LAPPEENRANTA-LAHTI UNIVERSITY OF TECHNOLOGY LUT
LUT School of Engineering Science
Chemical Engineering

Master's thesis

Anna Lankila

Removal of pharmaceutical compounds by adsorption

Examiners: Professor Mika Mänttäri
D.Sc. (Tech.) Laura Kaijanen

ABSTACT

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The aim of this work was to evaluate the efficiency of two activated carbons and sawdust adsorbents in the removal of selected pharmaceutical compounds. The efficiency with which these adsorbents removed pharmaceuticals found in wastewater samples was studied under different conditions. The factors that were studied included temperature, adsorbent dosage and contact time. The experiments were performed using a batch adsorption set-up. Additionally, background information for pharmaceuticals and adsorption are examined in the theoretical part. Typical contacting systems for adsorption, common adsorbents used in wastewater treatment, and different factors that affect adsorbent performance are also discussed briefly.

With the highest adsorbent dosage 0.5 g/L, the powdered activated carbon (PAC in short) and granular activated carbon (GAC in short) used in the experiments reached over 90 % removal efficiency of all detected pharmaceuticals from wastewater samples. However, GAC's suitability for pharmaceutical removal decreased significantly with the decrease of temperature, contact time and dosage. Pharmaceutical removal was also successful using spruce sawdust, albeit less efficient than with PAC or GAC.

TIIVISTELMÄ

Lappeenrannan-Lahden Teknillinen Yliopisto LUT
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Lääkeaineiden poistaminen adsorptiolla

Diplomityö

2022

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Tarkastajat: Professori Mika Mänttäri, TkT Laura Kaijanen

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Tämän diplomityön tarkoituksena oli tutkia eri adsorbenttejä lääkeaineiden poistamisen kannalta. Tutkittavina adsorbentteinä olivat kaksi eri aktiivihiiltä sekä kaksi eri kuusipurua. Lääkeaineiden erotustehokkuuksia tarkasteltiin eri olosuhteissa käyttäen oikeita jätevesinäytteitä. Tutkittavat parametrit olivat lämpötila, adsorbentin annostus sekä kontaktiaika. Kokeet puolestaan suoritettiin panostyyppisellä adsorptiokoejärjestelyllä. Kirjallisuuskatsaus osassa annetaan taustatietoa lääkeaineille sekä adsorptiolle jäteveden puhdistukseen liittyen. Lisäksi tarkastellaan tyypillisiä adsorptiokontaktisysteemejä, yleisiä jäteveden puhdistuksessa käytettyjä adsorbenttejä, sekä ominaisuuksia, jotka vaikuttavat adsorbenttien suorituskykyyn.

Suurimmalla aktiivihiilien annostuksella 0.5 g/L päästiin yli 90 % erotustehokkuuksiin kaikilla jätevedestä havaituilla lääkeaineilla. Kuitenkin tutkitulla rakeisella aktiivihiilellä (GAC) erotustehokkuudet huomattavasti heikentyivät laskettaessa lämpötilaa, kontaktiaikaa tai adsorbentin annostusta. Edellä mainittujen parametrien vaikutus ei ollut yhtä merkittävä testatulla hienojakoisemmalla jauhemaisella aktiivihiilellä (PAC). Lääkeaineiden erotus onnistui myös kuusipurunäytteillä, ollen kuitenkin selkeästi vähemmän tehokasta.

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1 INTRODUCTION

For as long as there has been a pharmaceutical industry, there have been pharmaceuticals entering the water cycle. The accelerating pace at which this is happening, and the increasing awareness of their potential to cause various adverse effects, have together become a cause of great concern among the global scientific community within the last few decades (Deblonde et al., 2011). As a sign of this recognition, pharmaceuticals are officially recognized as emerging contaminants (ECs) by the EU as well as across the world. This underlines the fact that the current understanding of their effect on the environment and human wellbeing is inadequate, as are the regulations and laws concerning them. (Geissen et al., 2015)

The primary way that pharmaceuticals become pollutants is via excrement, where consumed pharmaceuticals can remain up to 90 % unchanged (Lindholm-Lehto et al., 2016). The accelerated pace of pharmaceuticals entering the water cycle can thus be attributed to widespread demographic trends, such as increases in median age and the population in general, or by societal trends such as increases in living standards and available pharmaceutical products (Boecking et al., 2012).

The full effects of pharmaceuticals on nature are extensive and difficult to evaluate or estimate, since pharmaceutical compounds by themselves may not necessarily be as concerning as the unique combinations and degradation products which they create after they have entered environments that they were not intended for. These effects are inherently very difficult to predict, and there is even less available data and research to draw from compared to regular pharmaceuticals (Lindholm-Lehto et al., 2016). Furthermore, even in low concentrations, pharmaceuticals can have extreme and unpredictable effects on not just humans and mammals, but also, for example, on fish and plant life. In some species, the effects might be similar to the original intended effect for human and veterinary use, while in others they may vary drastically. Furthermore, as pharmaceuticals accumulate in a natural ecosystem through continuous exposure, microbial strains in the ecosystem become more resistant to antibiotics. (Fent et al., 2006; Pal, 2018)

The purpose of this thesis was to evaluate activated carbons and spruce sawdust as adsorbents and their capability for pharmaceutical removal. In the literature part of the work, background information for adsorption in the context of wastewater treatment is given, and typical adsorbents in wastewater treatment are discussed. Additionally, various factors affecting the performance of adsorbents are presented. In the experimental part of the work, the effect of three different factors in wastewater adsorption are examined. These factors are temperature, contact time and adsorbent dosage, and the focus is on their impact on the removal efficiency of pharmaceuticals.

LITERATURE REVIEW

2 PHARMACEUTICAL COMPOUNDS IN WASTEWATER

2.1 Pharmaceutical waste sources

Measurable concentrations of pharmaceuticals can be found today in surface water, ground water, effluents and even tap water, usually in the range of $\mu g l^{-1}$ to $n g l^{-1}$. (Garric & Ferrari, 2005) Pharmaceutical waste pervades all phases of the water cycle, with most of it being produced by companies in the pharmaceutical industry, but increasing volumes of said waste also comes from domestic and hospital wastewater. (Pal, 2018)

Shortcomings in both technology and regulation have adversely affected the removal rate of pharmaceutical waste. However, even under more rigorous regulatory conditions than those that exist today, companies are not typically inherently incentivized to reduce their pollution so much as outsource it or conceal its magnitude. (Pal, 2018)

2.2 Classification, composition and typical pharmaceuticals in wastewater

Although pharmaceuticals have so far been framed as a singular group due to the commonalities in their intended uses, the term actually encompasses a large group of different compounds that are chemically very diverse and thus have very different properties

(Pal, 2018). This group contains more than 4000 different molecules and 10,000 different specialty products (Beausse, 2004). Pharmaceuticals created for human use are bioavailable by design, but the increased amount of attention given to trace amounts of pharmaceuticals in the environment and the effects that they might have is a relatively recent development in the scientific community (Monteiro & Boxall, 2010). This attention has mostly been concentrated on therapeutic classes of drugs, such as antibiotics, sex hormones or lipid-lowering and anti-inflammatory drugs. Combined, these account for a large part of pharmaceutical pollution. (Martín et al., 2012)

Traditional treatment systems for wastewater treatment were not designed with the removal of pharmaceutical compounds in mind. Despite this, some of them can be removed by existing systems more effectively than others. (Monteiro & Boxall, 2010)

2.2.1 Antibiotics

Antibiotics are a group of pharmaceuticals that function as antimicrobials, treating fungi, parasites or pathogenic bacterial infections by either suppressing their growth or killing them. Antibiotics include natural substances as well as synthetic or chemically modified natural compounds, which in total amount to about 250 different antibiotics for human and veterinary pharmaceutical use. In the past, antibiotics used to refer only to natural compounds, the first being penicillin, and they were produced from bacteria or fungi. (Jafari Ozumchelouei et al., 2020; Kümmerer, 2009)

Typically, antibiotics are small but complex molecules, more often than not possessing multiple functionalities. Because of these different functionalities, antibiotics can be neutral, cationic, anionic, or zwitterionic depending on the pH conditions, which may change the properties of the antibiotic, such as its sorption behavior. Antibiotics can be categorized according to their action mechanism or their chemical structure. When grouped on the basis of chemical structure, the most important classes of antibiotics include aminoglycosides, glycopeptides, macrolides, ß-lactamase, sulfonamides, tetracyclines, and quinolones. (Kümmerer, 2009)

In many countries, antibiotics are more commonly used for veterinary purposes than they are for human consumption. In 2012, the use of antibiotics for veterinary antimicrobials in Germany was more than three times higher than for human medicine, and in Spain, the equivalent ratio was over six times as much in 2014. (Szymańska et al., 2019)

The increasing amount of resistance to antibiotics in bacteria is an important public health issue and a cause of concern across the world. This phenomenon can be largely attributed to excessive and often unwarranted application of antibiotics across multiple sectors. (Szymańska et al., 2019) Examples of this include the preventive placement of antibiotics in fishponds, the use of antibiotics in various crops to prevent plant disease, and the inclusion of antibiotics in livestock feed either as a preventative measure or as growth promoters. (Hirsch et al., 1999; McManus, 2014; Szymańska et al., 2019)

Humans and animals generally metabolize antibiotics quite poorly, causing antibiotics to enter the water cycle via feces carried in wastewater (Szymańska et al., 2019). The removal rate of antibiotics in wastewater treatment is around 50 % on average. However, there are drastic differences in the removal rates of specific antibiotics, as well as the removal rates at specific wastewater treatment plants with different methods. At one extreme of the studied antibiotics is Tetracycline, with a 95 % removal rate, while at the other is Trimethoprim, with only a 1.4 % removal rate. (Deblonde et al., 2011)

2.2.2 Beta blockers

Beta adrenergic antagonists are pharmaceuticals which block beta-adrenergic receptors. They are usually referred to as beta blockers, or just β-Blockers in short. This medical class has extensive usage for the treatment of many illnesses, such as treatment of hypertension, anxiety, cardiac arrhythmias and angina. (Scheurer et al., 2010) Due to their wide range of applications, beta blockers are high on the list of most descripted pharmaceuticals, ranking 4th in the United States, for instance (Iancu et al., 2020).

The amino moiety of beta blockers leads them to be positively charged and protonated in neutral pH conditions. All beta blockers are also weak bases, and their acidity constant values are above nine. (Maurer et al., 2007; Ramil et al., 2010) Typical beta blockers in

common commercial use include atenolol, betaxolol, bisoprolol, metoprolol and propranolol. (Iancu et al., 2020)

Typically, beta blockers are not efficiently removed in wastewater treatment plants due to their slow degradation rates. After consumption, the beta blockers are metabolized to different degrees depending on the compound. For example, atenolol medication can remain approximately 90 % unchanged, unlike propranolol, which can be metabolized extensively, over 90%. Like many pharmaceuticals, beta blockers can have undesirable effects when coming into contact with the environment. Propranolol is particularly toxic to aquatic life, even in low concentrations; its effects on green algae are well-studied. (Gabet-Giraud et al., 2014; Maurer et al., 2007; Ramil et al., 2010)

3 ADSORPTION IN THE CONTEXT OF WASTEWATER TREATMENT

3.1 Fundamentals of adsorption

Adsorption is a phenomenon where the adsorbent accumulates adsorbate to its surface, bonding generally due to van der Waals forces (physisorption), covalent bonding or electrostatic attraction (chemisorption). In chemisorption, the adsorbate and the adsorbent are bonded with stronger forces in a monolayerlike fashion, and are consequently harder to separate. Depending on the case, only one of these processes could occur, or possibly both at same time. (De Gisi et al., 2016) This is one of the ways to explain and define adsorption as a surface process, where the adsorbate collides with the adsorbent and intermolecular forces of attraction cause the adsorbate to be deposited on the surface of the adsorbent. Adsorption can happen between solid-liquid phases, which are solid porous adsorbent and absorbable solute. This is the most important case in water treatment contexts, but there are also other types of adsorption processes, namely solid-gas, liquid-liquid and liquid-gas. (Dąbrowski, 2001; Hu & Xu, 2020; Sadegh et al., 2017)

Another way to explain the adsorption process is as a mass transfer process, where substance moves from one phase to another, becoming bonded to it in the process, such as from liquid

to a solid surface (Sadegh et al., 2017). The adsorption process is usually reversible, and that reversed process is referred to as desorption (Artioli, 2008). In this way, adsorbents can sometimes be regenerated and reused after their initial usage (Lata et al., 2015).

3.2 Adsorption mechanism

The adsorption process is always divided into three major steps in typical adsorption diffusion models. The first step is known as external or film diffusion, meaning the diffusion of the adsorbate from solution through the liquid film that surrounds adsorbent particles. The second step is internal diffusion or intraparticle diffusion, where adsorbate is migrated into pores of the adsorbent or along the pore walls. The last step is adsorption, where the adsorbate is attached into the adsorbent surface site. This last stage is considerably faster than the first two of the aforementioned steps, so adsorption rate is mostly controlled by the first two. (Qiu et al., 2009; Viegas et al., 2014)

3.3 Adsorption isotherms and kinetic models

The adsorption process has been classically modeled and calculated with isotherms, which are equations that describe the amount of adsorbate adsorbed per unit weight of adsorbent as an equilibrium concentration function at a given temperature in bulk solution. The equilibrium stage is where the adsorbent has reached its capacity, or in other words, the adsorption rate is the same as the desorption rate. (Artioli, 2008; Sadegh et al., 2017; S. Singh & Kaushal, 2017) Temperature is an important factor in adsorption, and isothermal parameters are highly dependent on it, as the word's etymology – *therme* meaning heat – suggests. However, the most famous and commonly used isotherm models are the Langmuir and the Freundlich equations, which are presented in Equation 1 (Langmuir) and 2 (Freundlich). There are several other models including Dubinin-Kaganer-Radushkevich, Temkin and Harkin-Jura, just to name a few. The Freundlich equation describes heterogeneous surface adsorption, whereas the Langmuir equation is related to monolayer adsorption. (Ali, 2014; Artioli, 2008; Sadegh et al., 2017) The classical isotherm models contain uncontrolled approximations and are not always representative of real-life applications as a result, but these equations are relatively easy to use and convenient, so isotherms are in widespread use (Dąbrowski, 2001).

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}K_1} + \left(\frac{1}{Q_{max}}\right) C_e \quad (1)$$

where Q_{max} is Langmuir constant

K_1 is Langmuir constant

C_e is equilibrium concentration, (mg L^{-1})

q_e is adsorbed adsorbates mass per unit amount of adsorbent, (mg g^{-1})

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

where $\frac{1}{n}$ is constant, relating to system characteristics

K_F is constant, relating to system characteristics

C_e is equilibrium concentration, (mg L^{-1})

q_e is adsorbed adsorbates mass per unit amount of adsorbent, (mg g^{-1})

The kinetic models for adsorption are used to describe the rate at which the adsorption process is progressing. Adsorption mechanisms can be also analyzed with these models. There are many kinetic models available, such as intra-particle diffusion models, pseudo-second-order (presented in Equation 5), pseudo-first-order (presented in Equation 4) and simple-first-order (presented in Equation 3). (Sadegh et al., 2017) The mass transfer rate of solution to the surface of the adsorbent controls the adsorption kinetics. Adsorption kinetics are usually a relatively slow process, where reaching the equilibrium stage can take several weeks. (Howe, 2012)

$$\log q_t = \frac{k_s}{2.303} t + \log q_e \quad (3)$$

where q_e is adsorbed adsorbate at equilibrium, (mg g^{-1})

q_t is adsorbed adsorbate at specific moment t, (mg g^{-1})

k_s is rate constant, (h^{-1})

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

where q_e is adsorbed adsorbate at equilibrium, (mg g^{-1})

q_t is adsorbed adsorbate at specific moment t, (mg g^{-1})

k_1 is rate constant, (h^{-1})

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where q_e is adsorbed adsorbate at equilibrium, (mg g^{-1})

q_t is adsorbed adsorbate at specific moment t, (mg g^{-1})

k_2 is equilibrium rate constant, (g mg^{-1} h^{-1})

3.4 Background of water treatment by adsorption

The oldest and most popular adsorbent in present day use is activated carbon, though it has a relatively short history in its current form (Çeçen & Aktaş, 2011; Yu & Han, 2015). However, the earliest forms of using carbon for water purification and treatment can be found in ancient times. Examples of this include Hindu records from as early as 450 BCE, which describe the use of sand and charcoal filters for the water purification, and a Sankrit document from around 200 AD, which describes the filtration of water through coal via the use of copper vessels and sunlight. (Çeçen & Aktaş, 2011)

In the present day, we live in what can be called a "Pollutant Removal Age", where the detrimental effects of pollutants caused by human activity are relatively well known, and numerous techniques are available for water treatment. However, within the last few decades or so, adsorption has gained importance within the field of water treatment. Adsorption as a process is technologically simple and does not require high pressure or temperature. It is economically viable while also producing high-quality water. All of these advantages makes it appealing from an industrial perspective. (Crini et al., 2018; Gul Zaman et al., 2021)

3.5 Different types of contacting systems

Deciding the right type of contacting system for any given case is essential for the optimal financial outcome as well as for the efficiency of the process. This is partly because the adsorbent performance is not only affected by the intrinsic properties of the adsorbent, but the process system also dictates adsorbent performance to some degree (Dichiara et al., 2015). The most important selection criteria are, unsurprisingly, the intended use of the

process and the target substances for the adsorbent process. Adsorption processes can be divided to and examined as two general groups: adsorption processes from dilute solution and adsorption processes from multiple component mixtures. In the field of water treatment, with solid-liquid systems, the most common adsorbent process types are the batch-type process and the fixed-bed-type process, which are used in both industrial and laboratory scale applications. In the batch-type process, the process is carried out discontinuously, whereas in the columns and fixed-bed process, it is sustained continuously. Other types of processes include moving mat filters, pulsed beds and fluidized beds which can be utilized, for example, to obtain experimental data for industrial applications. (Ali, 2014; Crini et al., 2018)

3.5.1 Batch process

The batch process is a simple and useful method especially for laboratory testing, but it is also used for more large-scale processes. The batch process is a single-step operation, where adsorbent is mixed with contaminated water. This can be done using a mixing tank, or simply in a flask or other equipment, but the key is that the volume of the contaminated water does not change during the process. (Crini et al., 2018; Desta, 2013; Dichiara et al., 2015; Vashi & Patel, 2015) After this, adsorption ensues and given enough time, equilibrium is reached (Vashi & Patel, 2015). It is important to note that reaching equilibrium completely can take as long as weeks, and it is not usually necessary to wait for it unless it is an essential part of the experiment, like in adsorption isotherm parameter determination (Howe, 2012).

The batch methods have many benefits, which are often related to the simplicity and controllability of the experimental setup. It is a practical approach, where the process parameters, such as pH, temperature and contact time can be easily adjusted. It is also a relatively cheap process that usually only requires readily available equipment. The experimental method is well-established, and the results are easy to interpret. (Aktar, 2021; Crini et al., 2018) This is why the batch method setup is used in many different experiments, including the investigation of adsorption rate and capacity. The batch adsorption treatment can be utilized for adsorption equilibrium measurements, kinetic mass transfer data measurements, adsorbent characterization, and attenuation predictions of pollutants. (Vashi & Patel, 2015) However, the batch method is a non-destructive process, where contaminants

only change phases. Thus, a major drawback to the batch method is sludge disposal after the adsorption process. Additionally, the batch method treats relatively small volumes of solution, which is another one of its drawbacks. (Crini et al., 2018)

3.5.2 Continuous process

While the batch adsorption process is primarily applied on a laboratory scale, continuous adsorption processes (fixed-bed adsorbers or columns) are often unnecessarily complicated in laboratory testing. They are instead mainly utilized on an industrial scale, where the continuous process is commonly – albeit not always - considered the superior out of the two. (Al-Degs et al., 2009; Ali, 2014; Crini et al., 2018; Dichiara et al., 2015) In the fixed-bed systems, the adsorbent layer is put in contact with fresh solution continuously, and given enough time to reach adsorption equilibrium, meaning that the adsorbent layer has reached its capacity and is unable to adsorb further adsorbate. There are some practical limitations to this in real-life situations, such as axial dispersion limiting the adsorbent efficiency, but in the end, a major part of the adsorbent layer is in equilibrium with the concentration of the feed. (Dichiara et al., 2015) After the adsorbent has reached its capacity and is considered spent, typically one of two actions are done: the adsorbent is either regenerated, or it is replaced. The chosen procedure depends on the properties of the adsorbent, as all adsorbent materials cannot be regenerated, and recovering the adsorbate is not even always desirable. The regeneration can considerably lower down-process costs since the adsorbent can be reused after regeneration. (Crini et al., 2018)

In fixed-bed systems, the adsorption efficiency depends on solute concentration, which is considered a major advantage over the batch method. Though the batch process may become a more efficient option than the fixed-bed process after effluent concentration is high enough. Fixed-bed columns generally have improved mass and heat transfer characteristics and better residence times when compared to batch systems. Additionally, given enough time in the fixed-bed process, the solution is completely removed of contaminants, which is not possible in a well-mixed batch method. However, complete removal is not always necessary, which also presents an opportunity to reduce adsorbent load (Crini et al., 2018; Dichiara et al., 2015)

3.6 Typical adsorbents in wastewater treatment

There are many ways to group adsorbents in water treatment, such as by making a simplified distinction between adsorbents that are commonly used adsorbents, and ones that are non-conventional. However, the more common way to categorize adsorbents is to group them by origin. (Crini et al., 2018) In the following chapters, different groups of adsorbents are presented. These are, in order of appearance, natural adsorbents, by-products and wastes of agriculture or industry, and lastly, modified natural adsorbents and manufactured adsorbents. Finally, the different types of adsorbents are compared to one another, and the removal rates for different pharmaceuticals in water treatment are presented visually.

A large number of different factors – such as cost, stability, adsorption capacity, reusability, and environmental effects – should be taken into account in selecting adsorbents (Bello & Raman, 2018). The one that is most commonly used in water treatment today is activated carbon, which is also the oldest and historically most widespread known adsorbent. Although the group of adsorbents that sees the most amount of commercial use is quite small, a lot of progress has been made in recent years in adsorbent development. These commercial adsorbents include, by decreasing rate of utilization: commercial activated carbons, zeolites, silica gel and commercial activated aluminas. (Crini et al., 2018; De Gisi et al., 2016; Yu & Han, 2015) In addition, new engineered adsorbent materials and composites have been used and developed, such as carbon nanotubes and chitosan-based composites. Engineered adsorbents refer to adsorbent materials that are developed with a specific purpose in mind, often for the removal of pollutants. Typical characteristics of engineered adsorbents are high levels of stability and adsorption capacity, as well as large surface areas. There has also been an increasing demand for low-cost adsorbents derived from easily accessible natural or waste-based materials, which can sometimes, if necessary, be modified for improved adsorption properties, but can also be used by themselves. (Bello & Raman, 2018; Rashed, 2013)

3.6.1 Natural adsorbents

Natural adsorbents are a group of natural materials which are typically characterized by easy availability and supply, low cost, relatively low adsorption capacity and good

modification potential (Bello & Raman, 2018; Bhatnagar, 2013; Rashed, 2013). The relatively cheap price of these adsorbents allows for the spent adsorbent material to be simply disposed, thus avoiding costly regeneration processes. On the other hand, due to their low adsorption capacity, more waste is generated compared to engineered adsorbents. (Bhatnagar, 2013) Adsorbent properties can be enhanced with chemical or physical modifications, but this obviously raises the associated costs (Bello & Raman, 2018).

Natural adsorbents can be inorganic or organic, and include, for example, zeolites, clay minerals, clay, chitosan, charcoal, ores and sawdust (Bhatnagar, 2013; Rashed, 2013). It is notable that sawdust, for example, can be classified as agricultural waste material, or as a natural adsorbent, depending on the context and the classification system in question (N. Singh, 2018; Vishnu et al., 2021). Clay minerals are perhaps the most investigated natural adsorbents due to their non-toxicity, inexpensiveness, abundance and good adsorption properties for organic compounds and cations. Clay minerals have a colloidal nature and negatively charged surfaces, but some modification to the surface is still usually needed to improve adsorption capacity. (Bello & Raman, 2018)

3.6.2 Agricultural and industrial wastes or by-products as adsorbents

Using agricultural and industrial wastes or by-products as adsorbent material repurposes them and lowers the amount of waste that requires treatment operations. Recycling and reusing these wastes can have a substantial positive environmental impact and can also be a cost-efficient solution. These wastes are generated in large amounts, mostly treated with costly and complex methods where the risk for secondary pollution is high. (Mo et al., 2018) From these factors come the greatest advantages of these adsorbents: good material availability, low cost, and environmental friendliness. However, these materials usually need modification to advance properties such as surface area and porosity. Typical modification technologies include activation, grafting, carbonization and nanostucturing. (Bello & Raman, 2018; Mo et al., 2018)

Wastes and by-products of agriculture include many lignocellulosic materials - materials containing lignin and cellulose components - such as sawdust, coconut husk, oil palm shell

or rice husk (Bello & Raman, 2018; Hegazi, 2013). Numerous studies have been conducted regarding the use of these materials to physically adsorb heavy metals ions such as Hg, Pb, Ni, Cu, Cr, Cd and As, especially with these lignocellulosic materials. The removal of organic pollutants has also been a common subject of interest. These adsorbent materials have other advantages in wastewater treatment, such as chemical stability and ease of regeneration. (Bhatnagar, 2013; Mo et al., 2018)

Wastes and by-products from industrial activity includes sludge, fly ash, red mud and sawdust. When comparing these low-cost waste-based materials to one another, one important parameter that stands out is the local availability of the material. It is also notable that these adsorbents cost information is rarely reported. (Bello & Raman, 2018; Hegazi, 2013)

3.6.2.1 Sawdust

Sawdust is a natural lignocellulosic raw material, which can be collected from many agricultural waste sources. Being a byproduct of wood, it is a relatively low-priced and readily available material. Sawdust main utilizations are as bedding material for cattle and as an energy source. Sawdust's usefulness in water treatment has been widely studied, and promising adsorption results have been found regarding the removal of total organic carbon, heavy metal and phenol. (Elboughdiri et al., 2021; Leiviskä, 2014; Zaidun, 2018) Although sawdust has noteworthy benefits over more typical adsorbent solutions like activated carbons, such as price and a lack of a need for regeneration, there are still many obstacles to overcome in the material's usage. The main challenges come down to modification and disposal problems. Sawdust has been studied without modifications as such and with them; modifications widen the range of possible applications, but every addition raises cost, and possibly has an effect on biodegradability. (Larous & Meniai, 2012; Leiviskä, 2014) Without modifications, sawdust has high carbon content and low ash content (Oladimeji et al., 2021).

3.6.2.2 Activated carbon

Activated carbon materials are widely used adsorbents in wastewater treatment. They can be utilized to remove wide varieties of pollutants from different water cycles, such as municipal

and industrial wastewater contaminated groundwater. The goal of activated carbon adsorption may be to achieve a more thorough treatment of the total flow, or to remove only a very specific group of pollutants. Although activated carbon materials have excellent adsorption ability, the drawbacks of the adsorbent somewhat limit its usage. These drawbacks include a high cost, low regeneration capacity, and problems with disposing of the spent adsorbent. Its remarkable adsorption ability is shown in related indicators. The specific surface area for activated carbon materials is between 500 – 2000 $m^2 g^{-1}$ and the iodine number is within the range of 500 – 1200 mg g^{-1}. (De Gisi et al., 2016; Yu & Han, 2015) These indicators are used for illustrating adsorbent ability, the iodine number meaning the ability to adsorb small molecules presented in milligrams of the iodine adsorbed per one gram of adsorbent. The specific surface area is related to adsorption capacity: typically higher specific surface area value indicates higher adsorption capacity. (De Gisi et al., 2016)

Activated carbon can be produced from relatively cheap raw materials, with natural materials and even agricultural and industrial wastes as possible options (Rashed, 2013). Although the range of utilizable raw material is quite large, it should be noted that the raw material that is used has an effect on the properties of the activated carbon product. For example, ash content depends on the utilized raw material, which has implications on adsorbent regeneration possibilities and the number of possible regeneration cycles. Typically, the regeneration cycle increases ash content by 0.5 % - 1.0 %, so if the ash content is already high, this limits possible regeneration cycles. Another important factor affecting adsorbent properties is the production method. Typically, there are two main routes to produce activated carbon material: one activation process is the chemical method and other one is the physical method. In the physical method, carbonized materials are placed in contact with a steam flow at a temperature between 800 – 1000 °C, and in the chemical method, acids are added to carbonized materials. (De Gisi et al., 2016; Yu & Han, 2015)

The two main forms of activated carbon used in the context of water treatment are granular activated carbon and powder activated carbon, with granular activated carbon being the one more often used out of the two (Yu & Han, 2015). Granular activated carbons have the advantage in cost, but their drawbacks include poor selectivity, slow kinetics, regeneration limitations and limited design flexibility. They are also at a disadvantage when it comes to working capacity, since the micropores in granular activated carbons are relatively

inaccessible. Powder activated carbons do not have this issue, since the powder form increases accessibility to pores with small particle sizes. But as a drawback, powder activated carbons cannot be used for filtration properly due to their powder form, which results in impractical pressure drops in the process. Other associated disadvantages include regeneration limitations, limited design flexibility and difficulties surrounding the disposal of spent adsorbent. (Yue & Economy, 2017)

Of course, there are other less used activated carbon materials that are available. Activated carbon fibers are a promising example, with higher adsorption capacity and adsorption kinetics than granular activated carbons, as well as a better porous structure that makes their micropores directly accessible from the surface of the fiber. However, the market for them is still underdeveloped relative to activated carbons due to the production costs associated with activated carbon fibers (Bottani & Tascón, 2008; Moreno-Castilla, 2004)

3.6.3 Comparison

The different types of adsorbent materials and their efficiency to adsorb various pharmaceuticals are presented in Table 1. The presented adsorbent materials include examples of various activated carbons and biochars. Table 1 shows examples of adsorption experiments made with commercial activated carbons (PAC and GAC) and less expensive alternates such as re-purposed waste-based biochar and activated carbon. It is noticeable how adsorbent material has an effect on selected adsorbent dosage, with commercial activated carbons using noticeably smaller dosages. Pharmaceutical compounds properties are also of great importance: as seen in Table 1, the same set-up with the same adsorbent but a different drug can have completely different results in terms of removal efficiency. All experiments are done in room temperature with a batch adsorption set up and 200 rpm stirring speed. Pharmaceutical solutions were prepared as either mixtures or as single drug solutions in pure water.

Pharmaceutical removal efficiency can be calculated using Equation 6, and the amount of adsorbate adsorbed per used adsorbent can be calculated using Equation 7. These

calculations can be used to compare the results of adsorption experiments. However, changing too many variables at the same time reduces the comparability of the experiments.

$$Removal\ efficiency\ (\%) = \frac{C_0 - C_t}{C_0} \times 100, \quad (6)$$

where C_0 is the adsorbate's initial concentration

C_t is the adsorbate's concentration at the time t. (Ndoun et al., 2021)

$$q_t = \frac{C_0 - C_t}{m} \times V \quad (7)$$

where C_0 is the adsorbate's initial concentration

C_t is the adsorbate's concentration at the time t

V is the solution volume and m is adsorbent mass. (Ndoun et al., 2021)

Table 1 Comparison of the efficiency of different activated carbons and biochars as adsorbents at pharmaceutical removal.

Adsorbent	Pharmaceutical	Removal efficiency	Experimental set up	Drug and adsorbent concentration	Source
Commercial granular activated carbon (MG 1050)	Acetaminophen	52 %	Contact time: 2 h, pH 7	Initial drug concentration: 3 mg/L Adsorbent dosage: 1 g/L	(Luján-Facundo et al., 2019)
Commercial granular activated carbon (MG 1050)	Diazepam	79 %	Contact time: 2 h, pH 7	Initial drug concentration: 3 mg/L Adsorbent dosage: 1 g/L	(Luján-Facundo et al., 2019)
Commercial granular activated carbon (MG 1050)	Caffeine	70 %	Contact time: 2 h, pH 7	Initial drug concentration: 3 mg/L Adsorbent dosage: 1 g/L	(Luján-Facundo et al., 2019)
Commercial granular activated carbon (MG 1050)	Ibuprofen	48 %	Contact time: 2 h, pH 7	Initial drug concentration: 3 mg/L Adsorbent dosage: 1 g/L	(Luján-Facundo et al., 2019)
Commercial powder activated carbon (BM 8)	Acetaminophen	99 %	Contact time: 1 h, pH 7	Initial drug concentration: 3 mg/L Adsorbent dosage: 0.5 g/L	(Luján-Facundo et al., 2019)
Commercial powder activated carbon (BM 8)	Diazepam	100 %	Contact time: 1 h, pH 7	Initial drug concentration: 3 mg/L Adsorbent dosage: 0.5 g/L	(Luján-Facundo et al., 2019)
Commercial powder activated carbon (BM 8)	Caffeine	100 %	Contact time: 1 h, pH 7	Initial drug concentration: 3 mg/L Adsorbent dosage: 0.5 g/L	(Luján-Facundo et al., 2019)
Commercial powder activated carbon (BM 8)	Ibuprofen	100 %	Contact time: 1 h, pH 7	Initial drug concentration: 3 mg/L Adsorbent dosage: 0.5 g/L	(Luján-Facundo et al., 2019)

Adsorbent	Pharmaceutical	Removal efficiency	Experimental set up	Drug and adsorbent concentration	Source
Reused powder activated carbon	Acetaminophen	95 %	Contact time: 1 h, pH 7	Initial drug concentration: 3 mg/L Adsorbent dosage: 0.5 g/L	(Luján-Facundo et al., 2019)
Reused powder activated carbon	Diazepam	94 %	Contact time: 1 h, pH 7	Initial drug concentration: 3 mg/L Adsorbent dosage: 0.5 g/L	(Luján-Facundo et al., 2019)
Reused powder activated carbon	Caffeine	95 %	Contact time: 1 h, pH 7	Initial drug concentration: 3 mg/L Adsorbent dosage: 0.5 g/L	(Luján-Facundo et al., 2019)
Reused powder activated carbon	Ibuprofen	75 %	Contact time: 1 h, pH 7	Initial drug concentration: 3 mg/L Adsorbent dosage: 0.5 g/L	(Luján-Facundo et al., 2019)
Low-cost activated carbon from olive waste-cakes	Diclofenac	94 %	Contact time: 26 h, pH 4.1	Initial drug concentration: 15 mg/L Adsorbent dosage: 3.3 g/L	(Baccar et al., 2012)
Low-cost activated carbon from olive waste-cakes	Naproxen	92 %	Contact time: 26 h, pH 4.1	Initial drug concentration: 20 mg/L Adsorbent dosage: 3.3 g/L	(Baccar et al., 2012)
Low-cost activated carbon from olive waste-cakes	Ketoprofen	78 %	Contact time: 26 h, pH 4.1	Initial drug concentration: 19 mg/L Adsorbent dosage: 3.3 g/L	(Baccar et al., 2012)
Low-cost activated carbon from olive waste-cakes	Ibuprofen	70 %	Contact time: 26 h, pH 4.1	Initial drug concentration: 10 mg/L Adsorbent dosage: 3.3 g/L	(Baccar et al., 2012)
Cotton gin biochar, pyrolysis temperature 700 ^{o}C	Sulfapyridine	70%	Contact time: 24 h, pH 8 - 11	Initial drug concentration: 10 mg/L Adsorbent dosage: 5 g/L	(Ndoun et al., 2021)

Adsorbent	Pharmaceutical	Removal efficiency	Experimental set up	Drug and adsorbent concentration	Source
Cotton gin biochar, pyrolysis temperature 700 ^{o}C	Docusate	98%	Contact time: 24 h, pH 8 - 11	Initial drug concentration: 10 mg/L Adsorbent dosage: 5 g/L	(Ndoun et al., 2021)
Cotton gin biochar, pyrolysis temperature 700 ^{o}C	Erythromycin	74%	Contact time: 24 h, pH 8 - 11	Initial drug concentration: 10 mg/L Adsorbent dosage: 5 g/L	(Ndoun et al., 2021)
Cotton gin biochar, pyrolysis temperature 350 ^{o}C	Sulfapyridine	50%	Contact time: 24 h, pH 8 - 11	Initial drug concentration: 10 mg/L Adsorbent dosage: 5 g/L	(Ndoun et al., 2021)
Cotton gin biochar, pyrolysis temperature 350 ^{o}C	Docusate	79%	Contact time: 24 h, pH 8 - 11	Initial drug concentration: 10 mg/L Adsorbent dosage: 5 g/L	(Ndoun et al., 2021)
Cotton gin biochar, pyrolysis temperature 350 ^{o}C	Erythromycin	37%	Contact time: 24 h, pH 8 - 11	Initial drug concentration: 10 mg/L Adsorbent dosage: 5 g/L	(Ndoun et al., 2021)
Guayule bagasse biochar, pyrolysis temperature 350 ^{o}C	Sulfapyridine	14 %	Contact time: 24 h, pH 8 - 11	Initial drug concentration: 10 mg/L Adsorbent dosage: 5 g/L	(Ndoun et al., 2021)
Guayule bagasse biochar, pyrolysis temperature 350 ^{o}C	Docusate	66 %	Contact time: 24 h, pH 8 - 11	Initial drug concentration: 10 mg/L Adsorbent dosage: 5 g/L	(Ndoun et al., 2021)
Guayule bagasse biochar, pyrolysis temperature 350 ^{o}C	Erythromycin	50 %	Contact time: 24 h, pH 8 - 11	Initial drug concentration: 10 mg/L Adsorbent dosage: 5 g/L	(Ndoun et al., 2021)

3.7 Factors that affect adsorbent performance

The adsorption process is a complicated phenomenon. The nature and properties of adsorbate, adsorbent and environmental factors all affect the outcome and efficiency of adsorption. Some of these important factors are examined in the following sections.

3.7.1 Properties of the adsorbent

The properties of the adsorbent itself is, somewhat predictably, an important factor in determining the practicality of the adsorption process. Typically speaking, properties which enhance cost efficient features are favorable to have, including, for instance, a long lifespan, high selectivity and great adsorption capacity. These attributes are influenced by various physicochemical characteristics in adsorbents. Particularly influential factors include pore structure, surface area, surface functional groups and particle size. It is important to note that adsorbate-adsorbent interactions are also driven by the physical and chemical properties of the adsorbate, with solubility being one of the most important factors. (Cossu et al., 2018; Pourhakkak et al., 2021; Zahid et al., 2020)

3.7.1.1 Particle size

The effects of particle size are complicated, since change in particle size affects the chemical and physical properties of the material, such as interface system properties. Reduction of particle size is especially impactful after a certain threshold, depending on the type of particle in question. (Ikenyiri & Ukpaka, 2016)

Adsorption rate is highly linked to particle size. Particle size can also function as an indicator of material quality as well as performance. Particle size can be measured at its simplest with sieve analysis, by weighing adsorbent amount passing through specifically sized sieves, or measuring the diameter of particles from SEM images, for example. (Ikenyiri & Ukpaka, 2016; Müller, 2010)

3.7.1.2 Pore sizes

The pore size and structure of an adsorbent are determined by activation treatments and the precursor, which can be optimized for specific adsorbates. For instance, microporous materials are typically regarded as a favorable choice of adsorbent for gas adsorption, due to the small gas molecules being similar in size as the pores (Cao et al., 2021). Porous materials can be classified into three categories by the diameters of their pores, with the aforementioned microporous materials being one of them. Macropores refer to pores with a diameter of over 50 nm, mesopores or transitional pores refer to pores between 50 nm and 2 nm in diameter, and finally, micropores refer to pores which are less than 2 nm in diameter. (Pourhakkak et al., 2021; Savova et al., 2003)

3.7.1.3 Surface area

Adsorption is a surface phenomenon. Typically, high surface area of an adsorbent is attributed as an important characteristic affecting the capacity of the adsorbent. Thus, the adsorbent materials are often measured on the specific surface area. The specific surface area functions as an important evaluator value to adsorption capacity and the activity of the adsorbent. However, an adsorbent with a higher surface area is not always the better option, depending on the case. In some cases, using an adsorbent with a high surface area may cause pressure drop issues in the process, or make recovery more difficult. (Ikenyiri & Ukpaka, 2016; Suresh Kumar et al., 2019)

It is important to note that pore size, surface area and particle size are all related to one another. The pores of the particle increases the surface area. Additionally, the smaller that the particle size is, the higher the specific surface area is as well. (Ikenyiri & Ukpaka, 2016)

3.7.2 Environmental factors

3.7.2.1 Temperature

Wastewater temperature in treatment plants can vary based on seasonal as well as daily difference, possibly to a drastic degree. The effects of that variation are surprisingly complicated. Reflecting on the fact that adsorption is typically a spontaneous exothermic process, the conclusion would be that the adsorption process is reduced with higher temperatures. However, the outcome may also be entirely opposite, or even that the

temperature does not have a significant effect on efficiency of the adsorption process at all. Target pollutants and their properties also have important effects on the outcome as well. For example, changes in temperature also change the solubility of a target pollutant, which in turn may drastically decrease the adsorption of some pollutants, such as organic substances. (Marczewski et al., 2016)

EXPERIMENTAL PART

The following chapter presents the experiments done for the purpose of this work and explains its experimental methods. The effect of three different factors in wastewater adsorption – temperature, contact time and adsorbent dosage – are examined, with a focus on their impact on the removal efficiency of pharmaceuticals. Additionally, specific ultraviolet absorbance, or SUVA in short, is calculated for some of the samples. Of all the adsorbents examined in this work, sawdust and its suitability for wastewater treatment was the one most experimented on.

4 Materials and methods

All experiments were performed at LUT university laboratories in Lappeenranta, Finland. Wastewater for the experiments was collected from a local domestic wastewater treatment plant. Pharmaceutical compound analysis was done by and outsourced to Eurofins company.

4.1 Materials

4.1.1 Activated carbon

Two different activated carbons were used in the experiments. The first one is powdered activated carbon (PAC in short), developed and marketed to be particularly suited for wastewater treatment purposes. Specifically, its market name is NORIT® SAE 2, it is manufactured by Dolder AG, and its particle size is under 0.180 mm. In this work, it is

simply referred to as PAC, since it is the only PAC in this experiment. Another activated carbon that was used is granular activated carbon (GAC in short) which has a particle size range of 0.5 – 1 mm, is manufactured by Merck, Supelco, and referred to as GAC in this work.

4.1.2 Sawdust

4.1.2.1 Washing process

Sawdust made from spruce tree was used in the experiments both as such and washed. The sawdust was washed in order to investigate the impact of washing, and because it was predicted to facilitate pharmaceutical analysis. All sawdust samples also underwent an extraction process, with a 4:1 water sawdust ratio. For washed sawdust, this extraction process was performed before the washing process. At the beginning, extraction was carried out for one hour at room temperature, and continuing for a span of 2 hours at 160 °C.

The sawdust washing process was carried out as follows (illustrated in Figure 1). First, 100 g of sawdust was mixed with 1000 g of water. The water amount was chosen to be 10 times of sawdust, which is a generous amount. In the first round of washing, the sawdust expectedly adsorbed some of the added water, roughly half, corresponding to 5 times of the sawdust's own weight. In further washing rounds, the weight of the washing water remained roughly the same. The mixture was mixed for 5 minutes, after which it was filtered with sieves. The washing water was collected, and its color was subjected to spectrophotometry analysis. The washing process was repeated until the value of the spectrophotometry measurement did not noticeably chance between the last two measurements. In total, the washing process was repeated 4 times.

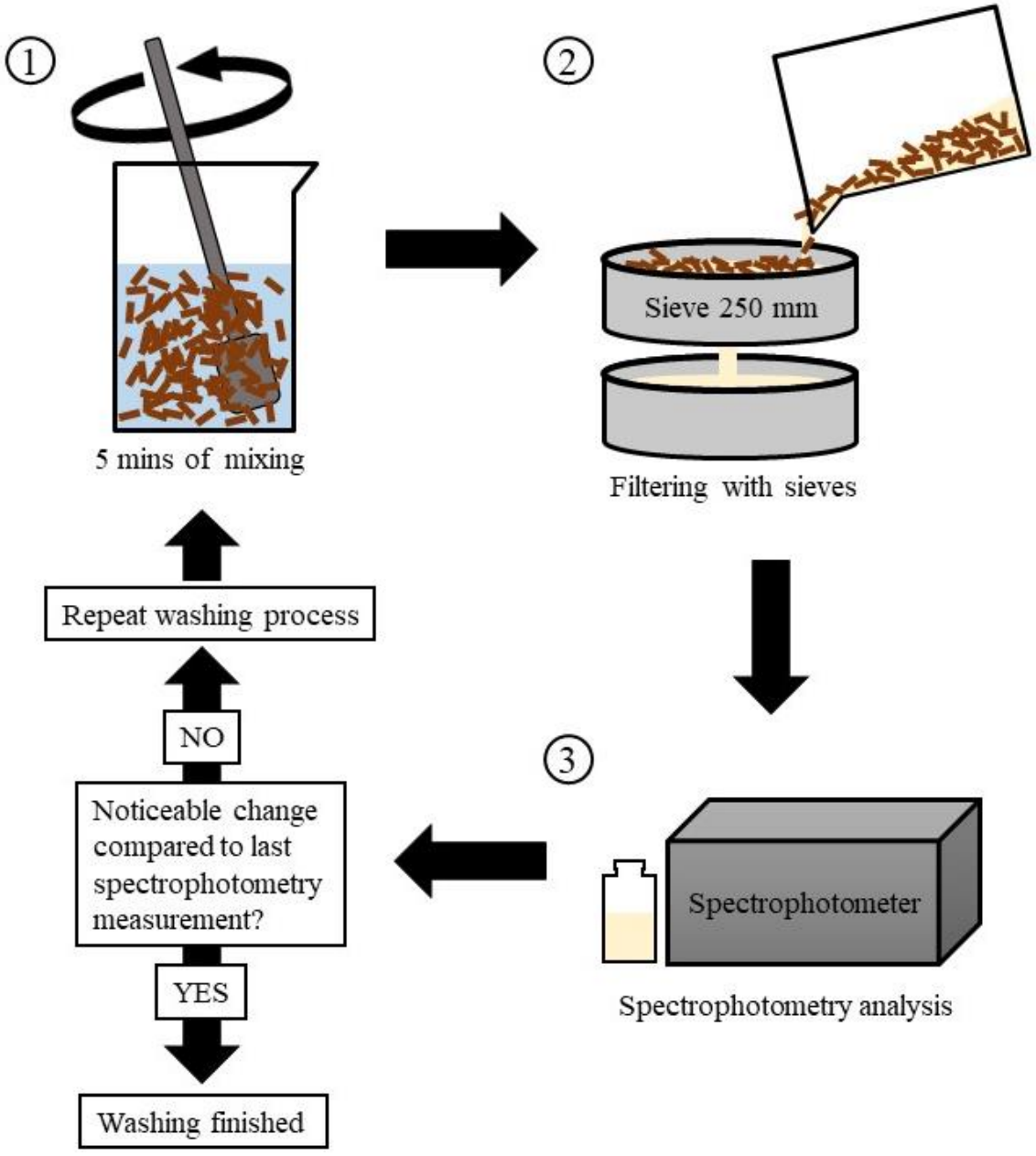

Figure 1 Illustration of the sawdust washing process.

After the washing process was carried out, the sawdust was dried of all moisture. The raw sawdust used for experiments was also dried in order to reach the same moisture percentage between all sawdust in order to maintain comparability. All sawdust was dried with Radwag MAC series moisture analyzer before the experiments, until 0 % of moisture was achieved. The washed sawdust was first dried out in the oven, since drying large quantities with only a moisture analyzer was found to be a highly inefficient and time-consuming process. The oven was heated to 90 °C, and the drying time was 4 hours.

4.1.2.2 Particle size distribution

The particle size distribution for sawdust was measured with a sieve analysis, using seven sieves that had openings of 2 mm, 1.40 mm, 1.00 mm, 0.710 mm, 0.355 mm, 0.250 mm and finally 0.125 mm. The experiment was done with a 75 g sawdust sample over the course of one hour. The sieve analysis was performed two times to ensure repeatability. Sawdust particle size distribution is presented in Figure 2, which shows the average results from two parallel experiments. During sample preparation for the adsorption experiments, the samples were not sieved, but the samples were homogeneous based on visual observation.

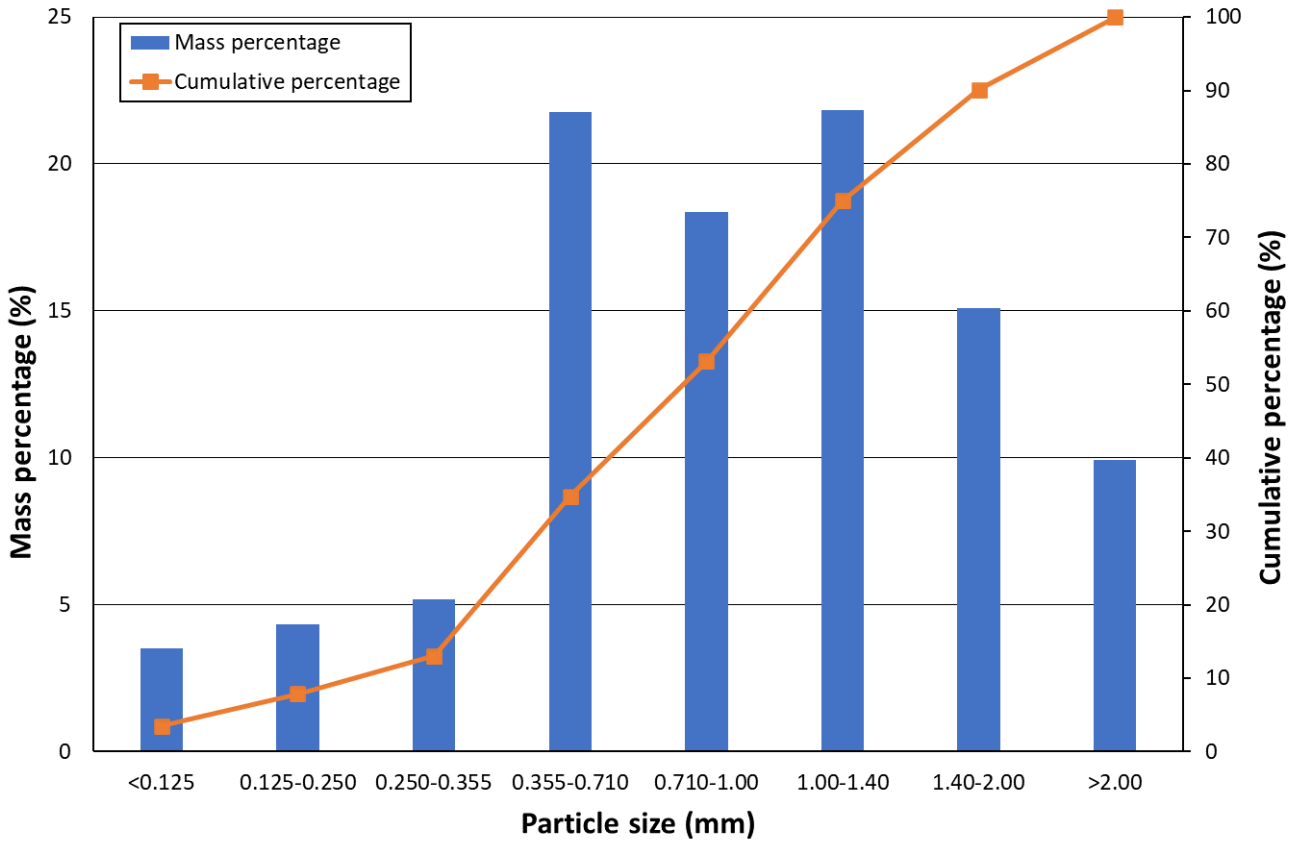

Figure 2 Particle size distribution curve for sawdust.

4.2 Experimental setup and procedure

4.2.1 Adsorption parameter experiments

The goal for the adsorption parameter experiments was to focus on relevant parameters, which highly affect both cost and efficiency of the adsorption process in wastewater treatment. The parameters that were selected for inspection were adsorbent dosage, contact time and temperature. Adsorbent dosage and the used adsorbent itself highly determine the removal efficiency of target pollutants. Roughly speaking, a larger amount of adsorbent used typically yields better results in terms of pollutant removal, but on the other hand, a large amount of adsorbent used, especially when dealing with expensive adsorbents, raises costs, sometimes making the process unviable to implement in practice. With regard to contact time, a longer contact time typically enables better pollutant removal, but long contact times are not always a practical option either. Lastly, there is temperature, which does not have the same impact in every wastewater treatment facility, as temperature variation is affected by seasonal changes in location. This parameter is particularly relevant to inspect in Finland.

Adsorbent parameter experiments were done using a GFL 3005 shaker as the mixing method. After the selected contact time for the test was carried out, samples were removed from the shaker and immediately filtered with Whatman Cat No 1001-110 filter paper. After that, finer filtration was needed for TOC analysis in the form of 0.45 µm syringe filtration, since the equipment could not endure suspended solids in the sample. For the samples sent for pharmaceutical analysis, the filtration phase was done using two different filter papers. The samples were then frozen in a cold room before being sent to Eurofins for analysis. An illustration of adsorbent parameter experiments is presented in Figure 3.

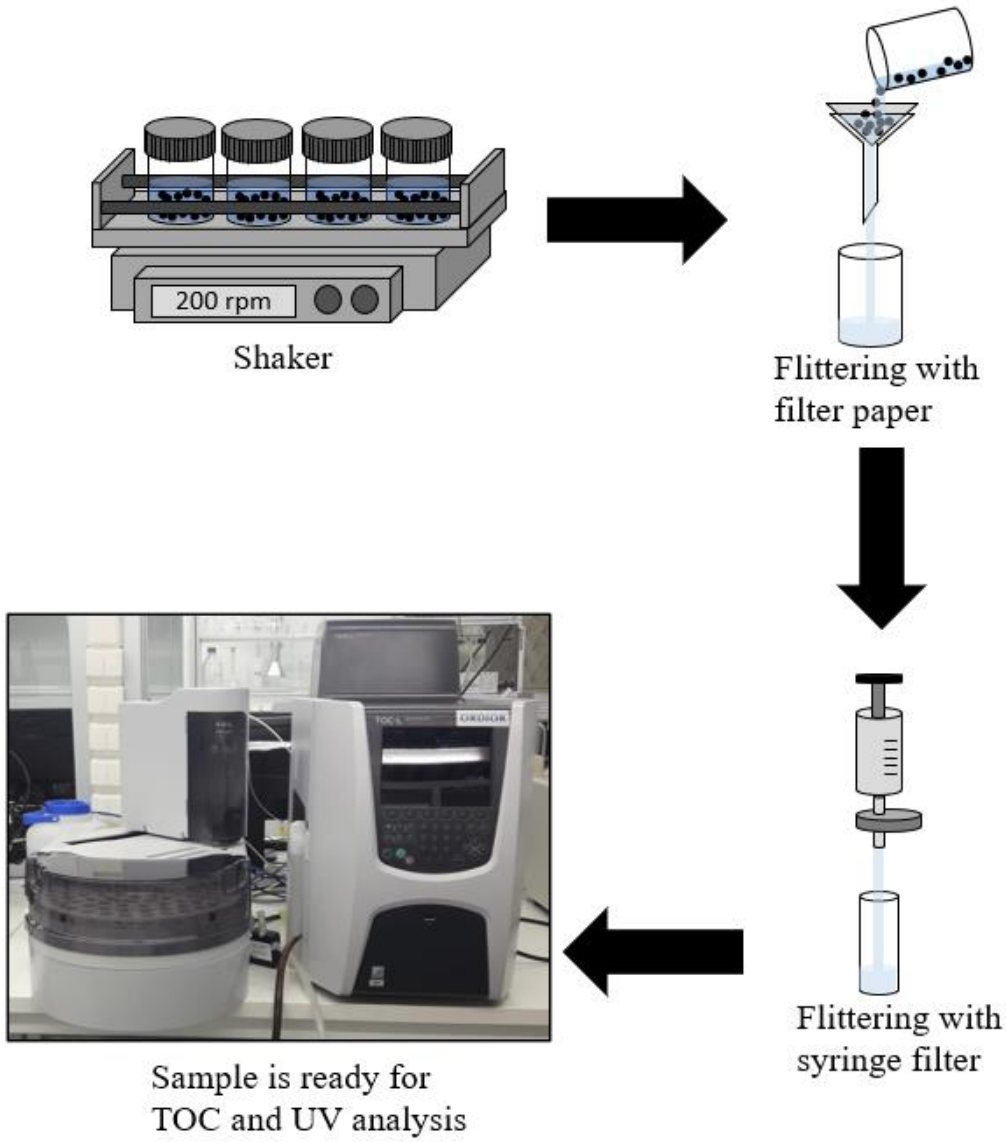

Figure 3 Visualization of batch adsorbent set-up and sample preparation for TOC and UV analysis.

4.3 SUVA analyses

SUVA is the ratio of specific UV absorbance at a given wavelength to the total organic carbon (or TOC in short) in a water sample. The typical chosen wavelength method is 254 nm, which was also the one chosen for this work. SUVA values were calculated using Equation 8. SUVA analysis may work as an indicator for chemical reactivity and aromaticity for water samples with organic content. In wastewater samples, organic matter is mainly

dependent on two factors: the wastewater treatment plant's performance and the initial quantity of organic matter. (Abd Manan et al., 2020; Musikavong & Wattanachira, 2007)

$$SUVA = \frac{UV_{254}}{TOC} * 100\ cm\ m^{-1} \quad (8)$$

where SUVA is specific ultraviolet absorbance, (L/mg-m)

UV_{254} is UV absorbance measured at 254 nm, (cm^{-1})

TOC is total organic carbon, (mg/L) (Abd Manan et al., 2020; USEPA, 2009)

The following chapter presents three different SUVA experiments. In addition to UV and TOC measurements, pH was measured where possible, since it has been found to have a potential effect on SUVA measurements (Weishaar et al., 2003).

4.4 TOC and UV procedures

TOC and UV analyses were executed in order to calculate SUVA values from samples with varying dosages of adsorbents. Two sets of experiments were performed, one for the same wastewater as used in pharmaceutical experiments, and one using tap water. SUVA values were also measured for water that was used, for the sake of comparison.

UV analyses were carried out with a Jasco V670 instrument, and the program used for experiments was fixed wavelength measurement. When measuring UV values for the samples with sawdust, sample preparation was often necessary. Dilution was often done for high concentration samples, ranging from 12.5 to 25 times. Additionally, pH was measured from all samples. TOC analyses were done with a Shimadzu TOC-L series total organic carbon analyzer.

5 Results and discussion

5.1 SUVA analyses

5.1.1 SUVA analysis for solutions collected from the sawdust washing process

All four solutions that resulted from the sawdust washing process were subjected to SUVA analysis. The results are presented in Table 2, where "1. Washing time" is referring to solution collected from the first washing round, "2. Washing time" refers to solution collected on the second washing round, and so on. The washing method is described in detail earlier, in the "Materials and methods" -section.

The difference between solutions was visible to the naked eye, with the first solution having a noticeably darker yellow tone in comparison to last two solutions. This was confirmed with a spectrophotometry analysis, where after the third washing round, the color was not significantly changed. Hence, unsurprisingly, the first solution had the highest TOC content, 829 mg/L. In the second solution, a 25 % reduction of TOC had happened, and after the third washing time the TOC reduction was 65 %. After the last washing round, the reduction was 82 % compared to the first solution. Respectively, the reduction of UV-254 was 38 % when moving on from the first washing to the second, 71 % after the third washing and 78 % after the last washing. SUVA value was not significantly affected between solutions, as it is a ratio of UV and TOC, and both values decreased at nearly the same rate.

Table 2 SUVA analyses for solutions collected from the sawdust washing process.

Solution	UV, 254.0 nm	TOC, mg/L	SUVA, L/mg-m
1. Washing time	7.45	829	0.90
2. Washing time	4.61	620	0.74
3. Washing time	2.15	289	0.75
4. Washing time	1.63	146	1.12

5.1.2 SUVA analysis for wastewater treated with activated carbons and sawdust

The SUVA analysis experiment was performed on wastewater treated with activated carbons and sawdust adsorbents, using an experimental set-up described earlier in the section "Adsorption parameter experiments". The experiments were done in room temperature with

a contact time of one day. Experiments on wastewater treated with PAC and GAC were executed with 100 mL wastewater volume, with the wastewater sample having been taken on the same day for both activated carbons. On a different day, the sawdust experiments were performed with a 50 mL wastewater volume, and the wastewater sample was again taken on the same day for both sawdusts. The results are presented in Table 3 and Table 4. The results of wastewater experiments with PAC and GAC are presented in Table 3 and the sawdust experiment results are presented in Table 4.

Table 3 SUVA analyses for wastewater treated with activated carbons.

Sample	pH	UV, 254.0 nm	TOC, mg/L	SUVA, L/mg-m
PAC 0.5 g/L	7.8	0.015	6	0.25
PAC 0.1 g/L	7.3	0.047	7	0.67
PAC 0.05 g/L	7.3	0.077	8	0.93
PAC 0.02 g/L	7.2	0.123	11	1.14
GAC 0.5 g/L	7.3	0.048	7	0.69
GAC 0.1 g/L	8.2	0.126	10	1.22
GAC 0.05 g/L	7.2	0.148	29	0.51
GAC 0.02 g/L	7.3	0.171	13	1.31
Wastewater	6.8	0.177	13	1.42

Table 4 SUVA analyses for wastewater treated with sawdust samples.

Sample	pH	UV, 254.0 nm	TOC, mg/L	SUVA, L/mg-m
Sawdust washed 20 g/L	6.7	3.131	156	2.01
Sawdust washed 10 g/L	7.2	1.826	103	1.77
Sawdust washed 5 g/L	7.7	1.284	65	1.97
Sawdust washed 2 g/L	7.4	0.660	33	1.99
Sawdust raw 20 g/L	6.8	4.773	481	0.99
Sawdust raw 10 g/L	6.9	3.023	268	1.13
Sawdust raw 5 g/L	7.7	2.108	156	1.35
Sawdust raw 2 g/L	7.6	0.948	63	1.51
Wastewater	7.4	0.180	10	1.85

As stated before, the wastewater sample were taken on different days when testing with activated carbons versus when testing with sawdust. The most notable difference between wastewater samples was pH, which was 6.8 in the activated carbon experiment and 7.4 in the sawdust experiment. The pH has an impact on cationic adsorption happening on the

surface of carbons, since surface properties change with pH, and the surface acts as either a base or as an acid based on pH (Savova et al., 2003). UV-254 value had only a minor difference between the wastewaters from different days that was within the margin of error. Also, wastewater tested in the PAC and GAC experiments (Table 3) had 3 mg/L higher TOC content compared to the wastewater in sawdust experiments (Table 4), which was also a relatively low difference.

All samples treated with sawdust experienced a significant increase in UV-254 absorbance compared to wastewater, although in the case of washed sawdust, the impact was less noticeable. With the sawdust's highest concentration of 20 g/L, the wastewater treated with washed sawdust had a 17 times greater UV-254 value than the wastewater sample, while wastewater treated with raw sawdust had a value 27 times greater. At the sawdust's lowest concentration of 2 g/L, the wastewater treated with washed sawdust had 3.7 times higher UV-254 value than wastewater, where wastewater treated with raw sawdust had 5.3 times higher. TOC values behaved similarly, decreasing along with sawdust concentration. With the highest concentration, the TOC of the wastewater treated with washed sawdust increased to 15.5 times of that of the wastewater sample, whereas with the wastewater treated with raw sawdust sample, and with same sawdust concentration, the increase was 48.1 times. TOC values decreased with the decrease in sawdust concentration, reaching only 3.3 times higher TOC value with washed sawdust at the lowest concentration, and 6.3 times using raw sawdust with same concentration. Washing the sawdust had a clear impact in this regard. The experimental set-up was not optimized for TOC removal, but under proper conditions TOC removal can be achieved with sawdust (Abudi, 2018). However, the increasing TOC is not desired in the context of wastewater treatment.

Results concerning the wastewater treated activated carbons were very different when compared to the results of the sawdust experiment. PAC with the highest concentration of 0.5 g/L had a 45 % reduction of TOC and 92 % reduction of UV-254 when compared to wastewater. In the PAC samples, UV-254, TOC and SUVA increased with decreasing concentration, as the lowest concentration of 0.02 g/L lowered UV-254 by 30.5 % and TOC by 15.4 %. PAC and GAC were tested using the same concentrations, so unsurprisingly PAC

performed better. However, it is important to keep in mind that PAC used in the experiment was the more expensive choice of adsorbent. With GAC samples, UV-254, TOC and SUVA also increased with decreasing concentration, with the exception of the concentration of 0.05 g/L, where TOC was increased to 2.2 times the value of the wastewater. This datapoint does not fit other results, which suggests a possible error in experimentation. GAC did not see an effect on TOC and UV-254 with the lowest concentration of 0.2 g/L, being lowered just marginally by 3.4 %.

5.1.3 SUVA analysis for tap water treated with raw sawdust

The kinetic experiment with tap water treated with raw sawdust was performed using an experimental set-up described earlier in the section "Adsorption parameters experiments". The experiment was done in room temperature 23.5 °C and with 50 mL of tap water volume. The adsorbent dosage for every sample was 10 g/L, or in other words, 1:100 adsorbent/water ratio. The results are presented in Table 5.

This kinetic experiment illustrates how using this set-up to tap water treatment with raw sawdust, TOC and UV-254 increase with contact time. Over the course of 24 hours, TOC increased from 193 mg/L at the 15-minute mark to 265 mg/L after the full 24 hours had passed. In the same time frame, UV-254 increased from 1.784 to 2.674. The fastest and most notable change happened within the first 2 hours. In the next 22 hours, TOC only increased by 8 %, and UV-254 by 18 %.

The 24-hour datapoint in this experiment and the 10 g/L dosage sample of raw sawdust from last chapter's experiment in Table 4 are otherwise identical, except for the water type used. Tap water predictably has lower UV-254, TOC and SUVA values than either of the previous wastewater samples. The test done with wastewater also gives higher UV-254, TOC and SUVA values than the test done with tap water, but the difference is not significant. The wastewater sample had 10 mg/L TOC, while tap water had 3 mg/L. Correspondingly, the sawdust with wastewater had 268 mg/L TOC, and sawdust with tap water 265 mg/L. The

increase of UV-254 was more impactful, increasing from 2.67 to 3.02 when changing from tap water to wastewater.

Table 5 SUVA analyses for tap water treated with raw sawdust at 1:100 adsorbent water ratio and 50 mL volume.

Time (h)	pH	UV, 254.0 nm	TOC, mg/L	SUVA, L/mg-m
0.25	7.4	1.784	193	0.92
1	7.2	2.044	206	0.99
2	7.2	2.188	243	0.90
4	7.2	2.296	244	0.94
24	6.5	2.674	265	1.01
Tap water	7.8	0.037	3	1.24

5.2 Experiments of impact of temperature, contact time and adsorbent dosage to pharmaceutical removal

5.2.1 Effect of adsorbent dosage on the removal of pharmaceutical compounds

The effect of adsorbent dosage was studied on PAC, GAC and sawdust samples. The studied dosages for activated carbons were 0.5 g/L, 0.1 g/L and 0.05 g/L and for sawdust samples 20 g/L, 10 g/L and 5 g/L. The experiment was performed in room temperature 24 °C and with 24 hours of contact time. The wastewater volume was 200 mL.

In this test series, a total of 23 different pharmaceutical compounds were detected in wastewater. The initial concentration of these pharmaceuticals in the wastewater sample, and the concentration in samples containing adsorbents, are presented in Table 6. In Table 7, the removal efficiency of pharmaceuticals is presented for all adsorbent dosages. A lot of datapoints are missing, particularly for sawdust samples. The reason for this is that the limit of quantification multiplied for these samples, leading it to be impossible to calculate or properly estimate concentration and removal efficiency. These datapoints are marked as "N/A" in all following tables.

Table 6 Concentration of pharmaceuticals in wastewater before and after treatment with adsorbents in varying dosages.

Concentration µg/l	Wastewater	PAC 0.05 g/L	PAC 0.1 g/L	PAC 0.5 g/L	GAC 0.05 g/L	GAC 0.1 g/L	GAC 0.5 g/L	SDR 5 g/L	SDR 10 g/L	SDR 20 g/L	SDW 5 g/L	SDW 10 g/L	SDW 20 g/L
Atenolol	0.036	0	0	0	0.01	0	0	N/A	N/A	N/A	N/A	N/A	N/A
Bezafibrate	0.058	0	0	0	0.04	0.026	0	0.052	N/A	N/A	N/A	N/A	N/A
Bisoprolol	0.38	0	0	0	0.074	0.025	0	0.16	N/A	N/A	N/A	N/A	N/A
Diatrizoic acid	0.88	0.35	0.11	0.028	0.68	0.62	0.069	0.46	0.49	0.73	0.94	N/A	N/A
Diclofenac	1.7	0.063	0.035	0.014	0.94	0.65	0.008	1.6	1.4	0.95	1.6	1.4	1
Furosemide	1.4	0	0	0	0.54	0.34	0	N/A	N/A	N/A	N/A	N/A	N/A
Carbamazepine	0.41	0.015	0.01	0.005	0.15	0.064	0	0.21	0.19	0.12	0.24	N/A	N/A
Quetiapine	0.018	0	0	0	0.007	0	0	N/A	N/A	N/A	N/A	N/A	N/A
Clarithromycin	0.043	0	0	0	0.014	0	0	N/A	N/A	N/A	N/A	N/A	N/A
Losartan	0.93	0.034	0.018	0.008	0.45	0.37	0	0.55	0.46	0.26	1.3	0.64	0.36
Metoprolol	0.42	0.009	0.006	0	0.089	0.029	0	0.23	0.21	0.15	0.19	N/A	N/A
Naproxen	0.11	0	0	0	0.057	0.036	0	N/A	N/A	N/A	N/A	N/A	N/A
Primidone	0.022	0	0	0	0.008	0.005	0	N/A	N/A	N/A	N/A	N/A	N/A
Propanolol	0.076	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Ramipril	0.04	0	0	0	0.024	0.02	0	N/A	N/A	N/A	N/A	N/A	N/A
Sertraline & Norsertraline	0.018	0	0	0	0	0	0	N/A	N/A	N/A	N/A	N/A	N/A

Citalopram	0.2	0	0	0	0.047	0.015	0	N/A	N/A	N/A	N/A	N/A	N/A
Sotalol	0.04	0	0	0	0.013	0	0	N/A	N/A	N/A	N/A	N/A	N/A
Sulfadiazine	0.055	0	0	0	0.031	0.018	0	N/A	N/A	N/A	N/A	N/A	N/A
Tramadol	0.54	0.018	0.015	0.006	0.21	0.09	0	0.28	0.24	0.17	0.27	N/A	N/A
Trimethoprim	0.33	0.008	0.005	0.002	0.084	0.034	0.002	0.087	0.064	0.037	0.079	N/A	N/A
Warfarin	0.005	0	0	0	0	0	0	N/A	N/A	N/A	N/A	N/A	N/A
Venlafaxine	0.7	0.024	0.021	0.009	0.25	0.12	0	0.29	0.22	N/A	0.24	N/A	N/A
Fluconazole	0.085	0	0	0	0.038	0.028	0	0.059	N/A	N/A	N/A	N/A	N/A

Table 7 Removal efficiency of pharmaceuticals when treated with different dosages of adsorbents.

Removal efficiency (%)	PAC 0.05 g/L	PAC 0.1 g/L	PAC 0.5 g/L	GAC 0.05 g/L	GAC 0.1 g/L	GAC 0.5 g/L	SDR 5 g/L	SDR 10 g/L	SDR 20 g/L	SDW 5 g/L	SDW 10 g/L	SDW 20 g/L
Atenolol	100	100	100	72	100	100	N/A	N/A	N/A	N/A	N/A	N/A
Bezafibrate	100	100	100	31	55	100	10	N/A	N/A	N/A	N/A	N/A
Bisoprolol	100	100	100	81	93	100	58	N/A	N/A	N/A	N/A	N/A
Diatrizoic acid	60	88	97	23	30	92	48	44	17	-7	N/A	N/A
Diclofenac	96	98	99	45	62	100	6	18	44	6	18	41
Furosemide	100	100	100	61	76	100	N/A	N/A	N/A	N/A	N/A	N/A
Carbamazepine	96	98	99	63	84	100	49	54	71	41	N/A	N/A

Quetiapine	100	100	100	61	100	100	N/A	N/A	N/A	N/A	N/A	N/A
Clarithromycin	100	100	100	67	100	100	N/A	N/A	N/A	N/A	N/A	N/A
Losartan	96	98	99	52	60	100	41	51	72	-40	31	61
Metoprolol	98	99	100	79	93	100	45	50	64	55	N/A	N/A
Naproxen	100	100	100	48	67	100	N/A	N/A	N/A	N/A	N/A	N/A
Primidone	100	100	100	64	77	100	N/A	N/A	N/A	N/A	N/A	N/A
Ramipril	100	100	100	40	50	100	N/A	N/A	N/A	N/A	N/A	N/A
Sertraline & Norsertraline	100	100	100	100	100	100	N/A	N/A	N/A	N/A	N/A	N/A
Citalopram	100	100	100	77	93	100	N/A	N/A	N/A	N/A	N/A	N/A
Sotalol	100	100	100	68	100	100	N/A	N/A	N/A	N/A	N/A	N/A
Sulfadiazine	100	100	100	44	67	100	N/A	N/A	N/A	N/A	N/A	N/A
Tramadol	97	97	99	61	83	100	48	56	69	50	N/A	N/A
Trimethoprim	98	98	99	75	90	99	74	81	89	76	N/A	N/A
Warfarin	100	100	100	100	100	100	N/A	N/A	N/A	N/A	N/A	N/A
Venlafaxine	97	97	99	64	83	100	59	69	N/A	66	N/A	N/A
Fluconazole	100	100	100	55	67	100	31	N/A	N/A	N/A	N/A	N/A

PAC performs the best out of the four adsorbents. In Figure 4, the removal efficiency results are visualized. The difference between the largest and the smallest dosages is not very noticeable. The removal efficiency values for all compounds but one show at least 96 % removal with all dosages. The exception is diatrizoic acid, where only 60 % removal efficiency is achieved with the lowest concentration, and 97 % removal efficiency is achieved with the highest concentration.

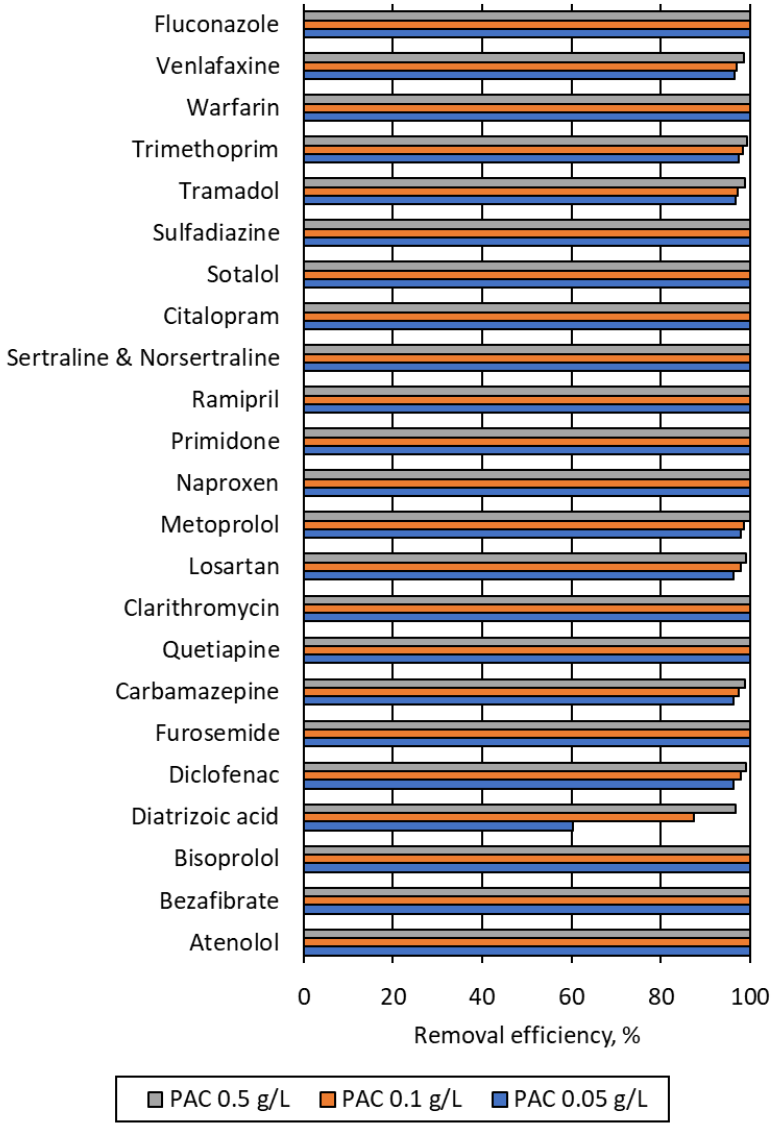

Figure 4 The effect of PAC dosage on removal efficiency of pharmaceuticals with 24 hours contact time, room temperature and volume of wastewater 200 mL.

Removal efficiency with different GAC dosages is visualized in Figure 5. The largest dosage, 0.5 g/L, reaches at least 99 % removal efficiency with all pharmaceuticals but diatrizoic acid, where 92 % efficiency is reached. The higher dosage leads to a higher removal rate, but unlike with PAC, lower dosages do not perform nearly as well. On average, a 0.1 g/L dosage leads to 80 % removal, and 0.05 g/L to only 62 % removal.

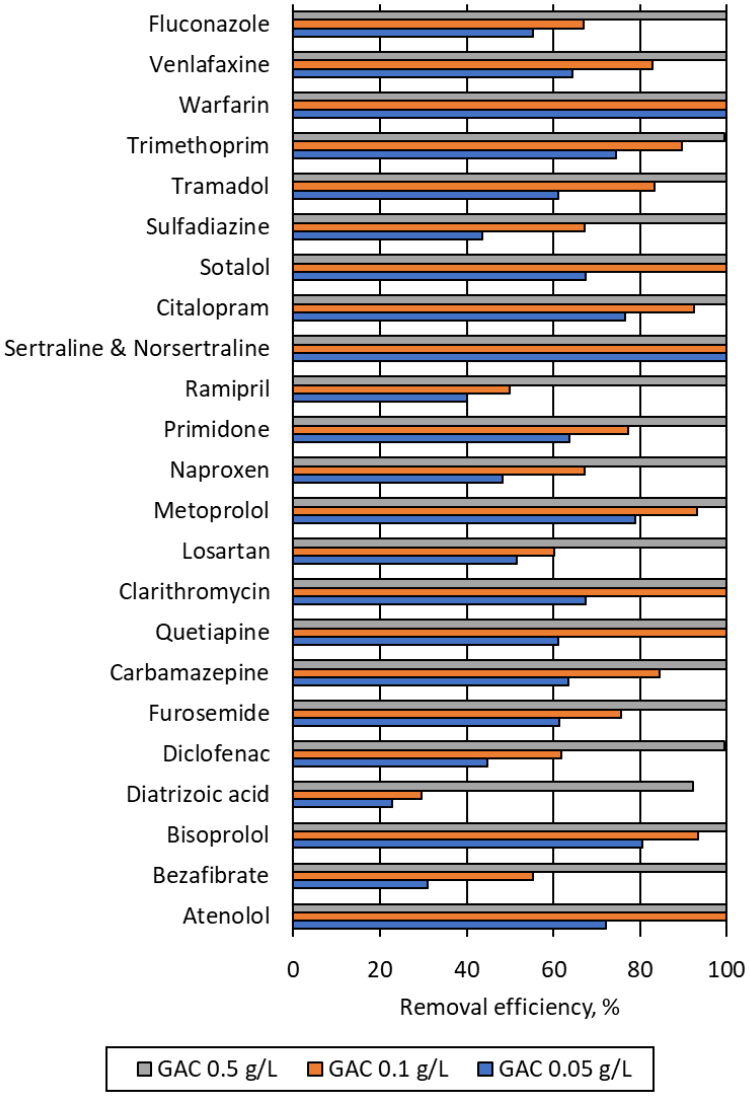

Figure 5 The effect of GAC dosage on removal efficiency of pharmaceuticals with 24 hours contact time, room temperature and volume of wastewater 200 mL.

The removal efficiency for both washed and unwashed sawdust is visualized in Figure 6. Analysis of the sawdust samples proved to be challenging: only 11 pharmaceuticals could

be identified, and they are thus the only ones with usable datapoints. Washing the sawdust did not ease analysis as predicted. A larger dosage usually leads to a higher removal rate, but the results are not as impressive as with activated carbons. The best results are achieved using unwashed sawdust and the largest dosage. It is notable that there are two negative removal efficiency values in Figure 6. This is not the only experiment where this happened, but in practice these values represent situations, where the separation of the given compound has not been successful with the adsorbent in question. These errors are most common with sawdust samples, and they occur when the measured pharmaceutical concentration in an adsorbent sample is higher than the concentration in a wastewater sample.

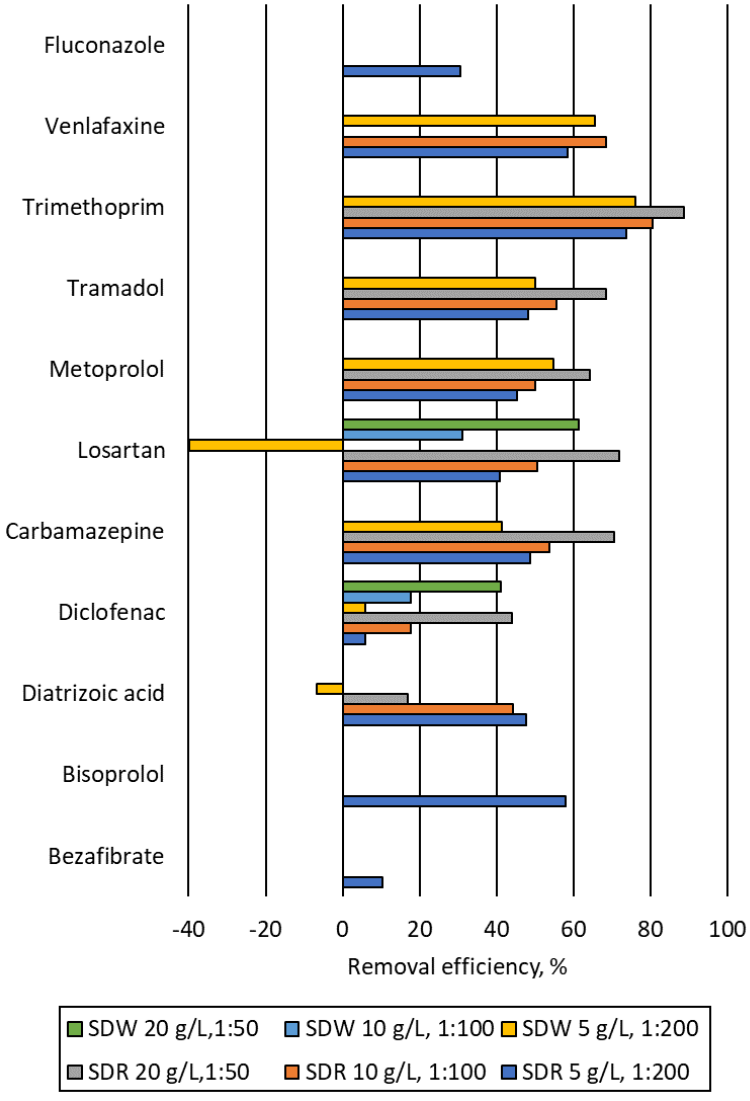

Figure 6 The effect of sawdust dosage on removal efficiency of pharmaceuticals with 24 hours contact time, room temperature and volume of wastewater 200 mL.

5.2.2 Effect of temperature on the removal of pharmaceutical compounds

The effect of temperature was studied on all four adsorbents studied in this work, PAC, GAC, and washed and unwashed sawdust. The three examined temperatures were 24 °C, 7 °C and 1 °C. The most common studied temperature for adsorption is room temperature, lower temperatures being less experimented on. That is partly the reason why the 7 °C and 1 °C points were selected. The 24 °C experiment was executed by taking advantage of room temperature, the 7 °C experiment was done in a cold room with a corresponding temperature, and the coldest temperature point, 1 °C, was obtained by performing the experiment inside a thermally adjustable fridge. Contact time for the experiments was 24 hours, with 200 mL wastewater volume. Concentration for activated carbons was 0.05 g/L and 5 g/L for sawdust. The initial pharmaceutical concentration in the wastewater sample and the samples with adsorbents are presented in Table 8, and the removal efficiency of pharmaceuticals is presented in Table 9.

Table 8 Concentration of pharmaceuticals in wastewater before and after treatment with adsorbents in varying temperatures.

Concentration µg/l	Wastewater	PAC 1 °C	PAC 7 °C	PAC 24 °C	GAC 1 °C	GAC 7 °C	GAC 24 °C	SDR 1 °C	SDR 7 °C	SDR 24 °C	SDW 1 °C	SDW 7 °C	SDW 24 °C
Atenolol	0.14	0.008	0	0	0.13	0.076	0.01	0.094	0.088	0.082	0.078	0.073	0.081
Bezafibrate	0.065	0.005	0	0	0.063	0.044	0.04	N/A	N/A	N/A	N/A	N/A	N/A
Bisoprolol	0.4	0	0	0	0.29	0.23	0.074	0.2	0.18	0.21	0.19	0.18	0.17
Diatrizoic acid	4.3	3.5	3.2	0.35	4.2	3	0.68	4.1	3.5	3.2	3.3	4	3.2
Diclofenac	2.6	0.18	0.099	0.063	2	1.5	0.94	1.6	1.8	2	1.7	1.7	1.9
Furosemide	1.9	0.14	0.068	0	1.7	1.3	0.54	1.8	2.1	2.2	1.8	1.9	2.2
Ibuprofen	0.19	0	0	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Carbamazepine	0.49	0.025	0.019	0.015	0.39	0.27	0.15	0.2	0.21	0.28	0.2	0.23	0.27
Quetiapine	0.012	0	0	0	0.015	0.01	0.007	N/A	N/A	N/A	N/A	N/A	N/A
Clarithromycin	0.026	0	0	0	0.021	0.021	0.014	N/A	N/A	N/A	N/A	N/A	N/A
Losartan	1.2	0.093	0.046	0.034	1.3	0.81	0.45	0.47	0.56	0.6	0.51	0.47	0.55
Metoprolol	0.61	N/A	0.005	0.009	0.46	0.35	0.089	0.33	0.29	0.29	0.34	0.21	0.21
Naproxen	0.51	0.045	N/A	0	0.57	0.44	0.057	N/A	N/A	N/A	N/A	N/A	N/A
Primidone	0.034	0.008	0.008	0	0.025	0.021	0.008	N/A	N/A	N/A	N/A	N/A	N/A
Propanolol	0.11	N/A	N/A	N/A	0.077	0.045	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Ramipril	0.035	0.015	0.008	0	0.034	0.028	0.024	N/A	N/A	0.052	N/A	N/A	N/A
Ciprofloxacin	0.053	0	0	N/A	0	0	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Citalopram	0.21	0	0	0	0.19	0.12	0.047	N/A	N/A	N/A	N/A	N/A	N/A
Sotalol	0.099	0	0	0	0.1	0.067	0.013	N/A	N/A	0.1	N/A	N/A	N/A
Sulfadiazine	N/A	0	0	0	0.025	0.013	0.031	N/A	N/A	N/A	N/A	N/A	N/A
Tramadol	0.66	0.062	0.034	0.018	0.56	0.38	0.21	0.38	0.31	0.33	0.34	0.3	0.28
Trimethoprim	0.35	0.014	0.003	0.008	0.25	0.17	0.084	0.048	0.056	0.091	0.044	0.05	0.083
Warfarin	0.014	0	0	0	0.015	0.01	0	N/A	N/A	N/A	N/A	N/A	N/A
Venlafaxine	0.77	0.045	0.029	0.024	0.58	0.46	0.25	0.42	0.43	0.45	0.39	0.37	0.38
Fluconazole	0.15	0.014	0.009	0	0.13	0.092	0.038	0.14	0.15	0.17	0.13	0.17	0.17

Table 9 Removal efficiency of pharmaceuticals when treating with different temperatures.

Removal efficiency (%)	PAC 1 °C	PAC 7 °C	PAC 24 °C	GAC 1 °C	GAC 7 °C	GAC 24 °C	SDR 1 °C	SDR 7 °C	SDR 24 °C	SDW 1 °C	SDW 7 °C	SDW 24 °C
Atenolol	94	100	100	7	46	72	33	37	41	44	48	42
Bezafibrate	92	100	100	3	32	31	N/A	N/A	N/A	N/A	N/A	N/A
Bisoprolol	100	100	100	28	43	81	50	55	48	53	55	58
Diatrizoic acid	19	26	60	2	30	23	5	19	26	23	7	26
Diclofenac	93	96	96	23	42	45	38	31	23	35	35	27
Furosemide	93	96	100	11	32	61	5	-11	-16	5	0	-16
Ibuprofen	100	100	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Carbamazepine	95	96	96	20	45	63	59	57	43	59	53	45

Quetiapine	100	100	100	-25	17	61	N/A	N/A	N/A	N/A	N/A	N/A
Clarithromycin	100	100	100	19	19	67	N/A	N/A	N/A	N/A	N/A	N/A
Losartan	92	96	96	-8	33	52	61	53	50	58	61	54
Metoprolol	N/A	99	98	25	43	79	46	52	52	44	66	66
Naproxen	91	N/A	100	-12	14	48	N/A	N/A	N/A	N/A	N/A	N/A
Primidone	76	76	100	26	38	64	N/A	N/A	N/A	N/A	N/A	N/A
Propanolol	N/A	N/A	N/A	30	59	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Ramipril	57	77	100	3	20	40	N/A	N/A	-49	N/A	N/A	N/A
Ciprofloxacin	100	100	N/A	100	100	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Citalopram	100	100	100	10	43	77	N/A	N/A	N/A	N/A	N/A	N/A
Sotalol	100	100	100	-1	32	68	N/A	N/A	-1	N/A	N/A	N/A
Tramadol	91	95	97	15	42	61	42	53	50	48	55	58
Trimethoprim	96	99	98	29	51	75	86	84	74	87	86	76
Warfarin	100	100	100	-7	29	100	N/A	N/A	N/A	N/A	N/A	N/A
Venlafaxine	94	96	97	25	40	64	45	44	42	49	52	51
Fluconazole	91	94	100	13	39	55	7	0	-13	13	-13	-13

The removal efficiency results for PAC are visualized in Figure 7. Datapoints for 24 °C are obtained from the adsorbent dosage experiment with the same concentration (0.05 g/L), meaning that the wastewater sample was taken from a different day. Generally, higher temperature leads to higher removal efficiency. The most sensitive pharmaceuticals to low temperature are diatrizoic acid (removal efficiency lowers from 60 % at 24 °C to 25 % at 1 °C), ramipril (removal efficiency lowers from 100 % at 24 °C to 57 % at 1 °C) and primidone (removal efficiency lowers from 100 % at 24 °C to 76 % at 1 °C).

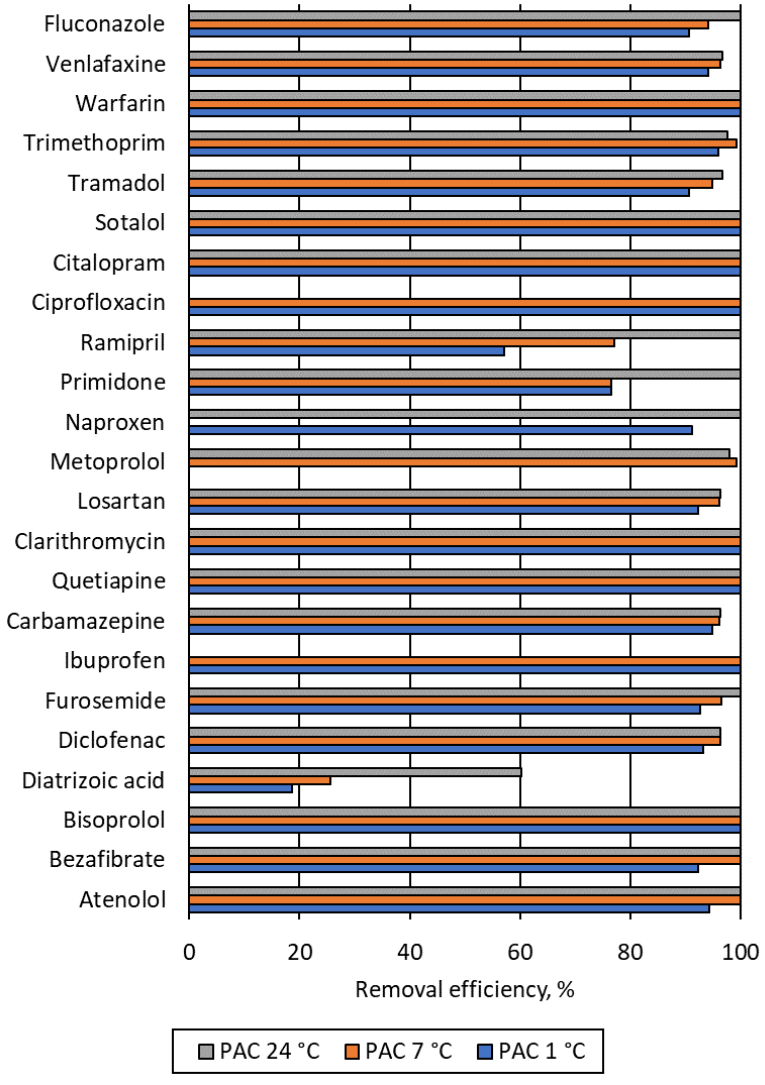

Figure 7 The effect of temperature on PAC removal efficiency of pharmaceuticals with 24 hours contact time, 0.05 g/L adsorbent dosage and volume of wastewater 200 mL.

The removal efficiency results for GAC are visualized in Figure 8. As with the PAC results, the datapoints for 24 °C are obtained from the adsorbent dosage experiment with the same concentration (0.05 g/L), meaning that the wastewater sample was taken on a different day. Again, higher temperature generally leads higher removal efficiency, but GAC is more sensitive to temperature compared to PAC. On average, the removal efficiency for all pharmaceuticals is 61 % at 24 °C. Respectively, at 7 °C it is only 39 %, and with 1 °C removal efficiency is decreased to only 15 % on average.

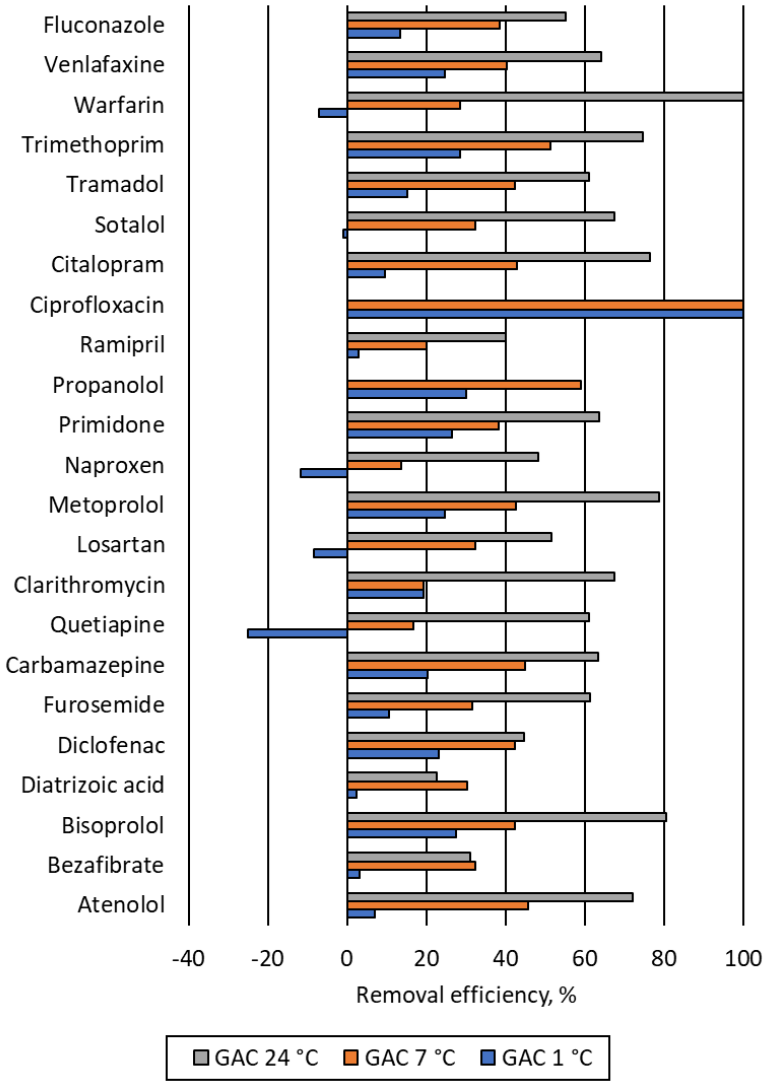

Figure 8 The effect of temperature on GAC removal efficiency of pharmaceuticals with 24 hours contact time, 0.05 g/L adsorbent dosage and volume of wastewater 200 mL.

Removal efficiency results for washed and raw sawdust are presented in Figure 9. Unlike with the activated carbons, temperature change did not have a great impact on the end results. However, sawdust has again less reliable analysis data compared to that of PAC and GAC. Unlike the clear trend with PAC and GAC, rising temperature in sawdust samples did not solely improve pharmaceutical removal.

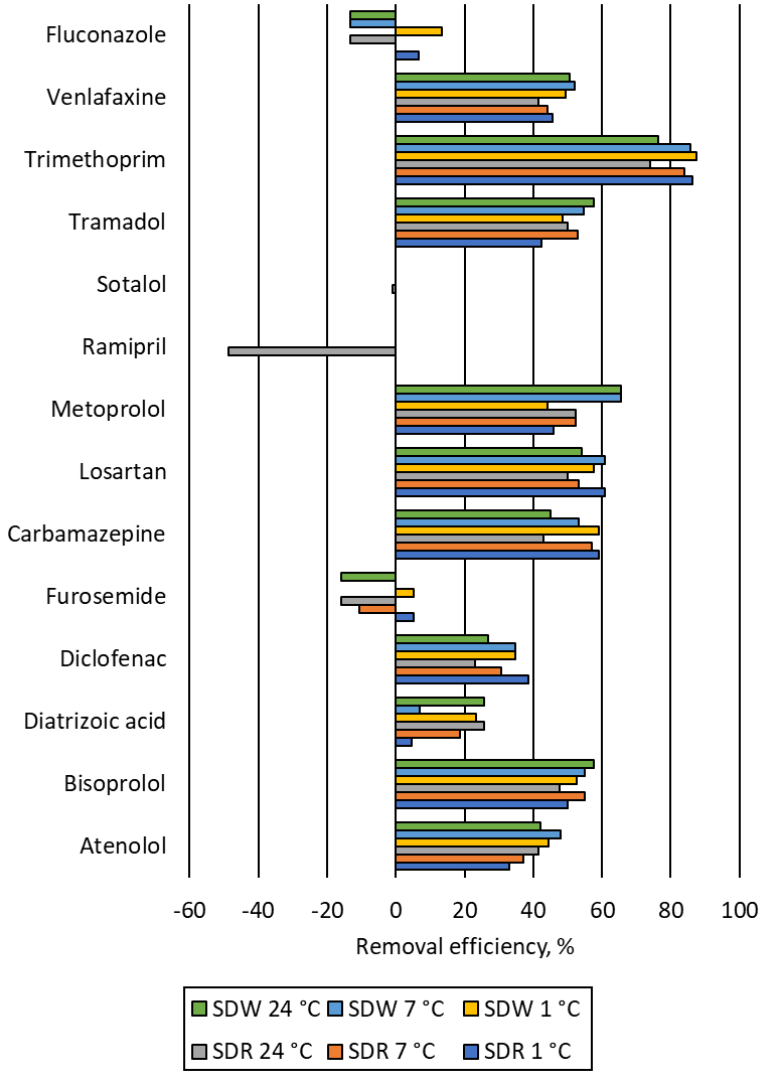

Figure 9 The effect of temperature on sawdust removal efficiency of pharmaceuticals with 24 hours contact time, 5 g/L adsorbent dosage (1:200 adsorbent wastewater ratio) and volume of wastewater 200 mL.

5.2.3 Effect of contact time on the removal of pharmaceutical compounds

The effect of contact time on adsorption was studied with a kinetic experiment that included four contact time points: 24 hours, 4 hours, 2 hours and 0.25 hours. The adsorbent dosage for PAC and GAC was 0.05 g/L and for sawdust it was 5 g/L. Wastewater volume was 200 mL. The initial concentration of pharmaceuticals for the wastewater sample and the samples with adsorbents are presented in Table 10 and the removal efficiency of pharmaceuticals is presented in Table 11.

Table 10 Concentration of pharmaceuticals in wastewater before and after treatment with adsorbents with varying contact times.

Concentration µg/l	Wastewater	PAC 15 min	PAC 2 h	PAC 4 h	PAC 24 h	GAC 15 min	GAC 2 h	GAC 4 h	GAC 24 h	SDR 15 min	SDR 2 h	SDR 4 h	SDR 24 h	SDW 15 min	SDW 2 h	SDW 4 h	SDW 24 h
Atenolol	0.14	0.03	0.009	0	0	0.15	0.15	0.12	0.01	0.12	0.11	0.11	0.082	0.098	0.093	0.11	0.081
Bezafibrate	0.065	0.027	0.006	0	0	0.072	0.069	0.058	0.04	0.059	0.062	0.055	N/A	0.059	N/A	N/A	N/A
Bisoprolol	0.4	0.028	0.014	0	0	0.38	0.35	0.27	0.074	0.33	0.31	0.25	0.21	0.33	0.28	0.25	0.17
Diatrizoic acid	4.3	3.6	2.7	2.7	0.35	4.1	3.6	3.5	0.68	3.3	3.2	3.8	3.2	3.1	2.9	3.5	3.2
Diclofenac	2.6	0.76	0.26	0.099	0.063	2.3	2.2	1.8	0.94	1.9	1.9	1.8	2	2	2.1	1.9	1.9
Furosemide	1.9	0.68	0.22	0.085	0	2	1.8	1.6	0.54	2	2	2	2.2	2.1	2.1	2.1	2.2
Ibuprofen	0.19	0.14	N/A	0	N/A	0.24	0.21	0.2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Carbamazepine	0.49	0.082	0.04	0.012	0.015	0.45	0.43	0.36	0.15	0.37	0.32	0.29	0.28	0.36	0.32	0.29	0.27
Quetiapine	0.012	0	0	0	0	0.019	0.016	0.014	0.007	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Clarithromycin	0.026	0	0	0	0	0.026	0.019	0.019	0.014	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Losartan	1.2	0.38	0.11	0.051	0.034	1.4	1.3	1.2	0.45	0.92	0.89	0.85	0.6	0.92	0.85	0.84	0.55
Metoprolol	0.61	0.056	0.022	0.006	0.009	0.55	0.53	0.44	0.089	0.39	0.35	0.31	0.29	0.38	0.3	0.3	0.21
Naproxen	0.51	0.2	0.072	N/A	0	0.63	0.65	0.52	0.057	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Primidone	0.034	0.017	0.01	0.008	0	0.028	0.026	0.023	0.008	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Propanolol	0.11	N/A	N/A	N/A	N/A	0.1	0.097	0.088	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Ramipril	0.035	0.014	0.014	0.007	0	0.04	0.036	0.031	0.024	N/A	0.066	0.059	0.052	N/A	0.052	N/A	N/A

Ciprofloxacin	0.053	0	0	0	N/A	N/A	0	0	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Citalopram	0.21	0.011	0.013	0	0	0.22	0.19	0.18	0.047	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Sotalol	0.099	0.045	N/A	0	0	0.17	0.14	0.093	0.013	N/A	N/A	N/A	0.1	N/A	N/A	N/A	N/A
Sulfadiazine	N/A	0	0	0	0	0.025	0.024	0.023	0.031	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Tramadol	0.66	0.14	0.09	0.035	0.018	0.65	0.61	0.59	0.21	0.6	0.47	0.43	0.33	0.55	0.44	0.48	0.28
Trimethoprim	0.35	0.029	0.022	0.004	0.008	0.31	0.34	0.27	0.084	0.2	0.13	0.1	0.091	0.19	0.13	0.12	0.083
Warfarin	0.014	0	0	0	0	N/A	0.014	0.014	0	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Venlafaxine	0.77	0.16	0.074	0.034	0.024	0.76	0.66	0.54	0.25	0.61	0.6	0.5	0.45	0.62	0.54	0.5	0.38
Fluconazole	0.15	0.052	0.023	0.012	0	0.16	0.13	0.12	0.038	0.16	0.2	0.18	0.17	0.17	0.17	0.17	0.17

Table 11 Removal efficiency of pharmaceuticals when treated with different contact times.

Removal efficiency (%)	PAC 15 min	PAC 2 h	PAC 4 h	PAC 24 h	GAC 15 min	GAC 2 h	GAC 4 h	GAC 24 h	SDR 15 min	SDR 2 h	SDR 4 h	SDR 24 h	SDW 15 min	SDW 2 h	SDW 4 h	SDW 24 h
Atenolol	79	94	100	100	-7	-7	14	72	14	21	21	41	30	34	21	42
Bezafibrate	58	91	100	100	-11	-6	11	31	9	5	15	N/A	9	N/A	N/A	N/A
Bisoprolol	93	97	100	100	5	13	33	81	18	23	38	48	18	30	38	58
Diatrizoic acid	16	37	37	60	5	16	19	23	23	26	12	26	28	33	19	26
Diclofenac	71	90	96	96	12	15	31	45	27	27	31	23	23	19	27	27
Furosemide	64	88	96	100	-5	5	16	61	-5	-5	-5	-16	-11	-11	-11	-16

Ibuprofen	26	N/A	100	N/A	-26	-11	-5	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Carbamazepine	83	92	98	96	8	12	27	63	24	35	41	43	27	35	41	45
Quetiapine	100	100	100	100	-58	-33	-17	61	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Clarithromycin	100	100	100	100	0	27	27	67	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Losartan	68	91	96	96	-17	-8	0	52	23	26	29	50	23	29	30	54
Metoprolol	91	96	99	98	10	13	28	79	36	43	49	52	38	51	51	66
Naproxen	61	86	N/A	100	-24	-27	-2	48	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Primidone	50	71	76	100	18	24	32	64	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Propanolol	N/A	N/A	N/A	N/A	9	12	20	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Ramipril	60	60	80	100	-14	-3	11	40	N/A	-89	-69	-49	N/A	-49	N/A	N/A
Ciprofloxacin	100	100	100	N/A	N/A	100	100	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Citalopram	95	94	100	100	-5	10	14	77	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Sotalol	55	N/A	100	100	-72	-41	6	68	N/A	N/A	N/A	-1	N/A	N/A	N/A	N/A
Tramadol	79	86	95	97	2	8	11	61	9	29	35	50	17	33	27	58
Trimethoprim	92	94	99	98	11	3	23	75	43	63	71	74	46	63	66	76
Warfarin	100	100	100	100	N/A	0	0	100	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Venlafaxine	79	90	96	97	1	14	30	64	21	22	35	42	19	30	35	51
Fluconazole	65	85	92	100	-7	13	20	55	-7	-33	-20	-13	-13	-13	-13	-13

Removal efficiency results for PAC are presented in Figure 10. Increasing contact time increases removal efficiency. The majority of pharmaceuticals reached nearly their maximum adsorption capacity at the 4-hour mark, and after that any further change was slow. However, three compounds stand out with slower kinetics. At the 4-hour mark only 37 % of diatrizoic acid was removed and 60 % removal was reached after a full day. Only 76 % of primidone was removed at the 4-hour mark, and 100 % removal was reached after a full day. Lastly, only 80 % of ramipril was removed by the 4-hour mark, and after a full day, 100 % removal was reached.

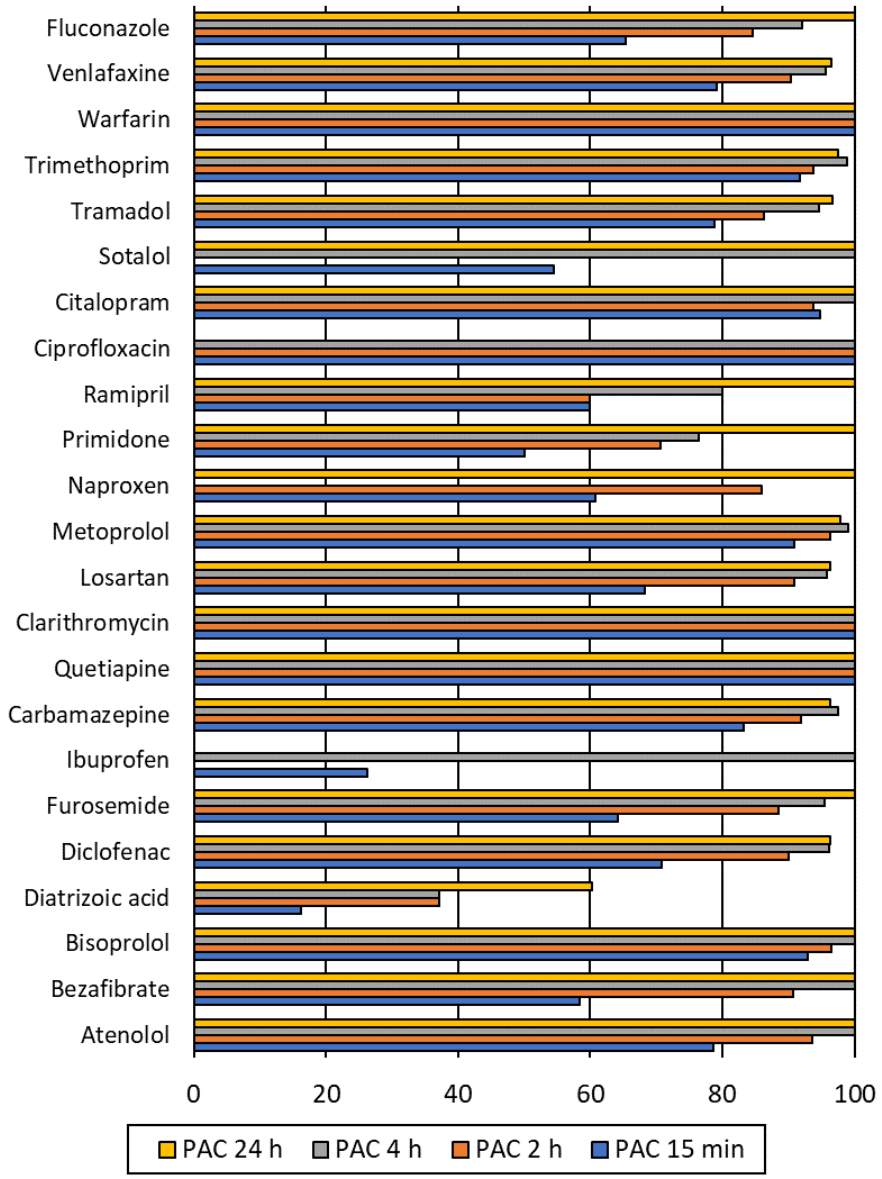

Figure 10 The effect of contact time on PAC removal efficiency of pharmaceuticals with room temperature, 0.05 g/L adsorbent dosage volume of wastewater 200 mL.

Contact time's effect on pharmaceutical removal with GAC is visualized in Figure 11. GAC has slower kinetics than PAC, and the full 24 hours are needed in order to reach over 40 % efficiency in the case of all compounds, with the exception of Ciprofloxacin.

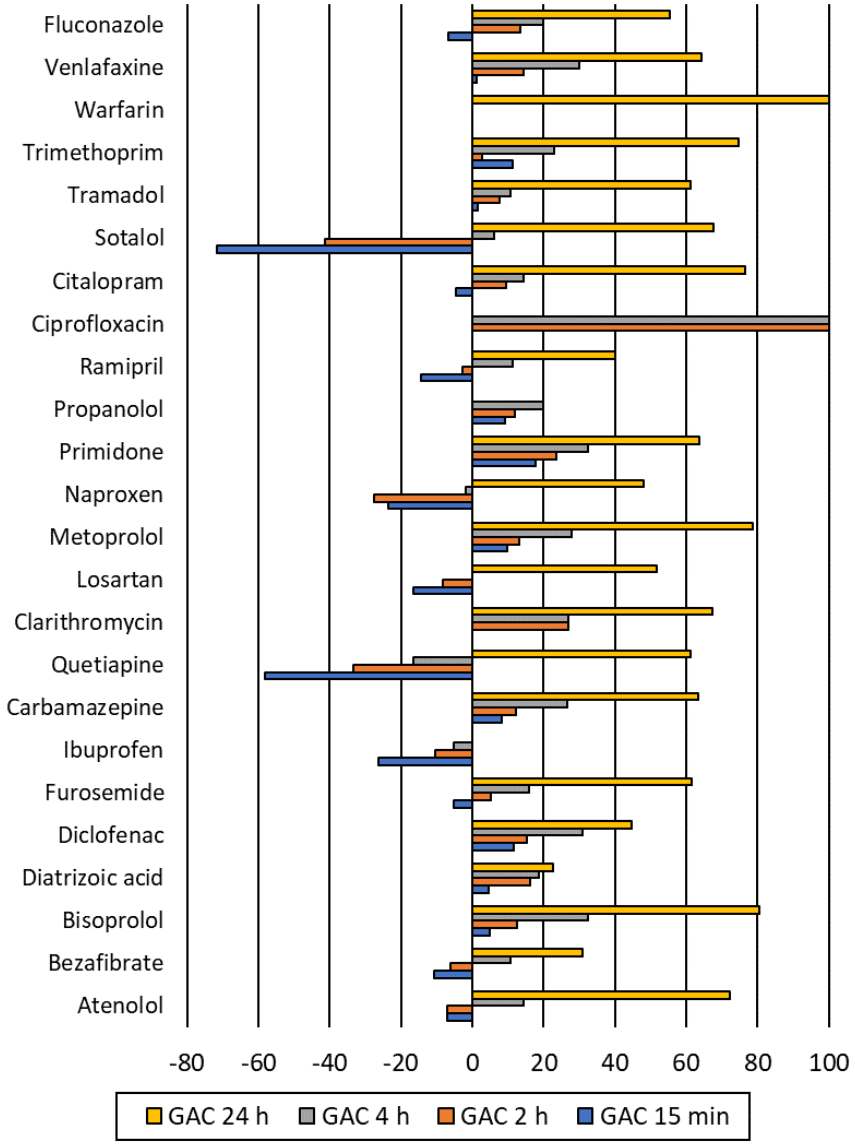

Figure 11 The effect of contact time on GAC removal efficiency of pharmaceuticals with room temperature, 0.05 g/L adsorbent dosage volume of wastewater 200 mL.

In Figure 12, the effect of contact time is explored for raw sawdust. Raising contact time increases removal efficiency. Long contact time is not as critical for sawdust as it was for GAC.

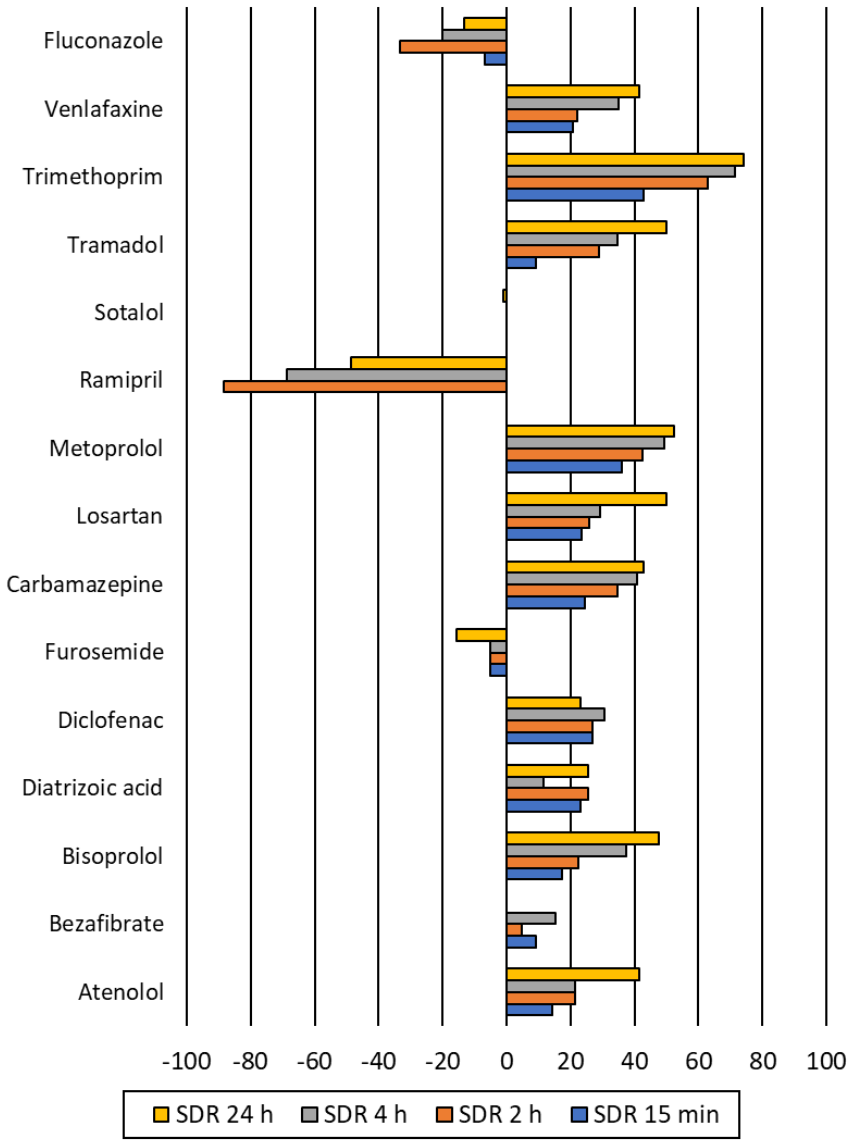

Figure 12 The effect of contact time on unwashed sawdust removal efficiency of pharmaceuticals with room temperature, 5 g/L adsorbent dosage (1:200 adsorbent wastewater ratio) and volume of wastewater 200 mL.

Finally, in Figure 13, the effect of contact time is explored for washed sawdust. Raising contact time again increases removal efficiency. As with raw sawdust, long contact time is not as critical as it was for GAC.

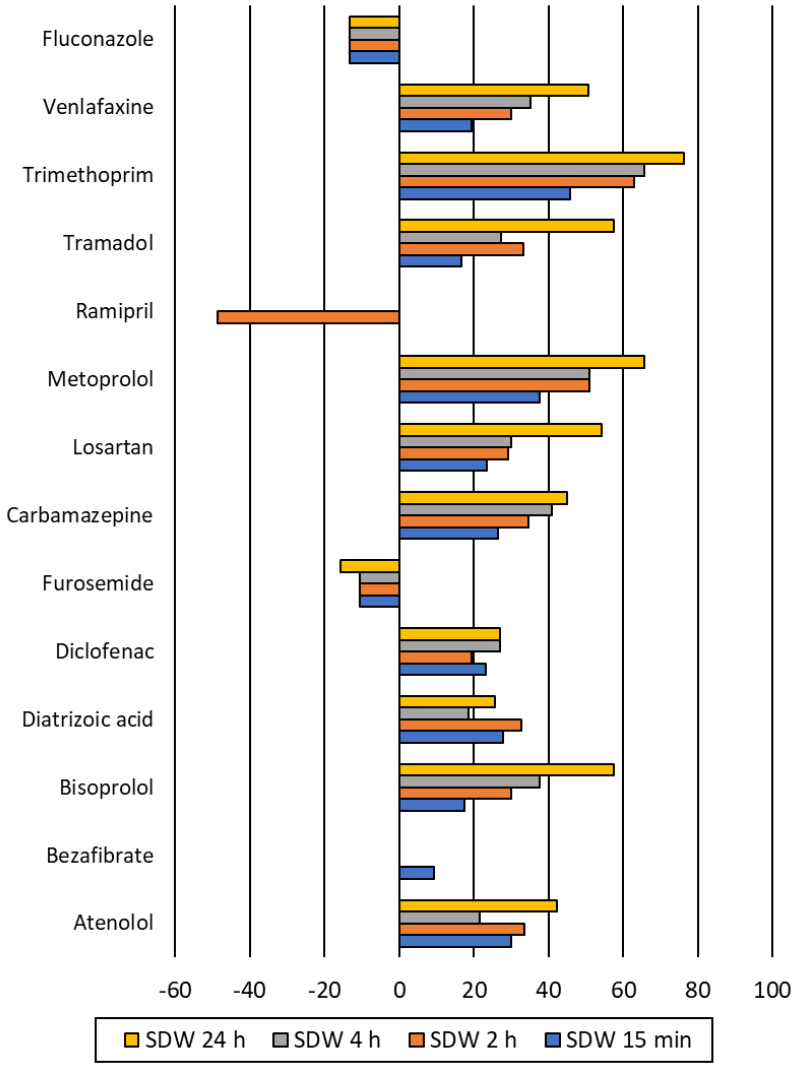

Figure 13 The effect of contact time on washed sawdust removal efficiency of pharmaceuticals with room temperature, 5 g/L adsorbent dosage (1:200 adsorbent wastewater ratio) and volume of wastewater 200 mL.

5.2.4 Pharmaceuticals found in all experiments

In total, 27 different pharmaceutical compounds were identified in the wastewater samples based on all pharmaceutical analyses. The limit of detection for pharmaceuticals varied between 0.005 – 0.25 µg/l and the uncertainty of measurement varied between 25 – 52 %. Wastewater samples from different days were not identical in terms of found compounds. The first wastewater sample contained sertraline and norsertraline (0.018 µg/l) and sulfadiazine (0.055 µg/l), whereas the second sample did not. The second wastewater sample contained ibuprofen (0.19 µg/l) and ciprofloxacin (0.053 µg/l).

All pharmaceuticals found in the experiments are presented in Table 12, along with some of their molecular characteristics. The listed Log K_{ow} value indicates the hydrophilicity or hydrophobicity of the compound, with 3.2 being the limit value for high hydrophobicity and tendency for absorption into wastewater. The acidity of substances is indicated with the acid dissociation constant, pKa. Typically, a lower pKa value indicates that the substance is charged and dissociated.

Out of all studied pharmaceuticals, diatrizoic acid stood out as being one of the most difficult compounds to remove. This was most noticeable in adsorbent dosage and temperature experiments with PAC and GAC adsorbents, requiring larger dosages and higher temperatures in order to enhance adsorption. Diatrizoic acid has also been found to have a low degree of removal in several other activated carbon adsorption experiments (Mahouachi et al., 2020) and the findings of this work are in line with that conclusion. Diatrizoic acid has bulky functional groups with aromatic ring, and the low removal rate may partly be due to the large size of three iodine atoms (Mahouachi et al., 2020). Possible ways to overcome low removal rates of iodinated contrast media, like diatrizoic acid, have been studied. One of the possible solutions is to add pre-treatments prior to the adsorption. Promising results have been found, as catalytic reduction of diatrizoic acid into reduction products with higher carbon loading greatly improves the adsorption process (Schoutteten et al., 2016).

A good example of an easily removed contaminant with PAC in this work was warfarin, having 100 % removal efficiency with only 15 minutes of contact time, with the lowest adsorbent dosage and in all studied temperatures. With sawdust samples, warfarin could not be detected and analyzed. However, among the detected pharmaceuticals, trimethoprim stood out in sawdust experiments by having over 80 % removal efficiency with 1:100 adsorbent wastewater ratio.

Table 12 Molecular characteristics of pharmaceuticals found in wastewater samples.

Pharmaceutical	CAS number	Classification	Molecular Formula	Molecular weight, g/mol	pKa, -	log Kow, -	Source
Atenolol	29122-68-7	Cardioselective beta blocker	$C_{14}H_{22}N_2O_3$	266.3	9.6	0.16	(PubChem, 2022)
Bezafibrate	41859-67-0	Drug for hyperlipidaemia treatment	$C_{19}H_{20}ClNO_4$	361.8	3.29	4.25	(ChemicalBook, 2022; PubChem, 2022; Thegoodscentscompany, 2022)
Bisoprolol	66722-44-9	Cardioselective beta blocker	$C_{18}H_{31}NO_4$	325.4	9.5	1.87	(PubChem, 2022)
Diatrizoic acid	117-96-4	Contrast agent, utilized in radiology	$C_{11}H_9I_3N_2O_4$	613.9	0.92	1.37	(ChemicalBook, 2022; Drugbank, 2022; PubChem, 2022)
Diclofenac	15307-86-5	Non-steroidal anti-inflammatory drug	$C_{14}H_9Cl_2NO$	278.1	4.2	4.5	(ChemicalBook, 2022; PubChem, 2022)
Furosemide	54-31-9	Loop diuretic	$C_{12}H_{11}ClN_2O_5S$	330.7	3.8	2	(ChemicalBook, 2022; PubChem, 2022)
Ibuprofen	15687-27-1	Pain killer	$C_{13}H_{18}O_2$	206.3	4.9	4	(ChemicalBook, 2022; PubChem, 2022)
Carbamazepine	298-46-4	Anti-epileptic agent, mood stabilizer	$C_{15}H_{12}N_2O$	236.3	13.9	2.5	(PubChem, 2022)
Quetiapine	111974-69-7	Atypical antipsychotic for bipolar disorder and schizophrenia treatment	$C_{25}H_{25}D_4N_3O_6S$	503.6	7.06	3.17	(PubChem, 2022)
Clarithromycin	81103-11-9	Semisynthetic macrolide antibiotic	$C_{38}H_{69}NO_{13}$	748.0	8.99	3.16	(PubChem, 2022)
Losartan	114798-26-4	Receptor blocker for diabetic nephropathy and hypertension treatment	$C_{22}H_{23}ClN_6O$	422.9	5.5	4.01	(PubChem, 2022)
Metoprolol	37350-58-6	Selective beta blocker	$C_{15}H_{25}NO_3$	267.4	9.7	1.9	(ChemicalBook, 2022; PubChem, 2022)
Naproxen	22204-53-1	Non-steroidal anti-inflammatory drug	$C_{14}H_{14}O_3$	230.3	4.2	3.2	(ChemicalBook, 2022; PubChem, 2022)

Primidone	125-33-7	Aromatic anticonvulsant for treatment of seizures	$C_{12}H_{14}N_2O_2$	218.3	12.3	0.91	(ChemicalBook, 2022; PubChem, 2022)
Propanolol	525-66-6	Nonselective beta-blocker	$C_{16}H_{21}NO_2$	259.3	9.42	3.48	(ChemicalBook, 2022; PubChem, 2022)
Ramipril	87333-19-5	Angiotensin-converting enzyme (or ACE in short)	$C_{23}H_{32}N_2O_5$	416.5	3.75	3.32	(ChemicalBook, 2022; HMDB, 2022; PubChem, 2022)
Norsertraline	87857-41-8	Metabolite of sertraline	$C_{16}H_{15}Cl_2N$	292.2	9.52	9.72	(Drugbank, 2022; PubChem, 2022)
Sertraline	79617-96-2	Antidepressant	$C_{17}H_{17}Cl_2N$	306.2	9.16	5.51	(LGC, 2022; PubChem, 2022)
Ciprofloxacin	85721-33-1	Antibiotic	$C_{17}H_{18}FN_3O_3$	331.3	6.09	0.28	(ChemicalBook, 2022; Drugbank, 2022)
Citalopram	59729-33-8	Antidepressant	$C_{20}H_{21}FN_2O$	324.4	9.59	3.5	(ChemicalBook, 2022; PubChem, 2022)
Sotalol	3930-20-9	Beta blocker and beta-antagonist	$C_{12}H_{20}N_2O_3S$	272.4	8.4	0.24	(ChemicalBook, 2022; PubChem, 2022)
Sulfadiazine	68-35-9	Antibiotic	$C_{10}H_{10}N_4O_2S$	250.3	6.36	0.25	(ChemicalBook, 2022; PubChem, 2022)
Tramadol	27203-92-5	Opioid analgesic	$C_{16}H_{25}NO_2$	263.4	9.41	3.01	(ChemicalBook, 2022; PubChem, 2022)
Trimethoprim	738-70-5	Antibiotic	$C_{14}H_{18}N_4O_3$	290.3	7.1	0.91	(PubChem, 2022)
Warfarin	81-81-2	Oral anticoagulant	$C_{19}H_{16}O_4$	308.3	5	2.7	(PubChem, 2022)
Venlafaxine	93413-69-5	Antidepressant	$C_{17}H_{27}NO_2$	277.4	10.09	3.2	(ChemicalBook, 2022; PubChem, 2022)
Fluconazole	86386-73-4	Antifungal agents for fungal infection treatment	$C_{13}H_{12}F_2N_6O$	306.3	1.76	0.25	(ChemicalBook, 2022; PubChem, 2022)

6 Conclusions

Pharmaceutical compounds are entering the water cycle at an accelerating pace, causing many different environmental and societal problems. Their full effects are extensive and difficult to fully evaluate due to the metabolization they undergo after entering environments that they were not intended for. Traditional wastewater treatment systems were not designed for pharmaceutical removal, leading only to a partial removal of pharmaceuticals. Adsorption may offer opportunities and economical solutions for more extensive removal in this regard.

In this work, four adsorbents – PAC NORIT® SAE 2, GAC Supelco Merck and washed & unwashed spruce tree sawdust – were examined in terms of adsorption capacity for pharmaceuticals found in wastewater, as well as other related attributes. Real wastewater was used in three experiments, which tested the adsorbents' sensitivity and reactions to different temperature, contact time and adsorbent dosage. Additionally, multiple SUVA experiments were performed on different solutions treated with the adsorbents, which found that TOC content increased over time when treated with sawdust. This phenomenon possibly interfered with and had an effect on later pharmaceutical analysis. Regardless of the challenges, spruce sawdust demonstrated potential for pharmaceutical removal. Furthermore, using sawdust as an adsorbent can be implemented in a cost-friendly manner by repurposing industrial waste material.

Overall, with the highest dosage of 0.5 g/L and a 24 h contact time, the GAC and PAC experiments successfully removed all detected pharmaceuticals with at least 90 % removal efficiency. However, degreasing adsorbent dosage, contact time or temperature highly decreased GAC efficiency and suitability. With PAC, maximum adsorption capacity was almost reached by the 4-hour mark. Efficiency in cold temperatures is also an important factor in a Nordic climate, making PAC more practical in a domestic context. Certain pharmaceuticals stood out for being hard to remove, demanding long contact times or being sensitive for temperature. Ramipril, primidone and diatrizoic acid stood out in particular.

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