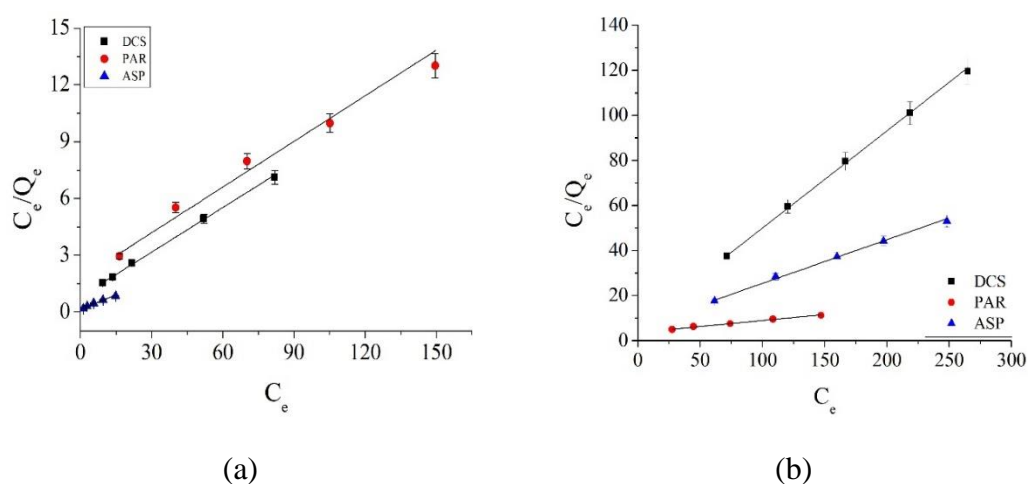
Figure 17. Langmuir isotherm models for the removal of DCS, PAR and ASP using (a) RGOM and (b) GONF.

The overall observed adsorption capacity is low for both adsorbents than the available adsorption capacities from the literature which can be attributed to the

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commercial nature of graphene oxide used for the experiments and the high initial concentrations of pharmaceuticals.

4.3.2. Freundlich isotherms. Data fitted according to Freundlich isotherm model is represented in Figure 18. The value of Freundlich isotherm constants (K_F and n) were calculated from the slope and intercept of the straight line obtained after plotting a graph between log Q_e at y-axis versus log C_e at x-axis. Large K_F values indicate a better adsorption capacity while the value of n correlates to adsorbent strength and the effect of concentration on the adsorption. A value of n more than 1 represents favourable adsorption [118]. The values of other parameters such as R^2 value and K_F values are shown in Table 4. The low values of K_F confirms the low adsorption capacities for both RGOM and GONF.

(a)   (b)
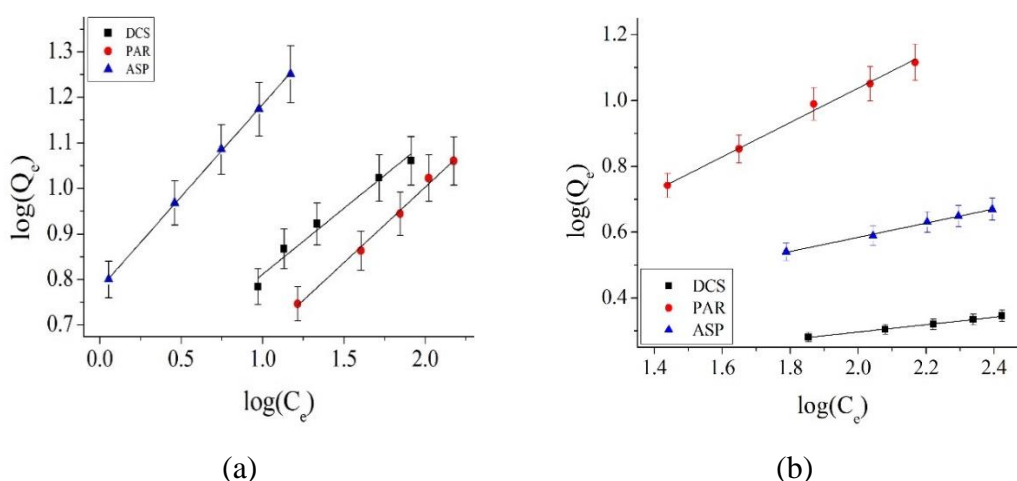
Figure 18. Freundlich isotherm models for the removal of DCS, PAR and ASP
using (a) RGOM and (b) GONF.

4.3.3. Temkin isotherms. Temkin isotherm models were obtained by plotting ln (C_e) vs Q_e and are shown in Fig 19. The validity of Temkin isotherm model depends on the concentration and is usually accurate only for intermediate concentrations [119].

Also, Temkin isotherm model is considered inapplicable to describe liquid adsorption data because of its complexity with respect to the gas phase adsorption [120]. Temkin isotherm constants, B and K_T, are calculated from the slope and intercept of the straight lines. The values of both constants are summarized in Table 5. A summary of all calculated values from isotherm models is presented in Table 5. It is

evident that the adsorption process carried out using RGOM showed promising results and better adsorption capacities as compared to GONF.

Correlation coefficient (R^2) is used to define the best adsorption model for each individual batch adsorption study. The closer the value of R^2 to unity, the better fitting it represents. The values of R^2 are very similar to each other and hence it is difficult to explain the adsorption process using only one model.

However, slightly better R^2 value shows that adsorption of all pharmaceuticals using GONF and adsorption of DCS using RGOM followed Langmuir isotherm. While the removal of PAR and ASP using RGOM observed to be best fitted by Freundlich Isotherm.

A comparison of the adsorption capacity of different adsorbent reported in literature is given in Table 6. It is evident from the table that the adsorption capacity of adsorbents usually remains on lower side for the removal of DCS, PAR and ASP. In case of Diclofenac sodium, single layered GO and 3D graphene aerogel showed very high adsorption capacity as compared to other adsorbents. On the other hand, activated carbon derived from biomass was found to be more efficient in removing aspirin. Paracetamol was best removed using magnetic AC.

(a)   (b)
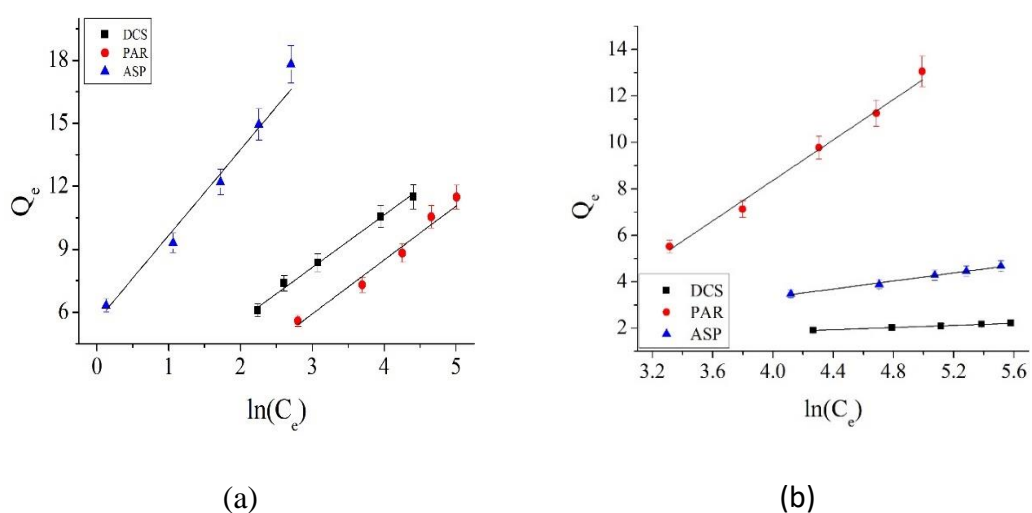
Figure 19. Temkin isotherm models for the removal of DCS, PAR and ASP using (a) RGOM and (b) GONF.

Table 5. Adsorption parameters for different isotherm models for the removal of DCS, PAR and ASP using RGOM and GONF

Model	Adsorption Parameters						
		RGOM			GONF		
		DCS	PAR	ASP	DCS	PAR	ASP
Langmuir	K_L (L/mg)	0.091	0.032	0.267	0.052	0.015	0.027
	Q_m (mg/g)	12.95	13.60	21.41	2.35	19.56	5.31
	R^2	0.999	0.988	0.989	0.999	0.996	0.997
Freundlich	K_F $(mg^{(1-1/n)} L^{1/n} g^{-1})$	3.39	2.15	5.95	1.17	1.12	1.41
	n	3.53	2.99	2.49	8.88	1.96	4.61
	R^2	0.978	0.995	0.999	0.998	0.996	0.996
Temkin	B (J/mole)	2.45	2.72	4.38	0.23	4.59	0.87
	K_T (L/mg)	1.37	0.41	3.15	52.28	0.12	0.83
	R^2	0.995	0.977	0.981	0.995	0.994	0.992

The low adsorption capacity in this study is justified by the use of commercial graphene oxide which reduces the operational cost by a great margin. The chemicals used in this study are readily available in commercial grade and hence the overall cost is greatly reduced. The studies showing very high adsorption capacity for adsorbent are prepared using analytical grade and even in the case of using biomass, the energy requirements to carbonize and activate the biomass are high. Using commercial grade adsorbent satisfies the objective of using this adsorption process on industrial scale. One -pot manufacturing process with the use of normal experimental conditions makes this study more economical and energy saving.

4.4. Kinetics

Kinetics study of adsorption is very important for practical implementation of the process. Two different kinds of kinetic models, pseudo first order (PFO) kinetic model and pseudo second order (PSO) kinetic model, were used to fit the data obtained by measuring the adsorption at different time intervals and keeping the other conditions at optimum values.

Table 6. Comparison of adsorbent capacities of different adsorbents

S. No.	Adsorbent	Max. Adsorption Capacity (mg/g)	Ref.
Adsorption of DCS			
1	Carbon nanotubes (CNT)	27	[121]
2	Commercial activated carbon	76	[122]
3	Activated carbon (AC) derived from cocoa shell	63	[123]
4	Single layered graphene oxide (GO)	750.0	[124]
5	Reduced graphene oxide (rGO)	59.67	[125]
6	3D graphene aerogel	596.71	[126]
7	CTAB-ZIF-67	54.31	[127]
8	CNT/HNO$_3$	24	[128]
9	AC derived from olive stones	11	[129]
10	RGOM	12.95	This study
11	GONF	2.35	This Study
Adsorption of ASP			
1	Graphene nanoplatelets	12.98	[130]
2	Activated carbon (AC) derived from rice hull	178.98	[131]
3	Activated carbon (AC) derived from tea leaves	178.5	[132]
4	N-CNT/β-cyclodextrin NC	72	[133]
5	Fe/N-CNT/β-cyclodextrin NC	71.9	[133]
6	Molecularly Imprinted polymer	0.03	[134]
7	Tyre Waste	40.40	[135]
8	RGOM	21.41	This Study
	GONF	5.31	This Study
Adsorption of PAR			
1	Activated carbon (AC) derived from rice husk	20.96	[136]
2	Activated carbon (AC) derived from rice husk	14.88	[136]
3	Activated carbon (AC) derived from sewage sludge	53.75	[137]
4	MWCNT	91.4	[138]
5	Graphene	18.9	[138]
	Magnetic AC	174.8	[139]
6	RGOM	13.60	This Study
7	GONF	19.56	This Study

4.4.1. Pseudo-first order kinetic model. Pseudo first order kinetic models for both RGOM and GONF are shown in Figure 20. According to the experimental results and obtained data, none of the adsorption process followed PFO model.

(a)   (b)
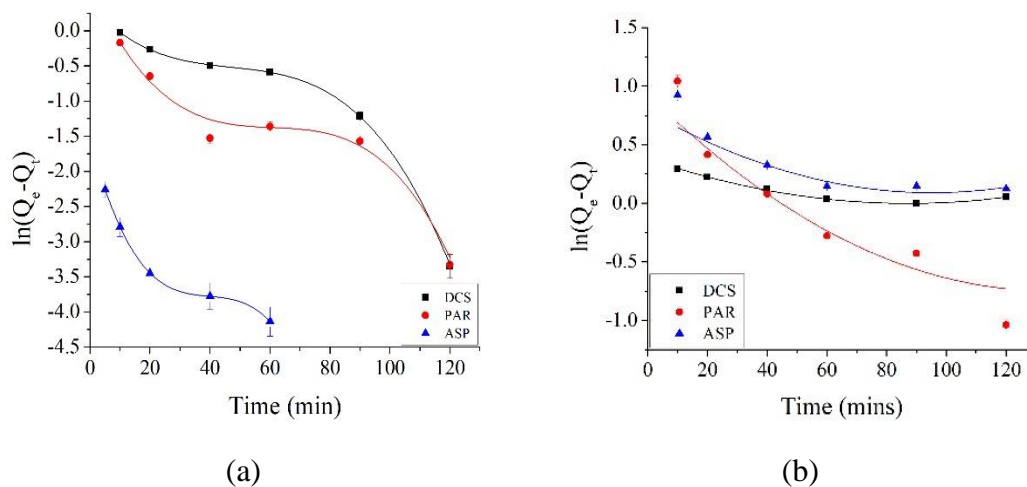
Figure 20. Pseudo-first order kinetic models for the removal of DCS, PAR and ASP using (a) RGOM and (b) GONF.

The obtained R^2 values for adsorption through RGOM were 0.829, 0.849 and 0.868 for DCS, PAR and ASP. For adsorption using GONF as an adsorbate the R^2 values were 0.696, 0.920 and 0.691 for DCS, ASP and PAR respectively.

4.4.2. Pseudo-second order kinetic model. Data fitted by pseudo second order kinetic model is shown in Figure 21. The correlation coefficient (R^2) values for PSO were very high as compared to PFO and hence the adsorption phenomena for all pharmaceuticals is governed by PSO.

In a recent study, a concern about the implementation of PSO kinetic model to adsorption process, which are fast in nature, was pointed out by Hubbe et. al. [140]. An adsorption process in which the attachment of adsorbate to active sites is the rate limiting step, PFO will provide better fitting of the kinetic data.

For a PSO model to fit the data better, it is assumed that the interactions between adsorbent and adsorbate molecules are faster than the diffusion. Hence fast adsorption processes following PSO model than the rate of adsorption slows down earlier than anticipated. A summary of different parameters such as kinetic rate constants and correlation coefficient calculated from pseudo first order and pseudo second order kinetic models are summarized in Table 7.

(a)   (b)
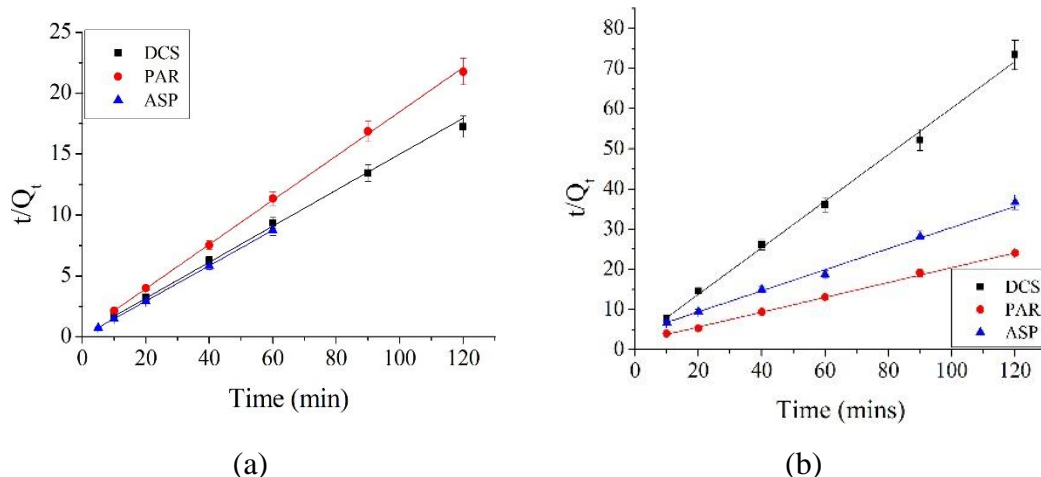
Figure 21. Pseudo-second order kinetic models for the removal of DCS, PAR and ASP using (a) RGOM and (b) GONF.

Table 7. Adsorption parameters for different kinetic models for the removal of DCS, PAR and ASP using RGOM and GONF

Model		Adsorption Parameters					
		RGOM			GONF		
		DCS	PAR	ASP	DCS	PAR	ASP
PFO	k_1	0.026	0.024	0.031	0.002	0.016	0.006
	R^2	0.829	0.849	0.868	0696	0.921	0.691
PSO	k_2	0.044	0.456	2.075	5.141	0.018	0.269
	R^2	0.998	0.999	0.999	0.996	0.998	0.997

4.5. Thermodynamics

To get a better insight of the adsorption phenomena, the calculation of thermodynamic properties such as change in Gibb's free energy (ΔG), change in enthalpy (ΔH) of the system and change in the entropy (ΔS) is very important. These thermodynamic properties were calculated using Sip's equation and the procedure is discussed in Chapter 3.

The first step is to obtain a plot between ln (K_{eq}), and $1/T$ called van't Hoff plot. K_{eq} was calculated for each temperature value by performing a regression analysis on

the adsorption data obtained after experiments. Another term K_{ads} is used for the regression analysis and is given as

$$K_{ads} = \frac{1}{K_{eq}} \tag{11}$$

The value of Sip's constant ns and K_{ads} is changed iteratively until the error is minimized and that values correspond to the constants obtained from isotherms. These values were than used to calculate K_{eq}. Table 8 shows the value of K_{eq} and n_s calculated for each adsorption process. The van't Hoff plots obtained from each individual study are given in Figure 22.

The van't Hoff plot gives a linear relation for adsorption of all pharmaceuticals except the adsorption of ASP onto RGOM. This employs that the change in enthalpy and entropy of the system does not remain constant with respect to temperature for ASP adsorption through RGOM. The calculated values of ΔG, ΔH and ΔS are summarized in Table 9 for RGOM and Table 10 for GONF.

(a)   (b)
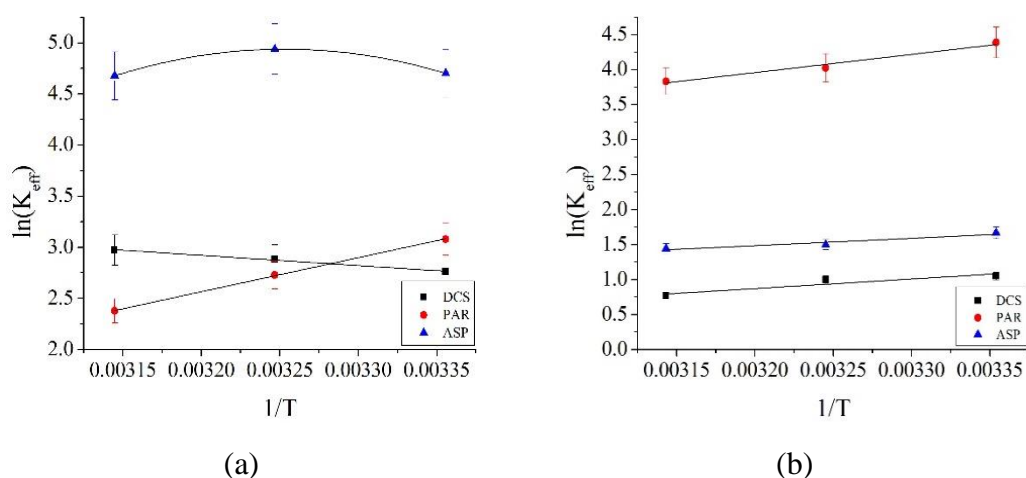
Figure 22. van't Hoff plot for the removal of DCS, PAR and ASP using (a) RGOM and (b) GONF.

It can be observed that the values of ΔG for all the adsorption reactions remains negative hence confirming the spontaneous nature of the process. Moreover, ΔG remains is less than 30 KJ/mol, hence one can safely assume that the adsorption is physical in nature. The adsorption of PAR on RGOM and DCS, PAR and ASP on GONF have negative value of ΔH thus illustrating the exothermic reaction while the

adsorption of DCS and ASP was followed by an endothermic reaction. The positive value of ΔS for the adsorption of pharmaceuticals onto GONF and DCS onto RGOM explains that the randomness of the system has increased as a result of adsorption, while change in entropy (ΔS) remains negative for the rest of the adsorption processes.

Table 8. Calculated Sip's parameters at different temperatures

Adsorbent	Drug	298 K		308 K		318 K	
		Keq	ns	Keq	ns	Keq	ns
RGOM	DCS	15.84	3.67	17.85	3.40	2.97	3.27
	PAR	21.76	2.95	15.33	2.88	10.78	2.74
	ASP	114.45	2.47	384.64	1.88	80.66	2.59
GONF	DCS	2.85	8.85	2.71	9.14	2.17	10.62
	PAR	80.57	2.02	56.11	2.20	46.31	2.30
	ASP	5.30	4.59	4.47	4.83	4.23	4.49

Table 9. Calculated thermodynamic properties for the removal of DCS, PAR and ASP using RGOM

	DCS			PAR			ASP		
T (K)	298	308	318	298	308	318	298	308	318
ΔG (KJ/mol)	-6.85	-7.38	-7.86	-7.63	-6.99	-6.29	-11.7	-14.7	-10.9
ΔH (KJ/mol)		8.32			-27.7		93.4	129.6	163.5
ΔS (J/mol K)		50.9			-67.2		-53.5	-172.9	-281.2

Table 10. Calculated thermodynamic properties for the removal of DCS, PAR and ASP using GONF

	DCS			PAR			ASP		
T (K)	298	308	318	298	308	318	298	308	318
ΔG (KJ/mol)	-2.59	-2.56	-2.05	-10.9	-10.3	-10.1	-4.13	-3.84	-3.81
ΔH (KJ/mol)		-10.7			-21.9			-8.93	
ΔS (J/mol. K)		27.0			37.2			16.22	

4.6. Reusability Study

Economic aspects of a chemical process demand materials which can be recycled and reused. In adsorption, a good adsorbent must possess the ability of reuse and should retain its capacity of adsorbing contaminants after several cycles. In this study, three cycles of reusability were performed, and the adsorption efficiency was calculated. Figure 23 depicts the reusability study for both RGOM and GONF in terms of removal percentage.
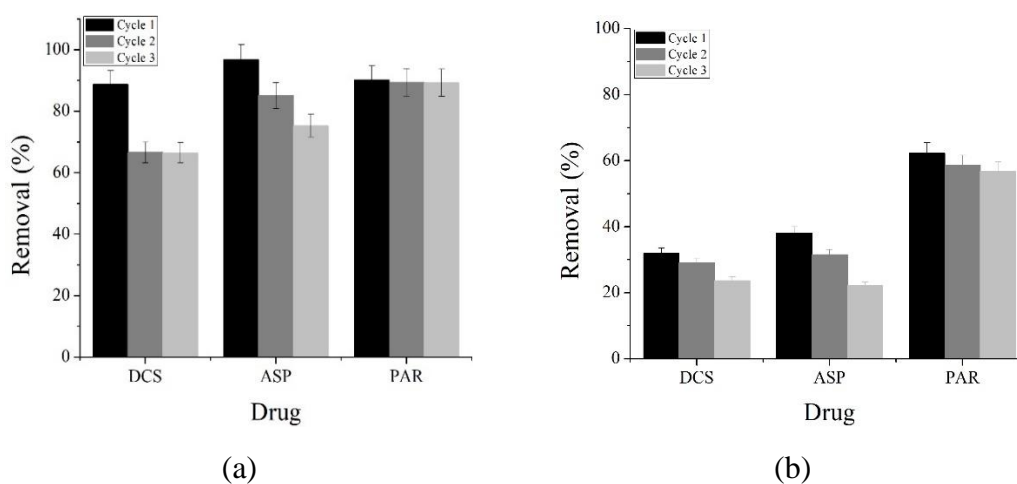
Figure 23. Reusability study for (a) RGOM and (b) GONF.

The removal of ASP followed a gradual decrease in the removal efficiency after 1st and 2nd cycle. The drop in the removal effectiveness of DCS by RGOM was high in the first cycle but then remained almost constant for 2nd and 3rd cycle. For PAR removal, however, the change was negligible for three cycles. On the other hand, the efficiency

of GONF to remove DCS, ASP and PAR showed a gradual decrease. The removal of PAR was the most efficient one and the change after 3 cycles was slight. However, the removal of DCS and ASP decreased more significantly with the removal efficiency dropping from 31% to 23% for DCS and from 38% to 22% for ASP.

4.7. Continuous fixed-bed adsorption study

Continuous fixed-bed column studies were carried out for RGOM only due to its higher removal efficiency and better adsorption capacity than GONF. The effect of bed depth and flow rate on the removal of pharmaceuticals was studied. The adsorption data was then fitted using four different models namely Thomas mode, Bohart and Adams model, Clark model and Yan et al. model.

4.7.1. Effect of bed depth. It The effect of bed depth of adsorbent in a fixed-bed column is shown in Fig. 24. It is evident from the figure that the increase in the bed depth form 1.8 cm to 3.6 cm results in the longer usage time of the column and more volume can be processed.
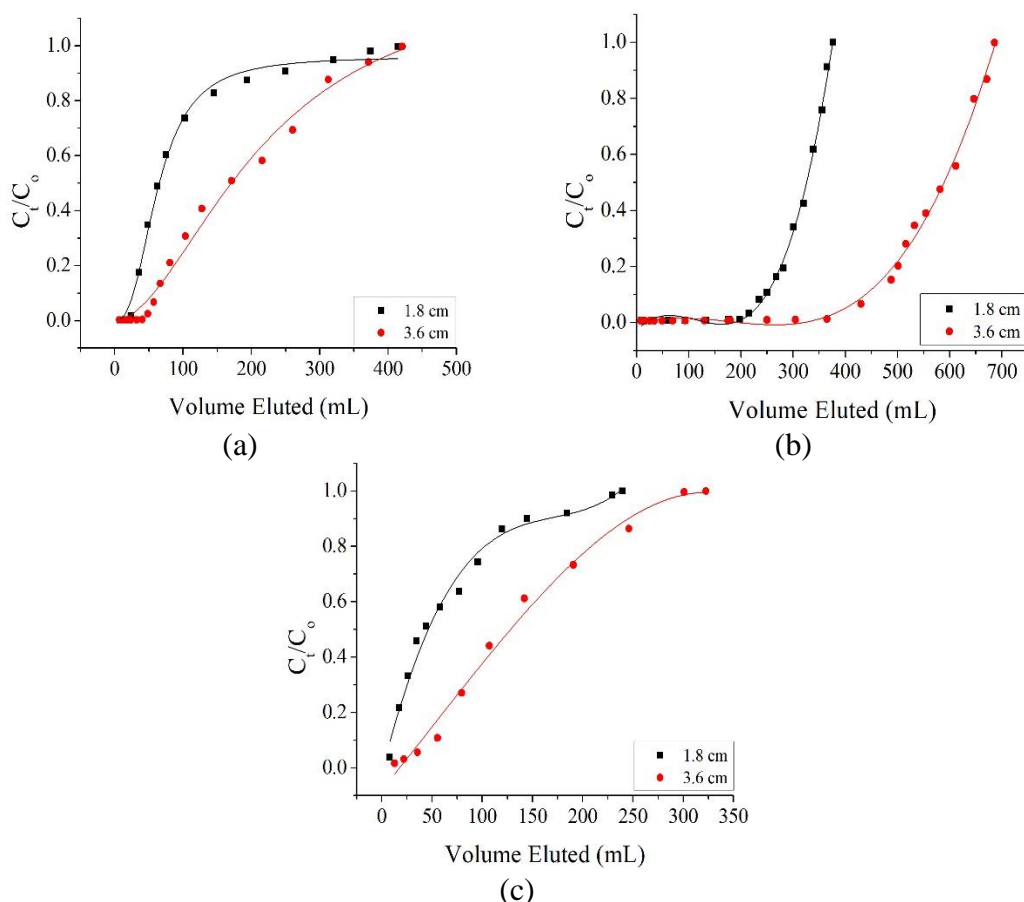
Figure 24. Effect of Bed Depth of RGOM on the removal of (a) DCS (b) ASP and (c) PAR.

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This increase in the processing time and volume is attributed to the availability of more active sites due to an increase in adsorbent mass. At lower bed depth, the adsorbate would not find sufficient time to diffuse into the active sites of the adsorbent [92]. The study was performed under optimum values of pH and temperature. The flow rate was kept at 0.45 mL/min. Initial concentration of all pharmaceuticals was 100 mg/L.

4.7.2. Effect of flow rate. The effect of flow rate of pharmaceutical containing water with an initial concentration of 100 mg/L of each pharmaceutical and bed depth of 1.8 cm on the performance of fixed bed column is shown in Fig. 25. Optimum pH and temperature values were used for each pharmaceutical.

A smaller value of flow rate will generate more volume of clean water because of the availability of more contact time between adsorbate and adsorbent. An increase in flow rate will result in lesser contact time and hence adsorption capacity and service time of column.
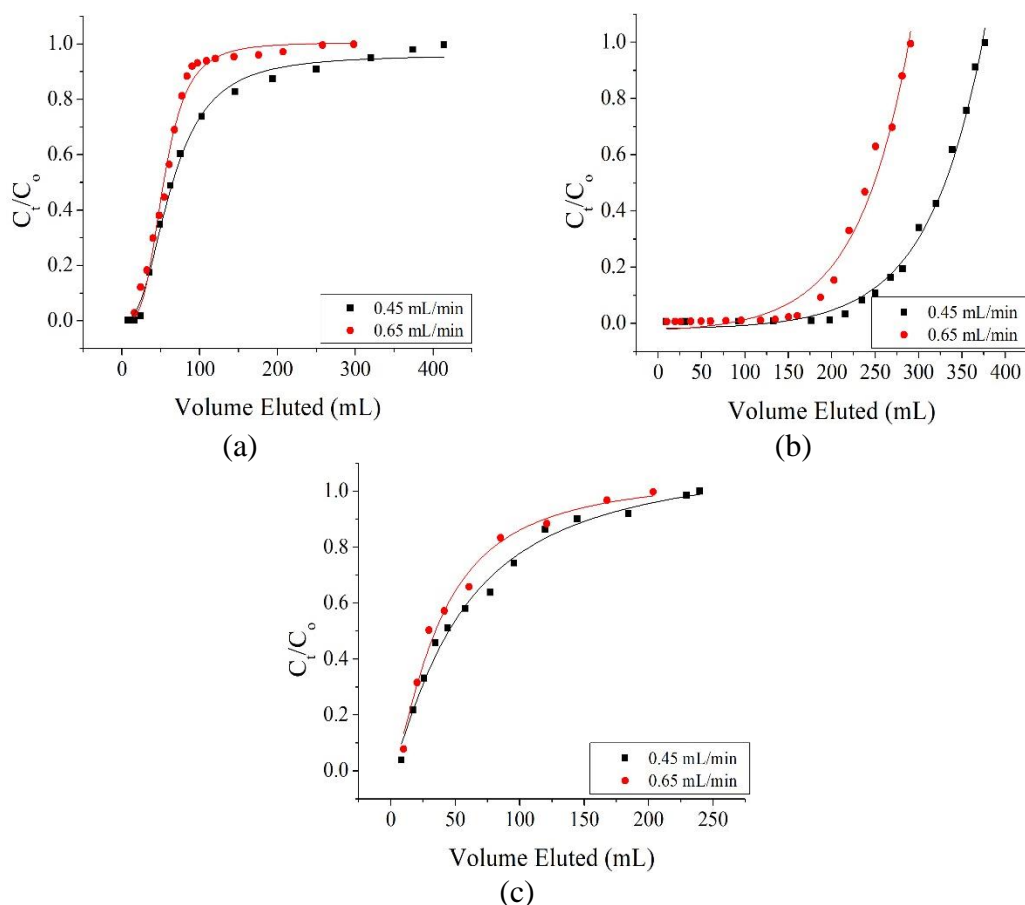
Figure 25. Effect of flow rate of solution on the removal of (a) DCS (b) ASP and (c) PAR by using RGOM.

4.7.3. Fixed-bed adsorption models. Four different kind of fixed Bed adsorption model were used to fit the adsorption data obtained for all pharmaceuticals. The linearized model fitting for DCS, PAR and ASP are shown from Fig. 26-28.

The calculated regression coefficients (R^2) along with different model parameters are summarized in Table 11. Observing the R^2 values, it is evident that the adsorption of PAR onto RGOM under continuous flow conditions was best described by Thomas model. Thomas model is based on the assumptions that the adsorption follows Langmuir isotherm, isothermal conditions of reaction and suggests that internal and external diffusion is not the rate limiting step in the process [115, 141]. On the other hand, highest value of R^2 for the adsorption of DCS was observed for Yan et al. model. Yan model takes the same assumptions in consideration [142] and the results are similar to previously reported studies [141].

Table 11. Continuous fixed-bed adsorption model parameters for the removal of DCS, PAR and ASP using RGOM

Adsorption Models	Parameters		DCS	PAR	ASP
Thomas	K_{TH}	$L.mg^{-1}.min^{-1}$	0.206	0.1418	0.182
	q_o	$mg. g^{-1}$	5.249	6.47	23.59
	R^2		0.859	0.946	0.8257
Bohart and Adams	K_{AB}	$L.mg^{-1}.min^{-1}$	0.049	0.051	0.128
	N_o	$mg. L^{-1}$	10227.2	7350.4	16830.5
	R^2		0.389	0.753	0.922
Clark	A	-	54.05	1198.7	13236
	r	min^{-1}	0.025	0.019	0.024
	R^2		0.742	0.946	0.867
Yan et al.	a	-	3.1414	2.919	2.112
	b	mL	48.522	79.402	336.771
	R^2		0.9583	0.799	0.5256

Bohart and Adams (B-A) model was found to fit the data obtained from ASP adsorption. It assumes that the rate of uptake of the adsorbate is proportional to the concentration of adsorbate in the bulk liquid and the residual adsorptive capacity of

adsorbent. B-A model takes several factors in account such as bed depth (cm) and superficial velocity (cm/min) of the fluid and the effect of each parameter can be approximately estimated [143].

Figure 26. (a) Thomas (b) Bohart and Adams (c) Clark and (d) Yan et al. model for fixed-bed adsorption of DCS using RGOM (Flow rate: 0.65 mL/min; Bed Depth: 1.8 cm; pH: 5±0.1; Initial concentration: 100 mg/L; Temperature: 25°C).

Summarizing the results, graphene oxide doped with metal particles on its surface offer a good approach to remove pharmaceuticals compounds from wastewater treatment. Both RGOM and GONF showed good capability to remove commonly detected pharmaceuticals. RGOM showed high removal efficiency which is in comparison to the studies found in the literature as shown in previous chapters. GONF, on the other hand, showed lesser removal efficiency. An insight of adsorption process was gained using different isotherm and kinetic models and calculating thermodynamic

properties. Most adsorption data followed Langmuir isotherm model while the remaining were best described by Freundlich isotherm model. Pseudo-second order kinetic models showed best fitting for the removal of all pharmaceuticals using both adsorbents. In the end, reusability study and continuous fixed-bed adsorption was carried out to gain better understanding of adsorption usage in industrial applications.

Figure 27. (a) Thomas (b) Bohart and Adams (c) Clark and (d) Yan et al. model for fixed-bed adsorption of PAR using RGOM (Flow rate: 0.45 mL/min; Bed Depth: 3.6 cm; pH: 5±0.1; Initial concentration: 100 mg/L; Temperature: 25°C).
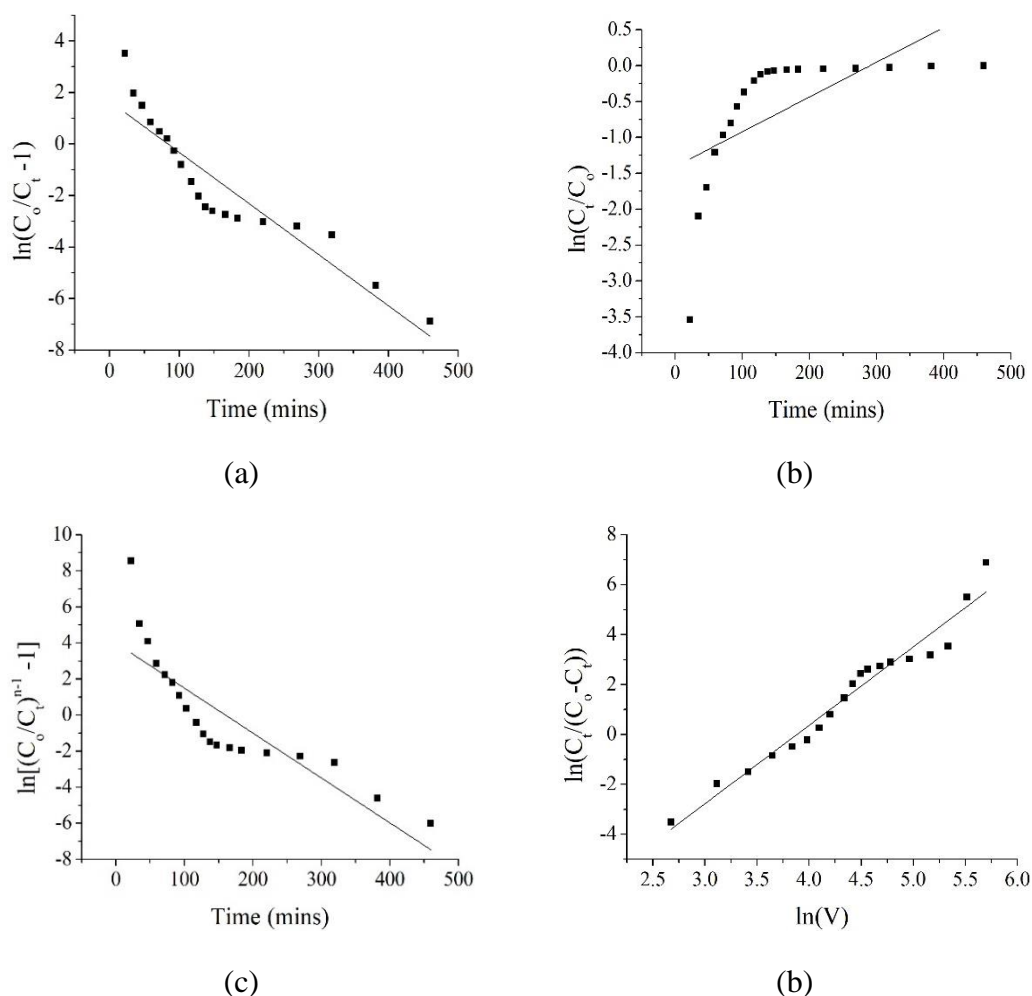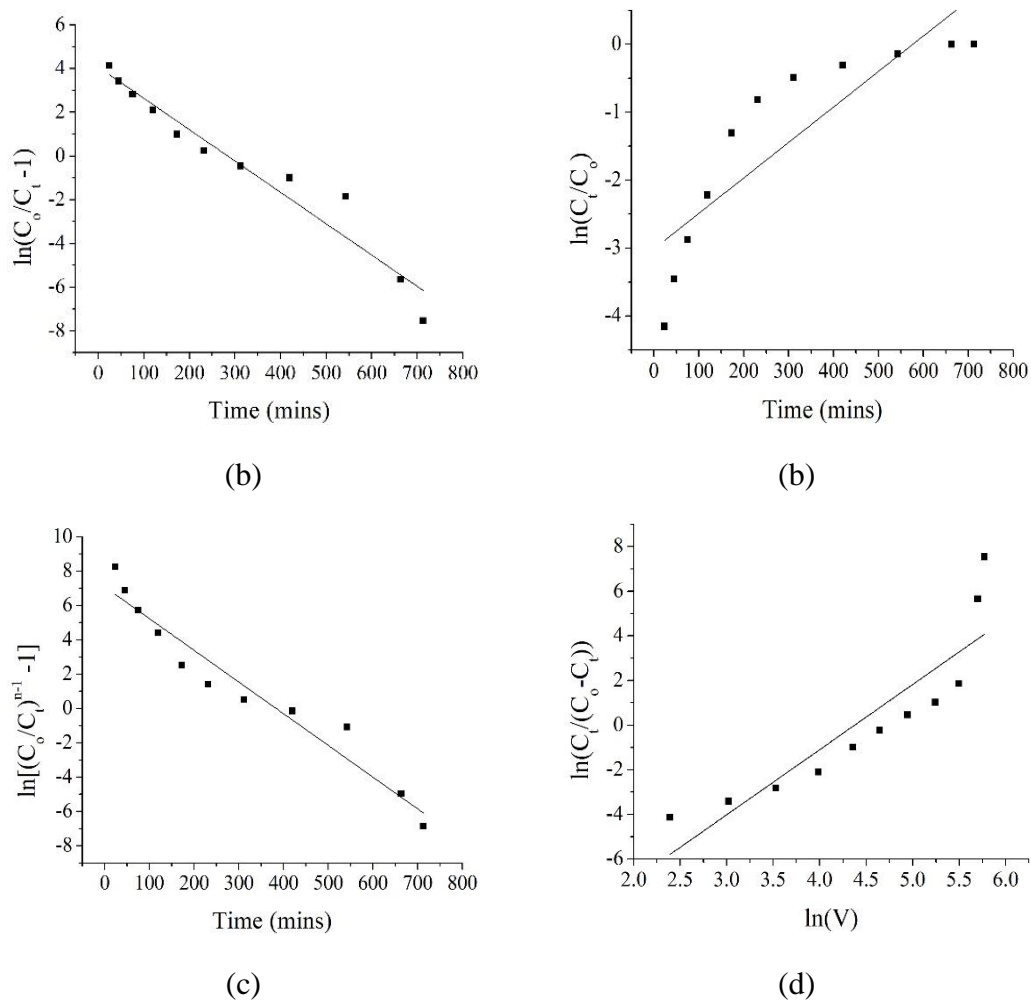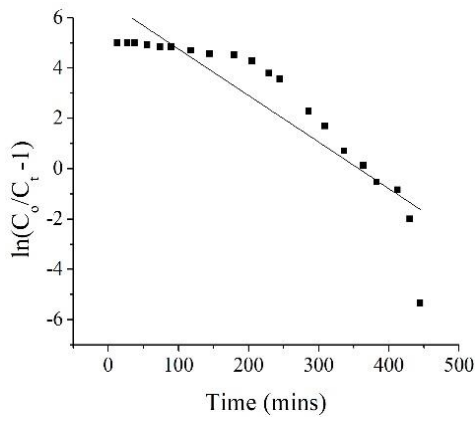
(a)
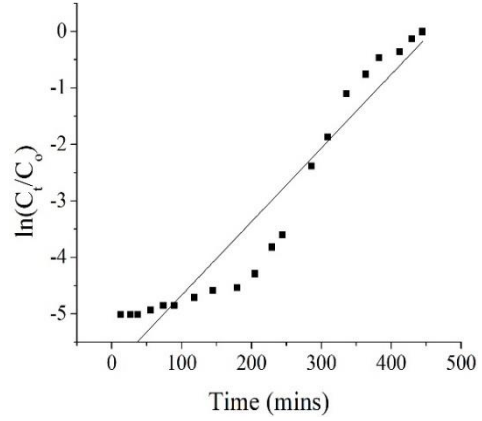
(b)
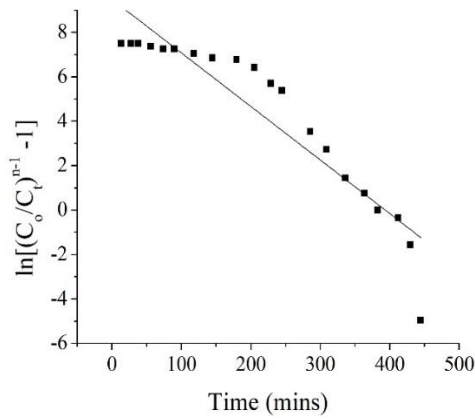
(c)
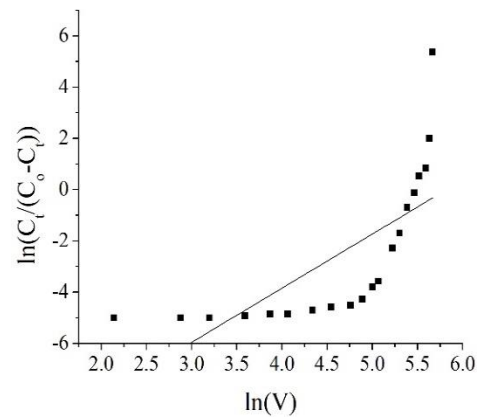
(d)

Figure 28. (a) Thomas (b) Bohart and Adams (c) Clark and (d) Yan et al. model for fixed-bed adsorption of ASP using RGOM (Flow rate: 0.65 mL/min; Bed Depth: 1.8 cm; pH: 3±0.1; Initial concentration: 100 mg/L; Temperature: 25°C).

Chapter 5. Conclusion and Recommendations

The use of adsorption as a primary method of removing pharmaceutical compounds from wastewater was studied in this work. Two graphene oxide-based nanocomposites (RGOM and GONF) were employed to remove three pharmaceuticals from water. Batch and continuous adsorption experiments were conducted to find optimum conditions for the removal of DCS, ASP and PAR. Isotherm, kinetic and thermodynamic study was completed to gain further insight of adsorption process. The use of RGOM showed good efficiency in removing the pharmaceuticals and exhibited better adsorption capacity than GONF. Optimum conditions were estimated, and the adsorption data was fitted using different isotherm, kinetic, thermodynamic and fixed bed column models. The study can be applied in industrial wastewater treatment given that the different material such as graphene oxide, iron chloride, nickel nitrate etc., used in this study are commercially available. This work is focused on the individual pharmaceutical compounds. However, pharmaceuticals can exhibit different behaviour in the vicinity of other compounds and a detailed study of using these adsorbents in a mixture of pharmaceuticals compounds is recommended.

Although the adsorption capacity was low, commercial availability, easy one-pot process for the manufacturing of both adsorbents and good reusability give an economic impact to the adsorption process and fulfils the objective of using adsorption process as a primary treatment method in the industry. The magnetite particles give extra advantage of easy separation of adsorbent from water which also contributes to a reduction in overall operational costs.

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Vita

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