Production of micro-mesoporous alternative carbonaceous adsorbents for high-efficiency sorption of the emerging organic micropollutants from wastewater effluent

Pourya Zojaji

A Thesis

In the

Department of

Building, Civil and Environmental Engineering

Presented in Partial Fulfillment of the Requirements

for the Degree of Master of Applied Science (Civil Engineering) at

Concordia University,

Montreal, Quebec, Canada

March 2020

CONCORDIA UNIVERSITY

School of Graduate Studies

This is to certify that the thesis prepared

By: Pourya Zojaji

Entitled: Production of micro-mesoporous alternative carbonaceous adsorbents for high-efficiency sorption of the emerging organic micropollutants from wastewater effluent

and submitted in partial fulfillment of the requirements for the degree of

Master of Applied Science (Civil Engineering)

complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

Signed by the final Examining Committee:

____Chair
Dr. Catherine Mulligan

____Examiner
Dr. Alex De Visscher

____Examiner
Dr. Chunjiang An

____Supervisor
Dr. Maria Elektorowicz

Approved by ____
Dr. Michelle Nokken, Graduate Program Director

March 17, 2020 ____
Dr. Amir Asif, Dean

Gina Cody School of Engineering and Computer Science

Abstract

Production of micro-mesoporous alternative carbonaceous adsorbents for high-efficiency sorption of the emerging organic micropollutants from wastewater effluent

Pourya Zojaji

A partial removal of emerging organic micropollutants (EOMs) in conventional wastewater treatment plants (WWTPs) results in their continuous release to the aquatic terrestrial systems. Subsequently, EOMs such as pharmaceutical compounds, their respective metabolites as well as hormones and herbicides need a complementary treatment, e.g. sorption. However, sorptive material supposes to follow sustainable development principles as much as possible. Thus, utilizing low-cost alternative precursors for the production of sorptive material was considered in this study. Wasted activated sludge (WAS) and wood waste were used as viable primary materials for this purpose. The main objective of the present work was to remove of EOMs from a WWTP's effluent by an effective alternative carbon adsorbent derived from the blends of sludge and woodchips. The study consisted of three stages. In the first stage, the presence of thirty multi-class EOMs was investigated in a WWTP effluent and its vicinity in Saint Lawrence River (SLR). Subsequently, the most popular EOMs were classified, then, target compounds were selected to be exposed to adsorption process. In the second stage, an effective method to produce pore enriched activated carbon from single-step activation of sludge with the additive of wood residues was developed. The produced new adsorbent increased the surface area from 1320 $m^2 g^{-1}$ to 1565 $m^2 g^{-1}$ after combining sludge precursor with hardwood chips. Also, the strength of the surface acidity and yield of products were mounted after wood addition. In stage 3, the sorption of an anti-depressant, venlafaxine (VEN), from aqueous solution onto the new adsorbent derived from the mixture of sludge and hardwood residues (SS:HW) was compared with a commercial granular activated carbon (CGAC). Maximum sorption capacity of the SS:HW was measured 131.57 mg g^{-1} from Langmuir isotherm while this value was 25.57 mg g^{-1} for CGAC. Then SS:HW adsorption efficiency was successfully validated on real WWTP effluent; while CGAC failed to remove a mixture of EOMs from the real matrix. The results revealed the new micro-mesoporous sludge-based (SS:HW) adsorbent could serve as an efficient tool for polishing WWTP effluent and protecting the quality of surface water resources.

Acknowledgment

Foremost, I would like to express my sincere appreciation to my supervisor Professor Maria Elektorowicz, for her motivation, immense knowledge, and her valuable and constructive suggestions. Her guidance helped me in all the time of research and writing of my thesis.

Also, I wish to acknowledge the financial support from Environment and Climate Change Canada (ECCC) [grant number EDF-PQ-2017G005].

I wish to pay my special regards to Dr. Shameem Jauffur and Dr. Esmaeel Kariminezhad from Envirogenique Company for their support and encouragement.

Special thanks to Mr. Marc-Antoine Vaudreuil from the University of Montreal for his valuable collaboration in the analysis of water and wastewater samples.

Dedication

To:

My beloved parents: Farima and Sasan

For nursing me with affection and love and their endless support in my life

My dear sister, brother-in-law, and my amazing nephew: Parisa, Hojjat and Parsa

For their unconditional love and for cheering me thorough this journey until the end.

Table of Contents

List of Figures

List of Tables

Abbreviation List

2OH-IBU	2-Hydroxy ibuprofen
4OH-DCF	4-Hydroxy Diclofenac
4N-SMX	4-Nitroso Sulfamethoxazole
AC	Activated carbon
ACB	Acebutolol
ATZ	Atrazine
AMX	Amoxicillin
AOP	Advanced oxidation process
BET	Brunauer-Emmett-Teller
CAF	Caffeine
CBZ	Carbamazepine
CBZ-DiOH	10,11-dihydro-10,11-dihydroxycarbamazepine
CGAC	Commercial granular activated carbon
CLT	Clarithromycin
COD	Chemical oxygen demand
DATZ	Desethylatrazine
DCF	Diclofenac
DVEN	Desvenlafaxine
DTG	Differential thermogravimetric
E1	Estrone
E2	Estradiol
E3	Estriol
EE2	Ethinylestradiol
EDA	Electron donor-acceptorr
EDC	Endocrine disrupting compound
EOMs	Emerging organic micropollutants
ESI	Electrospray ionization

FLX	Fluoxetine
FTIR-ATR	Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance
GAC	Granular activated carbon
HRT	Hydraulic retention time
HW	Hardwood
IBU	Ibuprofen
LC-MS/MS	Liquid chromatography tandem mass spectrometry
log K_{ow}	Octanol-water partition coefficient
NFLX	Norfluoxetine
NSAIDs	non-steroidal anti-inflammatories drugs
PAC	Powder activated carbon
PhACs	Pharmaceutical active compounds
PFO	Pseudo first order
pK_a	Dissociation constant
PSO	Pseudo second order
PZC	Point of Zero Charge
SBA	Sludge-based adsorbent
SEM	Scanning electron microscopy
SLR	Saint Lawrence River
SMX	Sulfamethoxazole
SPE	Solid phase extraction
SS	Secondary sludge
SW	Softwood
TGA	Thermogravimetric analysis
VEN	Venlafaxine
WWTP	Wastewater treatment plant

1. Introduction

1.1. Problem statement

The advent of more precise analytical instruments enabled the researchers to detect numerous new unregulated trace organic chemicals in the aquatic environment. These chemicals are commonly named as emerging organic micropollutants (EOMs). The occurrence of EOMs such as pharmaceutical active compounds, their respective metabolites, and hormones as well as herbicides at the concentrations ranging between a few ng L^{-1} to µg L^{-1} in surface waters and wastewaters have been recently highlighted in several studies around the world.

As a result of the new findings, unprecedented concerns have also emerged. For instance, many of these chemicals are unexpectedly behaving as endocrine active agents causing adverse health effects in intact aquatic organisms (Fuhrman et al. 2015). It is revealed a cocktail of pharmaceuticals can pose synergic ecotoxicology which is greater than each compound solely (Vasquez et al. 2014). Yet the impact of many of these chemicals on human health and environment are not well-understood.

Removal of the EOMs in conventional wastewater treatment plants (WWTPs) which can occur through, degradation (biologically, hydrolysis, oxidation), sorption to sludge or particulate matters and volatilization is not effective (Guerra et al. 2014). Hence WWTPs have been recognized as the source of EOMs' spread and the removal of micropollutants within the treatment plants by a complementary methodology has become a matter of urgent need during recent years.

Adsorption of EOMs to solid matrices as a complementary treatment has shown promising results. Activated carbon (in granular and powder forms) is the most frequently used adsorbent which exhibits very satisfactory removal rates due to its high surface area and the combination of a wide network of porosity and the surface chemistry properties (Álvarez-Torrellas et al. 2016b). Commercial activated carbons are commonly produced from wood, coal (bituminous and sub-bituminous varieties), lignite, and coconut shells (Wang et al. 2006). Unluckily, this resulted in a high cost of production in the large-scale application of activated carbon and restricts its applicability (Cabrita et al. 2010). As a consequence, great attempts have been made by researchers to introduce alternatively available and low-cost sources for the production of activated carbon.

Treated secondary sludge, as a leftover from biological operations in conventional WWTPs, attracted much of attention. Sludge is produced in immense quantities worldwide. Moreover, its difficulty in disposal became a bottleneck in the WWTPs. Sludge is potentially suitable for the production of carbonaceous adsorbent because of its carbonaceous nature, low cost, and wide availability (Ocampo-Pérez et al. 2012).

Production of sludge-based adsorbents (SBA) for wastewater remediation proposes has a twofold ecological benefit, it is not only ecofriendly to solve the problem of secondary pollution associated with the sludge itself, but also allows its reuse in water treatment applications. However, the high inorganic (ash) content of the sludge constraints the porosity development of resulting carbon products derived from the sole carbonization of it (Zeng et al. 2018; Smith et al. 2009a). This deficiency could impact the sorption capability of the SBAs while many wastewaters industrial applications demand efficient alternative adsorbents that they could be comparable with the available commercial activated carbon.

Recently, co-carbonization of the sludge with other carbonaceous biomasses demonstrated promising results to enhance the textural properties of SBA (Li et al. 2016; Xu et al. 2015). In addition, the co-processing of two precursors led to recycling more waste to valorized materials. However, this technique has been under development and depends on the thermal condition antagonistic interactions between two waste samples were also observed (Huang et al. 2017). Hence, more investigations should be conducted to produce suitable alternative SBA from the co-processing of sludge and carbon-rich materials.

1.2. Research objectives

The main purpose of the present thesis is to develop a new adsorptive material, which is efficient in removing emerging organic micropollutants from a WWTP effluent in the province of Quebec (Canada), in order to protect the quality of St. Lawrence River.

Detailed objectives are:

1. Finding the representative multi-class of EOMs in the selected WWTP wastewater effluent and its recipient St Lawrence River;
2. Applying waste to produce new adsorptive material at lower costs;
3. Developing an effective process for the production of a pore enriched sludge-based adsorbent with the additive of wood residues;
4. Defining the efficiency of the produced adsorptive material in the removal of target micro-pollutants from an aqueous solution;
5. Verifying the efficiency of new adsorptive material on real WWTP effluent.

1.3. Organization of thesis

The thesis consists of five chapters. Chapter 1 includes a short introduction, including the problem statement and the scope of the research. Chapter 2 presents the review of the existing relevant literature on the occurrence of EOMs in the WWTPs, the potential of novel technologies particularly adsorption with activated carbon as a remediation technique and finally potential of pyrolysis to produce sludge-based adsorbent. Chapter 3 presents a detailed description of the methodology, including materials and chemicals, water and wastewater sampling, SBA's synthesizing procedure, characterization facilities, and experimental procedure, as well as the analytical method. Chapter 4 presents results obtained from the environmental sample collection, laboratory experiments, and their discussion. Finally, Chapter 5 gives a conclusion and explores research contributions and recommendations for future work.

2. Literature Review

2.1. Emerging organic micropollutants (EOMs)

The adverse effect of chemical pollution has traditionally focused on conventional or legacy priority pollutants like nutrition, heavy metals, PAHs, PCBs, and petroleum hydrocarbons. However, our ever-growing society is using a continuously increasing number of chemicals which currently can be estimated in hundreds of thousands of compounds (most of them organics). Consequently, a wide range of man-made organic compounds, designed for use in various consumer goods is also emitted as xenobiotics to the environment.

While these chemicals have long been present in the environment, they have not gained scientific attention until recently (Thomaidi et al. 2015). The advent of highly sensitive analytical instruments enabled the scientific communities to detect numerous new unregulated trace organic chemicals, commonly known as emerging organic micropollutants (EOMs), in the aquatic environment. EOMs are commonly observed in waters at very minute concentrations, ranging from a few ng L^{-1} to several µg L^{-1}. The trace concentration and diversity of organic micropollutants not only complicate the associated detection and analysis procedures but also create new challenges for water and wastewater treatment processes (Luo et al. 2014).

Because EOMs are so numerous, diverse and ubiquitous, they are frequently lumped into categories that describe their purpose, use or other characteristics (Raghav et al. 2013). Some common categories are as follows (Yan et al. 2009):

- Pharmaceutical active compounds (PhACs) and their metabolites
- Natural and synthetic hormones
- Pesticides including herbicides, insecticides, fungicides
- Plasticizers
- Personal care products
- Flame retardants
- Nanomaterials
- Other emerging organic compounds.

2.2. Main source of EOMs entry to the aquatic environment

Many of EOMs are found in the consumer products used in the daily life of urban and industrial for different kinds of proposes. After use, these chemicals could be disposed in different ways. Most of them are potentially flushed down into the domestic wastewater sewer. As an example, pharmaceutical compounds used in human medical care are not eliminated in the human body. They are metabolized to a different extent and excreted as unchanged as well as metabolized compounds and finally end up to WWTPs (Heberer 2002). Furthermore, many of the microcontaminants could also end up to domestic WWTPs through the combined sewer system collecting urban runoff and drain of industrial discharge.

In the basic biological WWTPs removal of EOMs can occur through, degradation (biologically, hydrolysis, oxidation), sorption to sludge or particulate matters, and volatilization (Guerra et al. 2014). Figure 2.1 demonstrates the processes involved in the fate of pharmaceutical active compounds (PhACs) in WWTPs.

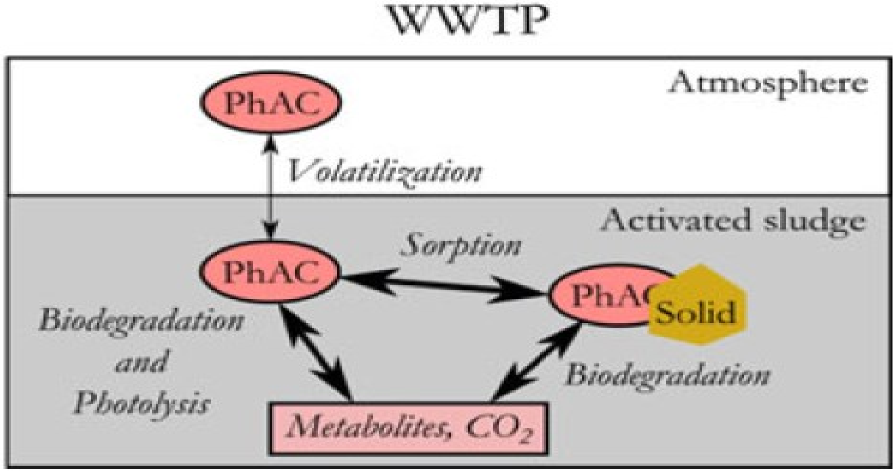


Figure 2.1 Fate of pharmaceutical active compounds in the conventional WWTPs (Mandaric et al. 2015)

It is revealed in the case of EOMs many of the aforementioned removal mechanisms in the conventional WWTPs are ineffective (Guerra et al. 2014; Verlicchi et al. 2012). For instance, pharmaceutical compounds are biologically stable that can inhibit microorganism activity. The sorption on the sludge depends on the type and properties of the suspended solids (sludge). Also, many of the EOMs have low vapour pressure as well as lack of hydrolysable functional groups. As a result, the removal of these microcontaminants is incomplete and continuous mass loads of

EOMs are permanently discharged from conventional WWTPs to the receiving surface water. This lack of treatment presented wastewater effluent and combined sewer overflows of conventional wastewater plants as the major sources of environmental EOMs release (Daneshvar et al. 2012).

2.3. Occurrence of EOMs at the conventional WWTPs

Local sale, consumption pattern, pharmacokinetics, and WWTPs performance are the factors influencing concentrations of the organic micropollutants in WWTPs effluent and recipient aquatic nature (Silva et al. 2015; Comeau et al. 2008). In the current section, the occurrence of well-known compounds belongs to three families of EOMs including pharmaceutical active compounds and their metabolites, hormones, and herbicides at the WWTPs was discussed.

2.3.1. Pharmaceutical compounds and their metabolites

Traditionally pharmaceuticals have not been recognized as environmental contaminants and have experienced several decades of unrestricted discharge to the environment. However, pharmaceutical active compounds (PhACs) are now classified as ‘‘new’’ or emerging contaminants to the environment (Hua et al. 2006). PhACs of environmental concern includes analgesics/non-steroidal anti-inflammatories drugs (NSAIDs), β-blockers, antibiotics and psychiatrics (Noguera-Oviedo and Aga 2016).

Analgesics are one of the most dispensed classes of pharmaceuticals worldwide. Analgesics such as Ibuprofen (IBU) and Diclofenac (DCF) are often sold by either prescription or non-prescription. The IBU and DCF are excreted only 25% and 15% unchanged from human’s body (Saunders et al. 2016). Both compounds with their metabolites have been observed in the inflow waste streams to the WWTPs (Comtois-Marotte et al. 2017; Guerra et al. 2014; Lishman et al. 2006). DCF is known as a recalcitrant compound showing little or no degradation in WWTPs (Vieno and Sillanpää 2014). Contrarily, IBU was reported as a compound that has higher removal efficiency in biological treatment. For example, more than 93% removal efficiency for the IBU and only 4–9 % for DCF were reported in WWTP utilizing activated sludge process located in Granby, province of Quebec, Canada (Gagnon and Lajeunesse 2012). One of the main metabolites of IBU is 2-Hydroxy ibuprofen (2OH- IBU). Surprisingly, this compound is also could be reproduced in the biological operations inside the treatment plants (Ebele et al. 2017).

In the five WWTPs, utilizing primary and secondary treatment, in the province of Quebec, 2-Hydroxy ibuprofen (2OH- IBU) was detected at the higher concentrations than IBU in the effluents and also less than 60% removal efficiencies was reported in the conventional biological WWTPs (Gagnon and Lajeunesse 2012).

Antibiotics are used for therapeutic treatment of bacterial diseases. They are comprised of different classes such as penicillin, sulfonamides, and macrolides. Among different antimicrobials, the most abundant ones were sulphonamides (Yan et al. 2009). A small average removal of 25 % was reported for the sulfonamide antibiotics in the conventional activated sludge process with the HRT ~ 25-h (Watkinson et al. 2007). Sulfamethoxazole (SMX) belongs to this group which has been frequently observed in the domestic waste streams (Segura et al. 2007; Miao et al. 2004). SMX is excreted as 15 % unchanged compound from the human body. It is reported 4-nitroso Sulfamethoxazole (4-N SMX) as one of SMX metabolites can induce more cytotoxic than the parent compounds (Bonvin et al. 2012). Yet 4-N SMX has not been reported in any aquatic environment (Bonvin et al. 2012). Amoxicillin (AMX) and Clarithromycin (CLT) are examples of antibacterials belonging to penicillin and macrolides, respectively. While high removal efficiency in the WWTPs and less stability in the surface waters were observed for AMX (Castiglioni et al. 2006), CLT was recalcitrant compounds in biological WWTPs. By adopting mass balance for the amount of CLT in the influent, effluent, and the sludge residue in two activated sludge plant (different HRTs; 12 and 24 hours) it was concluded due the presence of CLT at the higher proportion in the effluent and also fewer than 25 percent in the biosolids, CLT is a resistant compound to biodegradation (Guerra et al. 2014). SMX and CLT were presented at the median concentrations of 243 ng L^{-1} for SMX and 87 ng L^{-1} for CLT, in the effluent of three WWTPs utilizing activated sludge process around Canada (Miao et al. 2004).

β-blockers are prescription drugs used to treat hypertension, congestive heart failure, and abnormal heart rhythms. In Canada, Acebutolol (ACB) is one of the heavily used antihypertensives with significant daily doses (Lee et al. 2007). It is excreted 39% as unchanged compounds from human bodies (Vieno et al. 2006). ACB was present at the median concentration of 308 ng L^{-1} in the samples collected from seven WWTPs' effluents utilizing conventional treatments in the province of Ontario, Canada where its removal efficiency was reported approximately 19% in all WWTPs (Lee et al. 2007).

The prevalence of psychiatric disorders resulted in an increased number of prescriptions for psychiatric pharmaceuticals worldwide. In Canada, psychotherapeutic drugs are the second most dispensed class of pharmaceuticals (IQVIA 2017). The increased prescription, as well as required chronic administration of such drugs, suggests a higher environmental exposure (Silva et al. 2015). Anti-depressants and anticonvulsants are the two frequently used families of psychotropics.

From the anticonvulsants Carbamazepine (CBZ) is quite well-known. It is one of the most frequently reported PhACs in aquatic environment in Canada and worldwide (Rivera-Jaimes et al. 2018; Bayen et al. 2016; Darwano et al. 2014). Extremely low degradability of CBZ in biological treatment plants (<10%) was typically reported in the literature. Low removal efficiency (less than 10%) was reported for carbamazepine in two biological systems; conventional activated sludge (HRT =12 hours) and membrane bioreactor (Celiz et al. 2009). A removal efficiency between 4 and 9 % for CBZ was reported in four biological WWTPs in the province of Quebec (Gagnon and Lajeunesse 2012). One of the main CBZ urine metabolites is 10,11-dihydro-10,11-dihydroxycarbamazepine (CBZ-DiOH). Interestingly, it may be also produced by wastewater treatment operation (Jelic et al. 2012). CBZ-DiOH had the highest concentrations in comparison to the other CBZ metabolites in both influent and effluent of a WWTP located in Peterborough, Ontario where the former and the latter acquired concentrations of 426.7 ng L^{-1} and 1325 ng L^{-1}, in the effluent, respectively (Miao and Metcalfe 2003).

Antidepressants can be divided into several classes, according to their structure and mode of action. The most important classes of antidepressants are selective serotonin reuptake inhibitors (SSRI). When the drugs belong to the SSRI are not effective, other efficient antidepressants from the group of selective serotonin and norepinephrine reuptake inhibitors (SSNRI) are prescribed (Silva et al. 2015). Fluoxetine (FLX) and Venlafaxine (VEN) are the well-known examples of the SSRI and SSNRI antidepressant, respectively. In the study conducted by Lajeunesse et al. (2008) ten antidepressant drugs and their metabolites were present at concentrations of 2–346 ng L^{-1} in samples collected at the Montreal primary WWTP where VEN and its hydroxylated metabolite, named O-desmethylvenlafaxine (DVEN), possessed the highest levels. It is noteworthy the O-desmethyl-venlafaxine was also observed as a transformation product in the microbial degradation of VEN (Boix et al. 2016). Modest removal of different antidepressant compounds (approximately 40%) was reported in a WWTPs utilizing conventional activated sludge and tertiary treatment, followed by UV-disinfection in the province of Ontario, Canada where the VEN, DVEN, FLX, and metabolite of FLX (Norfluoxetine, (NFLX)) were detected in the effluent at the concentrations of 0.8, 1.64, 0.122, 0.005 μg L^{-1}, respectively (Metcalfe et al. 2010). In the meticulous study conducted in five WWTPs across Canada, VEN, DVEN, and FLX demonstrated low mean removal efficiencies of 19, 10, and 36%, respectively (Lajeunesse et al. 2012).

Caffeine (CAF) is the main stimulating ingredient in coffee, tea and is also found in other widely consumed products such as pharmaceuticals. Due to its vast consumption rate, caffeine often presents at relatively higher concentrations in comparison to the rest of microcontaminants in the raw sewage worldwide (Afonso-Olivares et al. 2017; Cardenas et al. 2016; Viglino et al. 2008). However, caffeine is not resistance to the conventional biological wastewater treatment process. As a result, its concentration is effectively decreased in the effluent. The concentration of caffeine was reduced by an order of magnitude or more in all the class B WWTPs in Northwest Ohio, USA (Spongberg and Witter 2008). The same result was reported in four secondary WWTPs using a variety of activated sludge process (anaerobic/anoxic/oxic [A2/O], anoxic/oxic [A/O] activated sludge oxidation ditch) in China (Yang et al. 2011).

2.3.2. Natural and synthetic hormones

Hormones could be excreted naturally from the human's body. The three major naturally occurring estrogens in women are estrone (E1), 17β-estradiol (E2), and estriol (E3) while testosterone is an androgen excreting from men. Among them, E1 has been recently added to the US EPA's fourth drinking water Contaminant Candidate List (CCL4). Also, synthetic hormones are used for various proposes like regulation of the reproductive system (Noguera-Oviedo and Aga 2016). Synthetic hormones such as 17α-ethinyl estradiol (EE2) and different progestogens are widespread in oral contraceptive formulations.

In Canadian and German WWTP discharges E1, E2, and EE2 were frequently detected within the lower ng L^{-1} range. The maximum concentration was found for E1 with 70 ng L^{-1} (Ternes et al. 1999). Yarahmadi et al. (2018) reported nine hormones including E1, E2, E3, EE2, and different progesterones were detected in both dissolved and particulate phases with mean concentrations from 21 ng L^{-1} to 389 ng L^{-1} in raw sewage and from 10 ng L^{-1} to 296 ng L^{-1} in treated wastewater of three WWTPs in the province of Quebec, Canada.

Degradation accounted for 78–99% and 73–96% of the removal of estrogens and progestogens from aerobic and anaerobic tanks (Fan et al. 2011). Sorption by particulate matters may also contribute to the significant part of the removal efficiency of hormones in the WWTPs (Andrási et al. 2013). In the investigation carried out by Servos et al. (2005) at the eighteen selected municipal treatment plants across Canada, reductions in E2 ranged from 40% to 99% and E1 reductions from −46% to 95% were observed. The non-complete removal of hormones could consequently enhance the estrogenic effect of WWTP effluent.

2.3.3. Herbicides

Herbicides are of non-point source origin because they are applied directly to the land for agricultural purposes. Nonetheless, due to their urban usage, they could be found in the municipal WWTPs as well.

S-triazine family of herbicides has been one of the highly intensive used herbicides worldwide. As such atrazine (ATZ) with 70,000 to 90,000 tones applied per year was one of the most widespread s-triazines in the world (Sivarajasekar et al. 2017). The occurrence of ATZ in the WWTPs effluent was previously reported in the literature. ATZ was present at the concentrations ranging from 4.8 ng L^{-1} to 20.9 ng L^{-1} in the secondary WWTP in the province of Ontario Canada (Hua et al. 2006). Also, a mean concentration of 14 ng L^{-1} was reported for ATZ inside two WWTP discharges in Canada (Daneshvar et al. 2012).

Very few scientific researches dealt with atrazine removal in urban biological wastewater treatment. Buttiglieri et al. (2011) reported less than 25% removal efficiency of ATZ in a pilot-scale membrane bioreactor. Campo et al. (2013) and Köck-Schulmeyer et al. (2013) declared none or negative removal efficiencies for the ATZ in the local conventional WWTPs. Deconjugation of transformation products of the herbicides inside the WWTP's biological operation may justify the negative efficiencies.

The main by-product of microbial biodegradation of Atrazine is named Desethylatrazine (DEA) (Cormier et al. 2015). The ATZ transformation product was also observed in the WWTP's effluent even at higher levels in comparison to the ATZ, itself (Daneshvar et al. 2012; Hua et al. 2006). Singer et al. (2010) reported a low average removal efficiency of less than 17±33% for the DEA in the conventional WWTP.

2.4. Impact of EOM's release to the recipient environment

There is an increasing concern about the environmental risks posed by EOMs. (Thomaidi et al. 2015) estimated the ecological threat associated with EOMs detected in the wastewater in the country level in Greece. The authors concluded a mixture of microcontaminants seems to pose a significant ecological risk even in the river with a high dilution effect.

Pharmaceuticals are coincident in the multi-therapeutic classes in the WWTPs effluent. Recent investigations proved the cocktails of PhACs originated from different therapeutic families could induce synergic or additive toxicities (Vasquez et al. 2014; Cleuvers 2003). As an example, Rice and Mitra (2007) revealed a mixture of 13 pharmaceutical compounds decrease 10–13% of human embryonic kidney cells growth after 2 days of exposure in vitro, while no effects were observed by each compound solely.

Furthermore, the long-term presence of antibiotics in the WWTPs outfall promotes the antibiotic resistance genes in the natural bacteria in the recipient environment (Hernando et al. 2006). The prevalence and persistence of antibiotic resistance in bacterial pathogens have become an emerging threat to public health, which is raising considerable concern (Gao et al. 2012)

Hormones are inherently potent endocrine disrupting compounds (EDC) causing alteration in the reproductive system of aquatic organisms. Moreover, other EOMs such as pesticides and some of the pharmaceutical active compounds behaved unexpectedly like EDCs to non-target organisms (Gonzalez-Rey and Bebianno 2012; Knudsen and Pottinger 1998). The feminization of male fish within WWTP's effluents is attributed to the presence of endocrine disrupters (Ternes et al. 1999). The study (Gagné et al. 2011) reported the endocrine-disrupting activity of municipal effluent caused feminization in wild mussel populations and the disruption in gonad physiology in the sites located in the downstream of the WWTPs outfalls in the province of Quebec, Canada.

In light of these concerns, the reduction of EOMs discharge into the receiving environment must be of the highest priority. Employing advance treatment methodologies dedicated to the removal of EOMs could potentially enhance the quality of the final WWTPs effluent discharge.

2.5. Complementary treatment of wastewaters containing EOMs

Despite the health risk of EOMs that are detected in the wastewater effluent has been highlighted by numerous studies, there is still a lack of measures to regulate maximum concentrations of EOMs in their source of emission. Particularly, in Canada national guideline has not yet been developed and just water quality guideline in certain estrogenic compounds exists in some provinces like British Columbia guideline for EE2 (Holeton et al. 2011).

Recently, the first regulation in Europe about EOMs (Office federal de l'environnement, Division Eaux, 2014), mandates removal of 80% in comparison to the wastewater influent for at least six pharmaceutical compounds among twelve micropollutants such as CBZ, CLT, DCF, and VEN. Nevertheless, to achieve such performances the implementation of non-conventional techniques in typical WWTPs needs to be more and more considered (Guillossou et al. 2019). As an example, Figure 2.2 shows the effectiveness of two commonly employed unconventional methods including activated carbon and oxidation with ozone in the elimination of organic micropollutants in comparison to the ineffective traditional biological methodology.

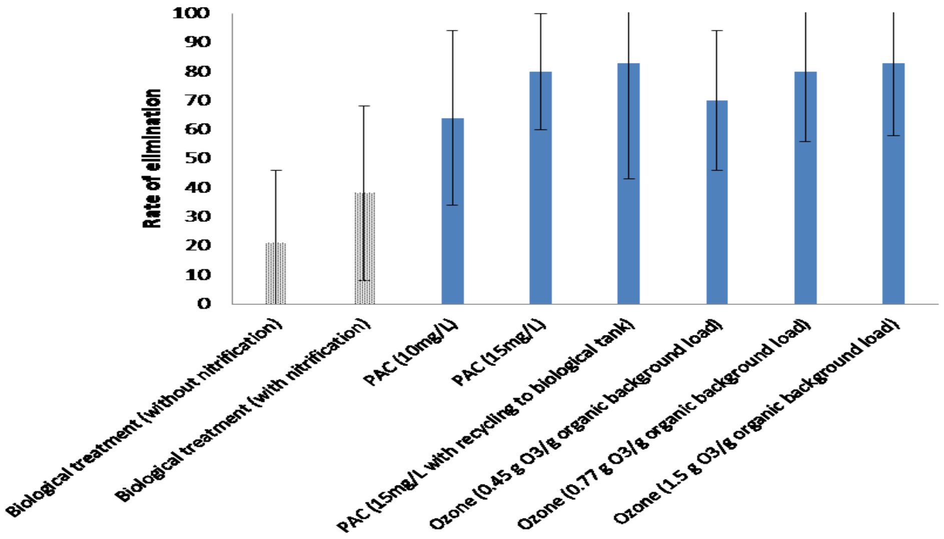


Figure 2.2 Capability of the biological treatment, powder activated carbon (PAC) and ozonation for removal of EOM (Abegglen and Siegrist 2012)

The complementary techniques should often be added as tertiary treatment to the available basic physical/biological treatment within a WWTP. As an example, Figure 2.3 presents a schematic of different segments of an advanced WWTP.

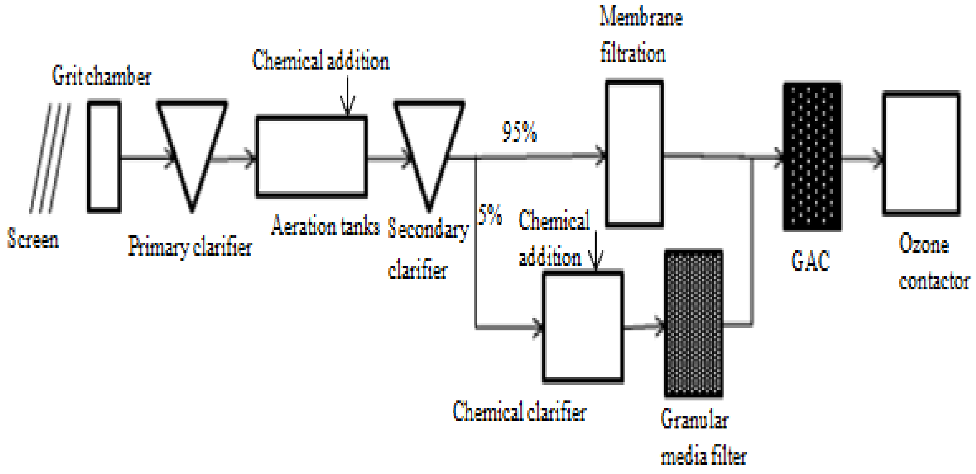


Figure 2.3 Schematic diagram of the complementary methodologies placement inside a conventional WWTP (Yang et al. 2011)

2.6. Main types of Complementary treatment

So far the non-conventional complementary treatment can be broadly divided into (Rodriguez-Narvaez et al. 2017);

- Complementary biological treatment
- Advanced oxidation process (AOP)
- Phase changing technologies

2.6.1. Complementary Biological treatment

The complementary biological treatments are placed after conventional biological purification systems in WWTPs. In the biological methodologies, organic pollutants are mainly broken down into smaller molecules through biologically catalyzed reduction induced by living microorganisms (Chamy 2013).

In last years many studies reported the ability of the fungal treatment to degrade the recalcitrant EOMs. White rot fungi (WRF) is known as a possible bioremediation candidate due to its potential enzymatic system which is able to degrade recalcitrant organic compounds. As an example, in a fluidized bed bioreactor, Trametes Versicolor could eliminate 83% of EOMs input inside a sterilized real effluent (Cruz-Morató et al. 2014). *T. versicolor* and *G. lucidum* were also used to biotransfrom VEN and DVEN. By both strains, removal efficiencies of 70% and 100% were achieved for VEN and DVEN, respectively. However, carcinogenic N-nitrosodimethylamine by-product was generated during VEN removal (Llorca et al. 2019). The white rot fungi technique is still a technology under study. Efforts should be made to examine them in a real urban wastewater condition where the crucial growth relevant parameter like the required amount of nutrition needs to be optimized.

Biological treatment could be also integrated with other tertiary treatments. A few studies propose the enzymatic membrane reactor (EMR) in order to degrade the micropollutants. A continuous membrane reactor containing laccase, an extracellular enzyme induced by fungal species, was designed by Lloret et al. (2012) to remove estrone (E1) and estradiol (E2) from the spiked aqueous solution. The residual estrogenic activity of the effluent was largely reduced up to 97 %.

Nguyen et al. (2014) employed a combined system comprising of the EMR with the addition of a natural redox-mediator compound and activated carbon. While EMR showed low efficiencies of 22% to 55% to remove four EOMs including CBZ, SMX, DCF and ATZ addition of the mediator and activated carbon enhanced the efficiency to the level of 65% to 80%. Despite the addition of redox-mediators can enhance efficiency, it was reported this sort of compound resulted in a cocontaminant increase in the toxicity of the effluent (Grandclément et al. 2017).

In a recent study, Ouarda et al. (2018) coupled a biological treatment (membrane bioreactor) with the electro-oxidation system to remove four EOMs including IBU, VEN, CBZ, and E2 from synthetic hospital effluent. The author concluded while both techniques were not individually effective to remove recalcitrant compounds like VEN and CBZ, the combined system could enhance the efficiency more than 97% for all EOMs. Despite the high efficiency in this technique, the author stated the production of by-products needs to be considered due to their potential of higher toxicity.

2.6.2. Advanced oxidation process (AOP)

Chemical oxidation is an effective technique in the removal of many recalcitrant organic contaminants. In recent years interest in advanced oxidation processes (AOP) has increased. AOP is based on the generation of radicals (OH·, O_2^-, HO_2) notably the hydroxyl radicals, highly reactive species with oxidation potential equals to 2.8 V that can attack many EOMs (Rivera-Utrilla et al. 2013). These free radicals are produced via different routes and specific work conditions.

Application of AOP based on ozone including O_3, O_3/OH·, O_3/H_2O_2, O_3/activated carbon systems for removal of EOMs from water and wastewater have gained much consideration. In general, ozone is a well-established and widely used end of pipe technique for the removal of many organic contaminants. Results from both pilot- and full-scale plants using ozonation after the conventional biological treatment reported removal efficiencies of about 95% for several micropollutants (Rúa-Gómez et al. 2012; Yang et al. 2011; Huber et al. 2005). Also in the case of low-quality effluent such as primary-treated effluent ozone oxidation was effective. For instance, in a pilot project conducted by Gagnon et al. (2008) O_3 at the dose of 20 mg L^{-1} was capable to remove EOMs including IBU, 2OH-IBU, DCF, CBZ as high as 70% from a primary treated wastewater. Despite the exceptional efficiencies, the major issue of concern arising from the ozonation of the wastewater is the oxidation by-products. For example, it was reported partially ozonation of pharmaceuticals could yield biologically still active oxidation products (Knopp et al. 2016).

Many of the EOMs contain aromatic rings, heteroatoms, and other functional groups that make them photoactive compounds. In spite of that, the removal percentages obtained by using UV radiation alone were quite low (lower than 30%) (Rivera-Utrilla et al. 2013; Gagnon et al. 2008). Giannakis et al. (2017) declared VEN demonstrated moderate photolysis under UV, and the addition of H_2O_2 with the simultaneous OH· generation enhanced the degradation potential of the chosen treatment in aqueous solution. However, in a real urban wastewater matrix, the presence of antagonists such as suspended solids, organic matters as well as reactive oxygen species scavengers significantly hindered the efficiency. As a consequence intensive treatment is needed for the actual condition.

Combination of UV with chlorine could generate highly oxidative radicals (OH· and Cl) which efficiently degraded the EOMs such as IBU, CBZ, DCF, SMX, EE2 and DEA (Wang et al. 2017; Xiang et al. 2016; Sichel et al. 2011). Despite the high degradation efficiencies formation of dangerous chlorinated intermediates/by-products such as Trihalomethanes (THMs) and N-Nitrosodimethylamine (NDMA) inside the wastewater is still the issue of concern in this sort of technique.

Employing photocatalyst under UV radiation could also enhance the hydoxyl radicals' formation. Titanium dioxide photocatalysis (TiO_2/UV) was used for degradation of VEN (Lambropoulou et al. 2017). VEN was quickly removed via photocatalytic reaction while a great number of intermediates were detected by high resolution LC–MS. Toxicity test demonstrated an increment in the acute toxicity in the first stages of the treatment (during 30 min) due to the formation and synergetic effect of toxic demethylated, N-oxide or other derivatives.

Finally, in oxidation techniques, the implementation of additional post-treatment processes seems to be necessary to minimize the risks that may arise due to the formation of toxic oxidation byproducts and to enhance the safety of the processes. Furthermore, AOPs usually imply the use of high chemical dosages and high energy consumption (Pérez-González et al., 2012) and thus they are often not considered sustainable cost-effective technologies (Sotelo et al. 2014).

2.6.3. Phase changing technologies

Technologies based on transferring contaminants from a liquid phase to a solid phase have been widely employed to remove EOMs. Adsorption and membrane filtration are the main examples of phase changing technologies.

In the membrane technology, forward and reverse osmosis, nanofiltration, as well as ultrafiltration membrane have been used for removing EOMs (Azaïs et al. 2014; Melo-Guimarães et al. 2013; Hancock et al. 2011). Size exclusion (sieving effect) is one of the prominent mechanisms for EOM removal in membrane filtration. This mechanism leads to concentrate the pollutants in the retentate which inevitably needs to be further treated. Furthermore, if the EOMs are not degraded, the concentration of solute on the filtrate increased by increasing the filtrate recovery and subsequently the overall performance would not be as high as expected (Taheran et al. 2016).

Among the possible techniques for advance wastewater treatment, adsorption to solid particles has proven to be superior to other techniques for a variety of reasons including (Silva et al. 2018a):

- producing high-quality effluent,
- simplicity of design,
- ease of implementation,
- wide range of applications,
- no unwelcome by-product,
- and possibility of adsorbent regeneration

Also, adsorption is a relatively low-cost technology. Depending on the type of adsorbent the cost of the treatment is estimated to be in the range from US $10 to US $200 per million liters, while when using other technologies like reverse osmosis, ion exchange, electrodialysis, and electrolysis, the cost can reach up to US $450 per million liters (Silva et al. 2019). Given all these benefits adsorption is considered one of the most promising, effective, and attractive approaches for complementary wastewater treatment.

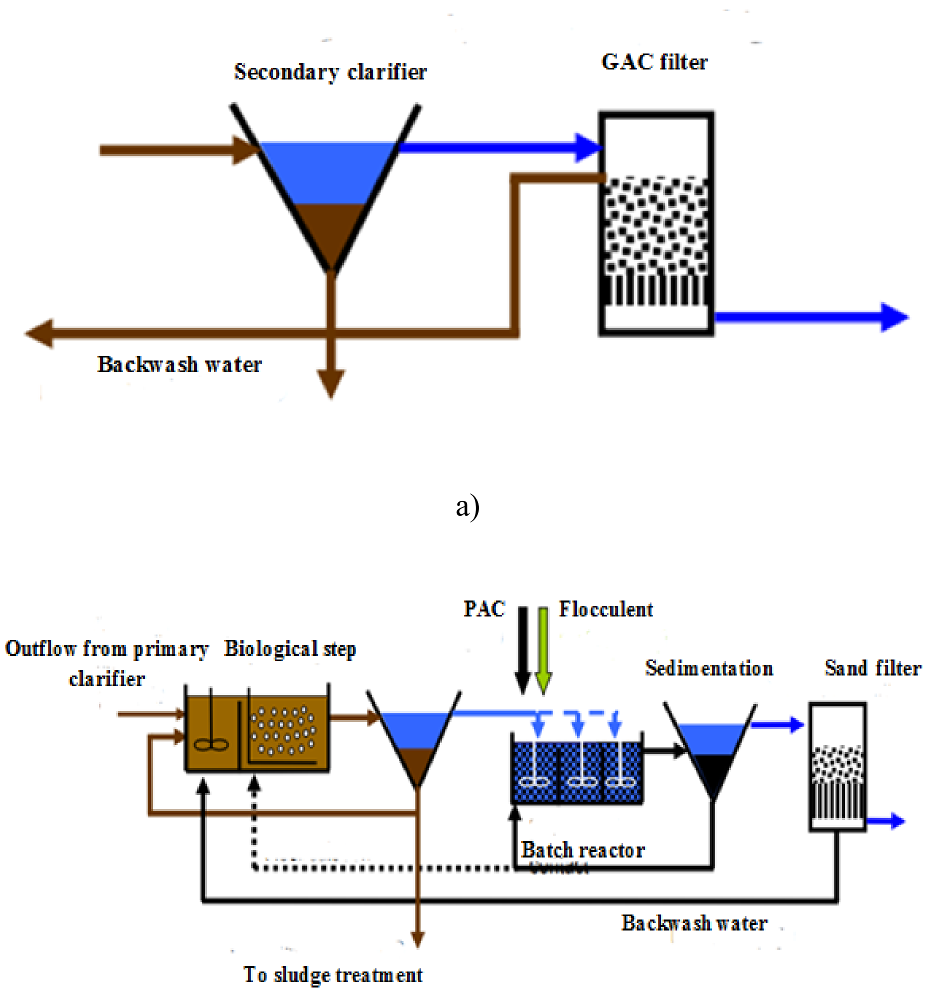
Different types of adsorbents were used for removing EOMs including activated carbon (Alves et al. 2018), zeolite (De Ridder et al. 2012), clay minerals (Mohd Amin et al. 2015) as well as metal oxides and metal nanoparticles (Akhtar et al. 2016). However, none of the adsorbents except activated carbon was capable of removing a wide range of EOMs from wastewater effluent (Abegglen and Siegrist 2012).

2.7. Adsorption with Activated Carbon

The term activated carbon (AC) refers to the large group of industrially produced materials which mainly consist of carbon atoms and acquire peculiarity of possessing valuable properties such as; surface area, the volume of pores with a tunable pore size distribution, and adsorption capacities (Linares-Solano et al. 2012). AC can possess a surface area of more than 1000 $m^2 g^{-1}$.

All these unique features and AC’s different morphologies can be tailored and developed according to their final application.

Conventionally, adsorption of natural and synthetic organic compounds is performed using either granular activated carbon (CGAC) and powder activated carbon (PAC) (Metcalf et al. 1972). According to the American Society for Testing and Materials (ASTM) (Standard No. 2652) the cut-off size between GACs and PACs is the mesh number of 80 (ca. 0.18mm) (Smith et al. 2012). The typical applications of GAC and PAC in the WWTPs were schematically demonstrated in Figure 2.4.



a)

b)

Figure 2.4 Application of activated carbon in the WWTP as a complementary treatment in the form of a) GAC and b) PAC (Abegglen and Siegrist 2012)

In general, GAC demonstrates advantages including facilitate regeneration, reactivation, and handling whereas PAC has a larger available specific surface area resulting in faster adsorption kinetics (Kårelid et al. 2017).

The United States Environmental Protection Agency (USEPA) had identified fixed-bed adsorption by granular activated carbon (GAC) as the best available technology for the treatment of regulated organic pollutants (Bo et al. 2016). Nevertheless, both morphologies of AC exhibited promising results in the EOMs adsorption.

2.7.1. Sorption of EOMs onto the activated carbon

2.7.1.1. Pilot-scale studies in WWTPs

Several studies employed activated carbon as a pilot-scale advanced treatment inside conventional WWTPs. In a very recent study (Guillossou et al. 2019), a complementary treatment consisting of AC's fluidized bed (CarboPlus®, Saur) was employed to treat part of a WWTP effluent (830 m^3 day^{-1}). A total of 48 EOMs were investigated. A dose of 10 g of fresh micro-grain AC per m^3 of water is applied. The authors concluded ACs treatment improved the removal of the EOMs, moderately eliminated in the WWTP, to an overall removal higher than 80%. ACs removed more than half of the EOMs that were not eliminated in the WWTP. Furthermore higher dosages of AC could enhance the overall removal efficiency.

Boehler et al. (2012) examined dosages of PAC addition to the different stages of a conventional WWTP including; an addition to secondary effluent with adsorption and sedimentation in a sequencing batch reactor (SBR) followed by a pilot textile filter (without/with PAC recycling to biology tank-single/double stage) as well as PAC addition directly to the activated sludge system at the pilot scale. It was concluded for reaching EOMs elimination efficiencies of more than 80% relative to the primary effluent adequate treatment of the secondary effluent (dissolved organic carbon 5–10 g DOC m^{-3}) is needed for 10–20 g PAC m^{-3} while a PAC dosage of 30–40 g m^{-3} influent directly to the biology tank reaches targeted EOM elimination as well.

In the study by Kårelid et al. (2017) complementary treatment with GAC and PAC was investigated. This method was compared in parallel operation at three different secondary WWTPs with the goal to achieve a 95% PhAC relative to the secondary effluent. The GAC system is composed of two sequential columns using a down-flow operation. The PAC system is composed of an initial mixing tank, three sequential contact tanks, a sedimentation tank, and a sand filter. Sorption by activated carbon in both forms was shown to be an efficient method for removal of 22 PhACs in the effluents of municipal wastewater treatment plants and the goal of 95% removal was reached for almost all tested ACs by the design of a relevant purification system.

Activated carbon has been also combined with other advance treatments like ozone. For example, Knopp et al. (2016) investigated the elimination of 33 EOMs from a secondary WWTP effluent with a combination of downstream advance techniques including, O_3 followed by GAC filter and expanded clay biofilter. The results revealed GAC system exhibited remarkable performance in which not only eliminated the remained EOMs from ozonation but also it adsorbed many of the oxidation's byproducts. Whereas biofiltration with expanded clay was ineffective to remove EOMs,

2.7.1.2. Batch adsorption experiments

To investigate the parallel removal of multi-class EOMs by activated carbon, the number of studies assessed the batch sorption experiments within either fortified water samples and/or real wastewater effluent samples.

In an exhaustive study conducted by Alves et al. (2018) sorption of 23 EOMs from spiked water (intial concentration of 20 μg L^{-1}) as well as real wastewater effluent onto the six different commercial activated carbons were investigated. After 48 hours of contact time the best-performing adsorbents achieved 78.6%- 88.5% global removal at the dosage of 20 mg L^{-1} in the spiked water whereas almost all ACs attained global removal efficiency of 88% at the dosage higher than 200 mg L^{-1}. At a similar dosage of 20 mg L^{-1} of adsorbent in the real wastewater effluent sample lower removal of EOMs was attained which was attributed to the presence of background organic matter.

Similarly, Mailler et al. (2016) pointed the positive effect of dosage of adsorbent in the batch sorption experiments. By the addition of 10 mg L^{-1} of PAC to the WWTP effluent, the average removal of the EOMs (including 17 pharmaceuticals and 2 pesticides) is 52% for the best performance PAC during 45 minutes contact time which was significantly increased (more than 80%) by doubling the dosages of the adsorbent.

De Ridder et al. (2011) reported sorption of 21 EOMs (2 μg L^{-1}) onto the GAC from distilled water. Different dosages of GAC (6.7 mg L^{-1}-22.2 mg L^{-1}) were contacted with the spiked solutions for eight weeks. Most solutes were removed at more than 85% at even the lowest GAC dose.

According to Stoquart et al. (2016) EOMs at the environmentally relevant concentrations (from 130 ng L^{-1} to 33 μg L^{-1}) were rapidly adsorbed from spiked water onto the PAC at the dosage of 1 g L^{-1}. The results indicated removal superior to 95% were reached within 5 min of contact time for all micropollutants investigated.

In the study by Bo et al. (2016), GAC were employed to remove 4 PhACs from spiked ultrapure water and a real wastewater effluent. In ultrapure water matrix, at contaminant's initial concentration of 500 μg L^{-1}, carbon dose of 133 mg L $^{-1}$ and 24 hour contact time the average adsorption efficiency of carbon was 74.1%, Lower removal efficiency (40.1%) was observed with carbon dosage of 250 mg L^{-1} in the wastewater effluent due to the presence of suspended solids and soluble organic compounds.

2.7.2. Mechanism of adsorption of EOMs onto activated carbon

Adsorption process is rather a complex phenomenon. In adsorption from dilute solution, this phenomenon is mostly governed by electrostatic interaction and non-electrostatic interaction (Calisto et al. 2015). The former could be either attractive or repulsive interaction appearing when the adsorptive molecule is disassociated or protonated in aqueous solution under experimental condition. The latter is always attractive and can include van der Waals forces, hydrophobic interactions, and hydrogen bonding (Calisto et al. 2015). Carbon and solute's characteristics can dictate the influence of these interactions.

Considering the adsorbent the following factors can affect the adsorption process (Moreno-Castilla 2004):

- Surface area and pore texture
- Surface chemistry

- Mineral matter content

The existence of high porosity in the ACs makes them excellent adsorbents. ACs contain carbon atoms grouping themselves into stacks of flat, irregular aromatic sheets in which the irregularities give rise to pores (Bansal and Goyal 2005). Pores' walls in ACs comprise two types of surface; internal surface or micropore surface and external surface. The micropores, which based on the International Union of Pure and Applied Chemistry (IUPAC) standard have diameters less than 2 nm, constitute 95% of the total surface area as well as micropore volume of AC (Bansal and Goyal 2005). The external surface constitutes the walls of the mesopores (diameter between 2 nm- 50 nm) and macropores (diameter >50 nm) as well as the edges of outward-facing aromatic sheets. Different analyses can be conducted to investigate the textural properties of AC such as gas adsorption analysis at 77 K, as well as Hg porosimetry. From gas adsorption data the specific surface area and pore volume can be determined from Brunauer-Emmett-Teller (BET) isotherm. The micropore volume also could be measured by Dubinin equations (Singh et al. 2017a).

It is favorable that ACs have a well-developed microporosity enhancing its surface area but also some meso and -macroporosity which functions as corridors to allow easy access to the micropores (Cabrita et al. 2010). It is noteworthy to say the efficiency of EOMs sorption to the ACs is well-correlated to the surface textural of the ACs by a few authors (Mailler et al. 2016; Rakić et al. 2015). Figure 2.5 demonstrates physical adsorption on the heterogeneous pore structure of AC.

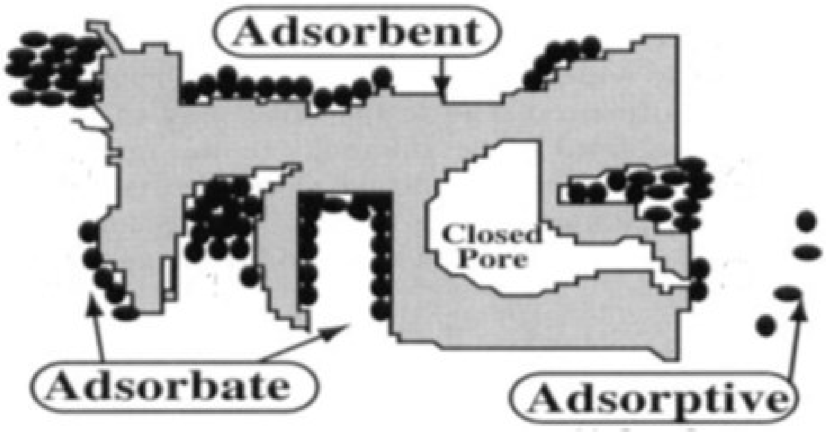


Figure 2.5 Physical sorption of contaminants to the AC surface (Marsh and Rodríguez-Reinoso 2000)

It is well-known the adsorptive capability of an AC is strongly influenced by the chemical composition of the carbon surface. The random ordering of the AC's aromatic sheets causes a variation in the arrangement of electron clouds in carbon which could influence its adsorptive properties (Bansal and Goyal 2005). Heteroatoms including oxygen, nitrogen, and hydrogen might be present at the edges and corners of aromatic sheets of the AC (Bansal and Goyal 2005). These atoms can determine the charge of the surface, hydrophobicity, and the electronic density of the carbon layers (Moreno-Castilla 2004). Spectroscopic methods such as infrared spectroscopy and X-ray photoelectron spectroscopy have been employed in several studies for identification and estimation of surface functional groups of carbon.

As an AC is immersed in an aqueous solution, it develops surface charges due to the dissociation of surface functional groups. The presence of carbon's surface charge causes electrostatic attraction/repulsion with polar EOMs. Carbon-oxygen surface groups are by far the most important surface groups (Bansal and Goyal 2005). They could make the adsorbents more hydrophilic which can influence the hydrophobic interaction with organic contaminants (Moreno-Castilla 2004). Finally, the potential of hydrogen bonding between the carbon-oxygen functional group and hydrogen bond acceptor of solute is the other aspect that heteroatoms can influence the EOMs adsorption. The rule of hydrogen bonding in the sorption of EOM by ACs has been proven by the researchers (Álvarez-Torrellas et al. 2016b; Calisto et al. 2015).

Mineral contents of the AC can affect the adsorption process. The nature and characteristic of the activated carbon precursor is the main factor determining its inorganic content. The mineral content could either exhibit deleterious effects such as pore blocking or positive effect like complexing as well as ion exchanging with the solutes (Fan et al. 2016; Nielsen and Bandosz 2016).

On the other hand, the characteristics of the EOMs' molecules could also play a significant role in the adsorption process. Molecular size, hydrophobicity (log K_{ow}), pK_a and the aromatic structure are the main characteristics. It is evident that the large organic molecule could not enter the micropores that could hinder the adsorption of the contaminants. Baccar et al. (2012) linked the adsorption of four pharmaceutical active compounds to the log K_{ow} and pK_a of target adsorbates. The benzene ring in some of the EOMs structure can play as a π-electron acceptor and the aromatic moieties and electron-rich OH group of carbon are strongly electron donor resulting in π-π electron donor-acceptor (EDA) interaction (Spessato et al. 2019; Chen et al. 2017). The mechanism of adsorption between a positive polar organic molecule and carbon material was schematically illustrated in Figure 2.6.

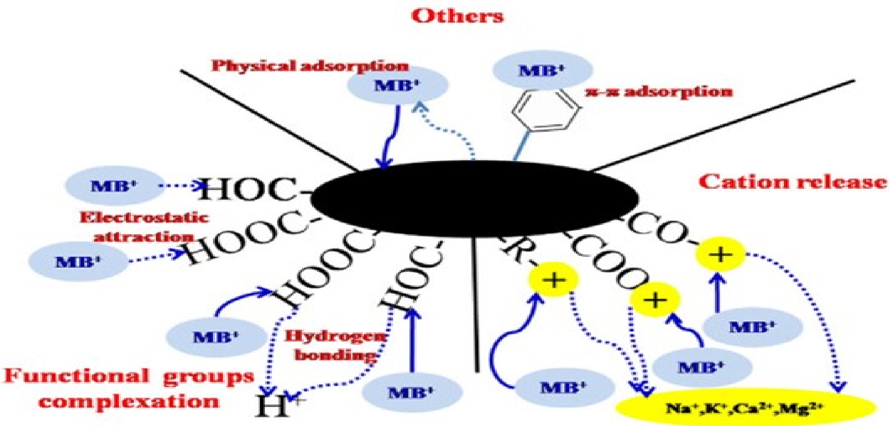


Figure 2.6 Involved mechanism in the sorption of a polar organic contaminant (MB) onto the activated carbon surface (Fan et al. 2016)

It is worthy to say when the number of solutes is increased, i.e. multicomponent solutions, there will be competition for active sites of adsorbent among the solutes which could influence the adsorption process. Sotelo et al. (2014) indicated that the adsorption capacity of GAC was reduced by 29.1% for CAF and 32.1% for DCF in cocktail solutions containing these two compounds compared to the single sorption system. Jung et al. (2015) attributed the lower efficiencies of multi-solute adsorption experiments to the lower binding energy, polarity, and π energy of the adsorbent and electrostatic repulsion from the cosolutes that occupied adsorption sites which all occurred due to the presence of adsorption competitors. In real wastewaters, the multiple contaminants and competitive sorption among them are generally present. Background organic matter can hinder the EOMs sorption onto AC by direct adsorption competition and pore blocking (De Ridder et al. 2011).

2.7.3. Adsorption of EOMs with alternative carbon adsorbents

Commercial activated carbons are commonly produced from wood, coal (bituminous and sub-bituminous varieties), lignite, and coconut shells (Wang et al. 2006). For example, approximately

80% of ACs used in the U.S. are produced from coal and coconut shell (Lussier et al. 1994). As a result, the implementation of ACs on large scale industrial applications is restricted due to poor economic feasibility associated with its manufacture (Cabrita et al. 2010).

In order to overcome the economic cornerstone for the use of AC in advanced water treatments based on adsorption processes using non-expensive materials could be a suitable alternative method. In this sense utilization of organic residue or by-products has been gained lots of consideration. The conversion of these residues to AC could be a “win-win” approach since not only it could be a sustainable technique for reducing waste and improving environmental health also the resulting product could be employed to protect the environment (Silva. et al. 2018b). So far pyrolysis (carbonization) of residues with chemical activators was employed as the principle valorization techniques (Silva et al. 2018b).

In order to adsorb EOMs different sorts of organic waste including, agricultural residue and industrial waste has been converted to the activated carbon. Most of the studies concentrated on the sorption of one particular micropollutant rather than parallel sorption of multi-class of EOMs.

The adsorption of IBU from aqueous solution onto the two ACs derived from peach stone and rice husk was investigated by Álvarez-Torrellas et al. (2016b). The adsorbent derived from peach stone acquired surface area of 1521 m^2 g^{-1} which was favourably compared with the commercial GAC in terms 1102 m^2 g^{-1} for GAC, showing its suitability as an alternative adsorbent.

Lin et al. (2017)employed agricultural waste to produce AC. The adsorption capacity of prepared carbon adsorbent was comparable to a commercial GAC. In comparison to the commercial carbon the carbonaceous product achieved 20% higher removal for SMX, but 10% lower for IBU indicating it could be a promising adsorbent.

Chen et al. (2017) investigated the sorption of CBZ onto the AC prepared from waste pomelo peel in the series of batch experiments. Prepared ACs possessed surface area of 904 m^2 g^{-1} and also adsorption capacity of CBZ onto waste carbon was reported significantly higher than the other reported organic and inorganic adsorbents.

Mestre et al. (2014) produced AC from a cork industry by-product for sorption of six PhACs. The surface area up to 950 m^2 g^{-1} was attained. Furthermore, high removal efficiencies between

80%- 100% were reported for the smaller molecules of PhACs due to a well-developed micropore structure of the carbon material.

Among the organic residues, wasted sludge derived from biological water treatment works attracted much attention. This sort of sludge is a carbonaceous material. In addition, it is being produced abundantly worldwide. As a result, it could be potentially presented as a cost effective alternative for AC production. The next section of the present thesis was dedicated to describing the common methods implemented for the production of sludge derived activated carbon.

2.8. Production of sludge-based carbon adsorbents

2.8.1. Sludge generation

Sludge is a residual suspension after wastewater treatment work procedure. Overall, the following sludge materials are considered: primary sludge collected from the primary clarifier, and secondary sludge, e.g. waste activated sludge (WAS) from the secondary clarifier (Smith. et al. 2009a). Also, sludge can be generated from utilizing tertiary treatment with the aim of phosphorous and nitrogen reduction. Generally, combined sludge (primary and secondary) is treated together. Figure 2.7 demonstrates the sludge generation in a wastewater treatment plant.

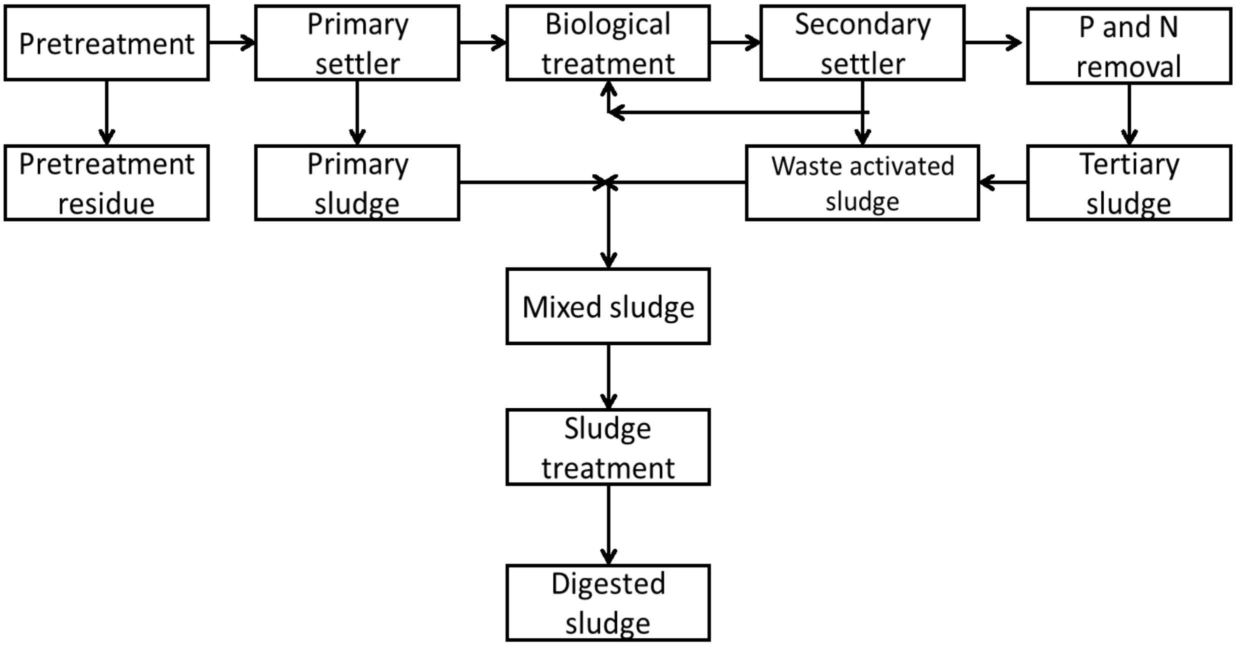


Figure 2.7 Sludge generation in a wastewater treatment plant (Raheem et al. 2018)

2.8.1.2. Post-treatment of secondary sludge

The waste activated sludge (WAS) retains a large amount of water (>0.95% by weight) resulting in extremely large volumes of residual solids produced (Pérez-Elvira et al. 2006). The composition of the sludge itself is affected by the pollution loads and the type of applied treatment method in the WWTP. It is an intricate mixture of numerous materials; organic matter, inorganics like heavy metals, and pathogens, as well as other contaminants. Therefore before disposal, it should be subjected to a series of treatments which includes but is not limited to thickening, dewatering, drying, and alkaline or biological stabilization (Metcalf et al. 1972).

Due to its biological nature, the secondary sludge is not easy to dewater. Therefore it is mixed with the primary sludge to increase its dewatering potential (Figure 2.7). Filter pressing and centrifugations are the most utilized technology to reduce the volume of the water at the first stage. Despite the dewatering process, the sludge still contains a large amount of water, which normally exceeds 70 wt% (Zhang et al. 2011). A drying process can be used to remove this part of water, which consumes a large amount of energy and raises the cost of disposal considerably.

The purpose of sludge stabilizing steps is to: reduce the pathogens, eliminate the offensive odors and inhibit, improve aesthetics and transportability (Yoshida et al. 2013). These goals are achieved by the biological reduction of organic content and the addition of chemicals to make the sludge unsuitable place for bacteria growth (Metcalf et al. 1972).

In fact, after drying sludge contains around 5–10 wt.% of water, 15–30 wt.% of carbohydrates, 2–17 wt.% of fats or lipids, 10–21 wt.% of proteins and 30–50 wt.% of inorganic matter (Wang et al. 2016b). Due to the organic fraction of activated sludge anaerobic digestion is a standard method in sludge treatment for reducing and stabilizing the wastewater solids. Anaerobic digestion can transform the organic content of the sludge to the biogas comprising of 60-70% methane, 30-40% carbon dioxide and traces of other gases (hydrogen, hydrogen sulfide, and nitrogen) (Pérez-Elvira et al. 2006). Apart from the biogas, a digestate containing organics and nutrition is generated in anaerobic fermentation as a final product. This digestate is the treated secondary (or combined) sludge, commonly known as biosolids, that is ready to be disposed off.

2.8.1.3. Traditional disposal methodology of treated secondary sludge

Upon the treatment, secondary sludge (i.e. biosolids) can be traditionally discarded using three main routes; reuse (farmland application), incineration, and landfilling (Paz-Ferreiro et al. 2018).

Farmland application

For several years treated sludge has been utilized in the agricultural application. Besides its organic matter the presence of nutritent mainly nitrogen, phosphorus, and potassium, render it very similar to the composition of farmland manure (Hadi et al. 2015). However, the utilization of sludge as a fertilizer is currently under the imposition of legislation to prevent health risks to humans and livestock. Potentially toxic components, heavy metals, pathogens, and persistent organic pollutants such as polychlorinated biphenyls (PCBs) and polychlorinated dibenzodioxins and furans are of primary concern in limiting its potential use as a fertilizer (Smith 2009b). These chemicals in sludge composition may cause secondary pollution problems in the environment (Samolada and Zabaniotou 2014).

Landfilling

The availability of the land is an important issue that needs to be taken into account for landfilling the biosolids. The lack of available land space in combination with increasingly stringent regulations governing the design and operation of new landfill have resulted in the surging cost and operation of the landfill (Samolada and Zabaniotou 2014). In addition, the biodegradable organic content of the biosolids contributes to the emission of gas that is rich in methane (CH_4) which has a greater greenhouse effect than CO_2 (Paz-Ferreiro et al. 2018). The Government of Québec increased the biosolids landfill disposal fees in the form of a green tax, fees that continue to increase and rose from \$10.95 in 2010 to \$19.50 per ton of dry solids in 2012 (CCME 2010). This increase leads to a huge financial burden on municipalities. Thereby, landfilling is also facing an increased public opposition over these concerns.

Incineration

Incineration is the controlled combustion of waste. Incineration is an exothermic reaction of biosolids resulting in the flue gas comprising of CO_2 and H_2O, ash and a certain amount of heat (Raheem et al. 2018). This technique can be done with or without energy recovery.

In fact, incineration is the technology to sludge minimization rather than for a complete disposing since 30 wt% of dry solids remain as ash (Samolada and Zabaniotou 2014). The residual ash contains concentrated heavy metals so it is a potential hazardous waste. Therefore, additional efforts are required to dispose of the resulted combustion waste. In addition, incineration can exhaust greenhouse gases and other toxic fumes such as dioxins and furans as well. Despite incineration is a well-established commercial technology in developed countries, sludge incineration has been laden by poor public perception and strict legislation. As a consequence, other novel methods of management are preferred.

2.8.2. Thermal conversion of sludge

The decline of the traditional disposal routes for sludge has created a high demand for emerging alternatives (Devi and Saroha 2017). Thermal conversion of sludge into value-added materials in the solid, liquid and gaseous forms appears as a viable option for waste management. Figure 2.8 demonstrates different forms of thermal conversion of residual organic waste into useful products.

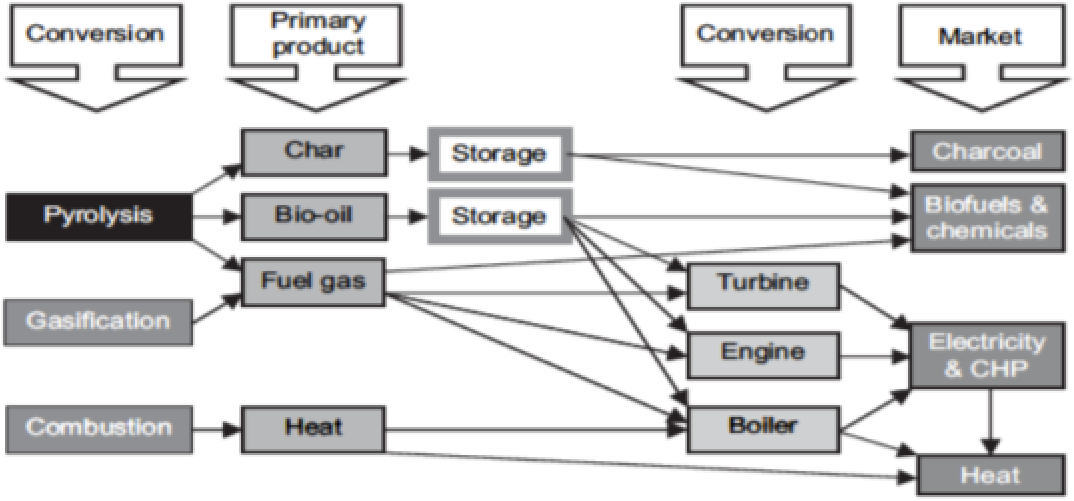


Figure 2.8 Products from thermal biomass conversion (Bridgwater 2012)

Among the available thermal methods including gasification, combustion, and pyrolysis, the former showed promising results. A comparative assessment of the three mentioned energy recovery methods was done based on SWOT analysis by Samolada and Zabaniotou (2014). In this type of analysis, technologies and methods were compared on the basis of economic, environmental and social metrics. Pyrolysis of sludge was identified as the optimal thermochemical treatment option compared to incineration and gasification. One of the main reasons supporting this conclusion is that pyrolysis is a zero waste method and also it has lower and acceptable gas emission.

2.8.2.1. Pyrolysis

Pyrolysis or carbonization is the thermochemical decomposition of materials occurring in the inert environment (absence of oxygen) (Fang et al. 2016). Pyrolysis is endothermal, i.e. needs energy to proceed. This energy is in the order of 100 kJ kg^{-1} (Raheem et al. 2018).

Over the years, the furnace has been used as a common heat source in pyrolysis. Inside the furnace, heat is transferred through conduction and convection to the outer surface of the sample. It slowly diffuses inwards as a result of the thermal gradient between the surface and the core material's particle. Figure 2.9 demonstrates a schematic diagram of the different parts of the regular furnace utilized for pyrolysis.

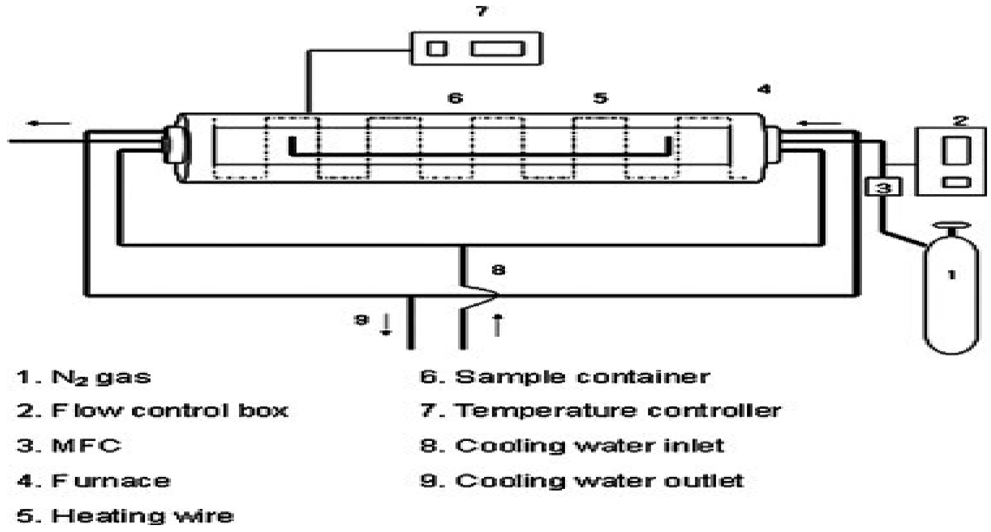


Figure 2.9 Schematic diagram of different parts of regular furnace (Hwang et al. 2008)

Another method of heating employs microwave irradiation. Although it shows benefits like less energy and time consumption, there are several critical issues concerning temperature control and thermal runaway, especially in the scaling-up of the microwave heating process (Hui and Zaini 2015).

The reactions involved in the pyrolysis of materials are quite complex. Their mechanisms are not fully understood. The products are results of multiple, parallel, consecutive, competitive and multiphase reactions. Sinha et al. (2000) enumerate the general changes that occur during pyrolysis:

1- Heat transfer from a heat source, to increase the temperature inside waste particles;

2- The initiation of primary pyrolysis reactions at this higher temperatures releases volatiles and forms char;

3- The flow of hot volatiles toward cooler solids results in heat transfer between hot volatiles and cooler unpyrolysed particles;

4- Condensation of some of the volatiles in cooler parts of the biomass, followed by secondary reactions, can produce tar;

5- Autocatalytic secondary pyrolysis reactions proceed while primary reactions (item 2, above) simultaneously occur in competition; and

6- Further thermal decomposition, reforming, water gas shift reactions, recombination of radicals, and dehydrations can also occur, which are a function of the process's residence time/temperature profile.

2.8.2.2 Main products of pyrolysis

Pyrolysis products can be classified into three groups (Raheem et al. 2018);

- Gaseous fraction containing the non-condensable low molecular gases such as CO_2, CO, H_2;
- Liquid or oil fraction containing the condensable volatile compounds;
- Char (the obtained solid residue).

Quality and quantity of pyrolysis products are influenced by the process conditions including temperature, reactor residence time and pressure as well as the original waste characteristics (Samolada and Zabaniotou 2014). It is important to distinguish pyrolysis from gasification. Gasification mainly transforms organic materials to combustible gas or syngas, using between 20 and 40% of the oxygen required for total combustion, whereas pyrolysis is a thermochemical reaction carried out at elevated temperatures (300–900 °C) and theoretically in an inert atmosphere (Fonts et al. 2012).

The maximum amount of solid carbon material is produced in the slow pyrolysis process where the feedstock is fully pyrolyzed (heating rate <100°C min^{-1}) at a moderate temperature with the holding time from 30 min to a few hours (Rawat et al. 2019). Contrarily fast pyrolysis yields more liquid byproduct. Significant higher heating rate (> 1000 °C min^{-1}) and shorter residence time and rapid quenching of the condensable vapour are the main fast pyrolysis futures (Rawat et al. 2019). Once the temperature rises to upper limits the production of non-condensable gasses is promoted.

2.8.3. Multipurpose solid residue from secondary sludge pyrolysis

The carbonaceous solid left from the pyrolysis of the sludge is porous nature materials which can be applied for different puroposes. It is mainly used as a soil amendment, organic and inorganic pollutants adsorbent and catalysts.

2.8.3.1 Sludge-based soil amendment

The resulting carbonaceous solid was first used for soil amendment, due to its advantages of carbon sequestration, soil fertility improvement, pollution remediation, and waste recycling (Bedia et al. 2018). For example, sludge-based carbon material could reduce nitrate emission from paddy soil by 96% or 98% depending on the dose applied and also resulted in the soil shifting from being a source to a sink of methane (Paz-Ferreiro et al. 2018). Hossain et al. (2010) prepared a sludge-based soil amendment in a fixed bed reactor at 550°C. They found that the treatment with biochar resulted in a 64% increase of cherry tomato yield when compared to the control. Furthermore, Waqas et al. (2015) reported in a soil amended by the sludge-based agent the concentrations of polyaromatic hydrocarbons in lettuce and cucumber were reduced by 56% to 67% and 44 to 57%, respectively, relative to the control soil without amendment.

2.8.4. Sludge-based carbon adsorbent

Secondary sludge is potentially suitable for the production of carbonaceous adsorbent because of its carbonaceous structure, low cost, and ready availability (Ocampo-Pérez et al. 2012). Production of sludge-based adsorbent (SBA) for wastewater remediation proposes has a twofold ecological prominence, it is not merely to ecofriendly solve the problem of secondary pollution associated with the sludge itself, but also to allow its reuse in water treatment applications (Xu et al. 2015).

One of the pioneering studies in the employment of a carbonized sludge for pollutant abatement purposes was carried out by Beeckmans and Ng in 1971. In their study, SBA exhibited intermediate adsorption capacity of violet dye and the authors proposed the potential application of SBA in the tertiary treatment of wastewater treatment. Since then the pyrolyzed sludge was used for removing numerous types of organic and inorganic contaminants such as heavy metals (Rozada et al. 2008), phenolic compounds (Martin et al. 2004), nutritions (Hwang et al. 2008) and miscellaneous compounds such as dyes (Li et al. 2011).

Several factors influence the pollutant removal capability of carbonized sludge, namely their porous structure and surface chemistry (Hadi et al. 2015). The factors may include but not limited to carbonization temperature, heating rate, dwell time and type of precursor. Multiple studies have shown the most important parameter affecting the textural properties of waste-based adsorbents is the carbonization temperature (Bedia et al. 2018; Sun et al. 2012).

2.8.4.1. Effect of temperature on textural properties of SBA

Through mass loss, during thermal decomposition and evolution of volatile matter product, the porosity of the precursor is generated (Xu et al. 2015). In general, with increasing the temperature the surface area and porosity of the carbon adsorbent increase. At higher temperatures, SBA deformation and degree of aromaticity are intensified leading to the formation of new porosity (Agrafioti et al. 2013). The reduction of the H/C, O/C, and N/C ratios of the precursor with increasing the temperature confirms the growth of aromaticity in the structure of the final carbon product. Furthermore, the temperature could change the strength and number of the carbon-oxygen functional group on the surface of the SBA affecting its adsorptive properties.

The widely used measure for showing changes in the surface development of the carbon adsorbents is the Brunauer, Emmett and Teller (BET) surface area (Smith. et al. 2009a). In a study by Rio et al. (2005b) specific surface area of SBA increases from 3 m^2 g^{-1} to 100 m^2 g^{-1} with increasing pyrolysis temperature ranging from 400 °C to 1000 °C. The results of chemical characterization of the carbonized residues showed that with increasing temperature, the amount of acid surface groups decreases, while the amount of basic surface groups seems to increase. It is well-known at the inert atmosphere acidic surface functional group such as carboxyl, phenols, lactones are decomposed in the temperature range of 350 °C to 700 °C. CO_2 is the main product in their thermal decomposition (Bansal and Goyal 2005; Moreno-Castilla 2004)

Increasing heating temperature from 300 °C to 500 °C resulted in an increase in SBA surface area from 4 m^2 g^{-1} to 18 m^2 g^{-1} (Agrafioti et al. 2013). Similarly, the study (Bagreev et al. 2001) reported an increase in the surface area of adsorbent, derived from secondary sludge, from 99 m^2 g^{-1} to 122 m^2 g^{-1} with an increase in the heating temperature from 600 °C to 900 °C. In their study raising temperature increased the microporosity. However the SBA was still dominated by mesopores.

Contrarily, many studies indicated increasing the temperature more than a certain limit could also have a detrimental effect on the SBA. Lu et al. (2013) investigated the effect of temperature in three secondary sludge collected from different WWTP. Increasing temperature from 300 °C up to 500 °C resulted in an increase in the SBA, however, at 600 °C samples showed a reduction in the surface area. The surface areas of the SBAs prepared from three types of sludge were ranging between 4 m^2 g^{-1} to 26.5 m^2 g^{-1}.

By varying the temperature between 500 °C to 700 °C the BET surface area was initially increased from 25.2 m^2 g^{-1} to 34.3 m^2 g^{-1} up to 600 °C while it was decreased to 28.7 m^2 g^{-1} for SBA prepared at the 700 °C (Lin et al. 2012). The same trend was observed for the total pore volume of SBA which was increased from 0.03 mL g^{-1} to 0.05 mL g^{-1} up to 600 °C. However it was dropped to 0.4 mL g^{-1} at 700 °C.

The surface area of the SBA prepared at a varying temperature between 500- 900 °C was investigated by Hwang et al. (2008). At the temperature of 700 °C the highest surface area of around 130 m^2 g^{-1} was obtained. Also, Zou et al. (2013) varied the temperature between 500-1000 °C to carbonize a secondary sludge pretreated by nitric acid. The highest surface area of 121.26 m^2 g^{-1} and the pore volume of 0.1 cm^3 g^{-1} were obtained at 600 °C. Both measures were almost became halved at the maximum temperature.

The decrease in the surface area probably due to the destruction of porous structure and development of shrinkage, cracking or blockage of micropores in SBAs (Xu et al. 2015).

The temperature could also significantly influence the final yield of SBA. All the above studies are in agreement with a decrease in the yield of the final SBA with raising the pyrolysis temperature. For example, in a study by Bagreev et al. (2001) the yield of SBA was reduced from 14.3% to 7.6% with a rise in the temperature from 600 °C to 900 °C. This may be attributed to the conversion of organic matters into biogas at high temperatures. Also Agrafioti et al. (2013)

reported with 60 min dwell time the yield of SBA was decreased from 58.1% at 300 °C to 27.0% at 500 °C.

2.8.5. Enhancement of sludge-based textural properties

As can be seen, the sole carbonization of sewage sludge could not result in a carbon adsorbent that acquired the surface area comparable to the commercially available activated carbon (typically S_{BET}>400 m^2 g^{-1}) (Álvarez-Torrellas et al. 2016b). The highest BET surface area of carbonized sludge reported in the literature lies in the range of 200 m^2 g^{-1} (Lillo-Ródenas et al. 2008).

Higher ash percentage (inorganic content) and hence lower carbon content of the sludge relative to the lignocellulosic feedstocks do not favor the development of high surface areas in the SBAs by carbonization (Agrafioti et al. 2013). Therefore there is a need to enhance the textural properties of SBA since many wastewaters industrial applications demand more efficient adsorbents. For achieving this goal two methods have been proposed in the literature;

1- Activation method;
2- Co-processing of sludge with other carbonaceous material.

2.8.6. Activation method

In order to develop the pore network in sludge-based carbon materials, the application of the activation method is often inevitable. There are two methods for manufacturing activated SBA, i.e., physical and chemical activation.

2.8.6.1. Physical activation

Physical activation is the development of porosity by gasification with an oxidizing agent at relatively high temperatures (Azargohar and Dalai 2008). This method usually is conducted in the two-step process. In the primary step, the carbonaceous precursor is carbonized at a relatively low temperature (typically 400-700 °C) in the absence of air (Xu et al. 2015). This step causes the breakage in the cross-linkage between carbon atoms leading to produce some pores in the resulting char. The second step involves the activation of the obtained char under an oxidizing atmosphere at higher temperatures (800-1200 °C) to further development of the SBA's porosity (Hadi et al. 2015).

The most used oxidizing gas is CO_2, steam, air, N_2, and a mixture of them. In a study by (Méndez et al. 2005) SBA was prepared in two-step heat treatment involving carbonization at 400 °C for 1 h inside a vertical electric furnace and subsequent air physical activation at 275 °C for 4 hours. The maximum S_{BET} surface area was reported 105 m^2 g^{-1}. During air activation at 275 °C, oxygen functional groups such as carboxylic acids and anhydrides, lactones, phenols, ethers, quinines were introduced to SBA leading to its acidic surface.

In the work conducted by Bosch et al. (1976), a secondary sludge was carbonized under the nitrogen atmosphere up to 700 °C for 4 hours. Subsequently, the produced carbonized sludge activated with steam or oxygen at 800 °C inside a horizontal tube furnace. Although the results from oxygen activation were unsatisfactory steam could enhance the SBA surface area to 200 m^2 g^{-1}.

The two-step preparation method was employed by Rio et al. (2006). Carbonization time fixed at 1 h at the optimum temperature of 600 °C. Steam was utilized as the activator which applied to the carbonized sludge at the optimum temperature of 760 °C and a dwell time of 30 min. BET surface area of the raw sludge and prepared SBA was reported 2.9 m^2 g^{-1} and 225 m^2 g^{-1}, respectively. The prepared SBA acquired mesoporous structure enabling suitable adsorption performance for organic macromolecules such as dyes rather than phenol having small molecular size.

Jindarom et al. (2007) employed single-step activation with the N_2 and CO_2 gas for preparation of SBA. The maximum surface area of the SBA is achieved with pyrolysis at 750 °C under the CO_2 atmosphere, 60.7 m^2 g^{-1} with mainly mesopores. The infrared spectroscopy analysis of the SBA prepared under both N_2 and CO_2 atmospheres indicated a decrease of acidic surface functional groups containing –OH, –NH and CO functionalities with increasing the pyrolysis temperature, corresponding to a decrease in the acidity of the char. It was reported that CO_2 can enhance the porosity of materials by removing the carbon atoms from the interior of the particle leading to the creation of new pores (Pastor-Villegas and Durán-Valle 2001).

Overall, physical activation proceeds by the progressive burn-off of the carbon fraction. The elimination of a large amount of internal carbon mass is necessary to obtain a well-developed carbon structure. However, the inorganic content of sludge, which is essentially non-porous, is high. Consequently, SBAs that have been produced by physical activation typically exhibit relatively low surface areas (Smith et al. 2009a).

2.8.6.2. Chemical activation

Chemical activation is generally made by mixing carbonaceous materials with chemical activating agents followed by carbonization at 400–900 °C. Contrarily to physical activation, this method consists of one stage (Hadi et al. 2015). Also, chemical activation is carried out at lower activation temperatures and shorter time relative to the physical approach (Hadi et al. 2015). More importantly, the textural properties of the chemically activated SBAs including surface area, pore volume, microporosity were remarkably more satisfactory than the physically activated SBAs. For example, Ros et al. (2006) reported physical activation of the secondary sludge by CO_2 was ineffective for preparation of proper adsorbent (maximum $S_{BET} = 62$ m^2 g^{-1}), whereas, chemical activation could yield the SBA with the BET surface area as high as 1686 m^2 g^{-1}. In spite of that, chemical activation has some disadvantages including the corrosiveness of the chemical agents and the necessary washing process to remove the chemical agents.

The chemical agents used in the chemical process are normally alkali and alkaline earth metal-containing substance and some acids. The most common activators include KOH, K_2CO_3, NaOH, $ZnCl_2$, H_3PO_4, and H_2SO_4 (Xu et al. 2015).

Two methods are often used to introduce activator to the precursor; solid physical mixing and wet impregnation. In the former chemical agent directly mixed with the feedstock at room temperature and in the latter the precursor is stirred for hours inside the concentrated solution of chemical agent, normally at above the room temperatures, followed by the filtration and drying.

In a study by Otero et al. (2009) the sludge immersed within a highly concentrated $ZnCl_2$ (98%) solution (weight ratio of 1:1 with respect to the sludge) for 48 hours. Dried impregnated sludge activated at 650 °C produced a mesoporous SBA with a surface area of 472 m^2 g^{-1}.

Chen et al. (2002) prepared SBA by activating anaerobically digested secondary sludge with 5 M $ZnCl_2$ and thereafter pyrolyzing it at 500 °C for 2 hours under nitrogen atmosphere. The produced SBA was found acidic and mesoporous in character with a BET surface area of 647.4 m^2 g^{-1}.

Various types of activated carbons were developed from secondary sludge using H_2SO_4, H_3PO_4, and $ZnCl_2$ at the temperature of 650 °C for 60 min by Zhang et al. (2005). Sludge was impregnated into the activators' solutions and dried at 105 °C for 24 h. While all the prepared SBAs were dominantly mesoporous and acidic, S_{BET} of the SBA activated by $ZnCl_2$ was reported 555 m^2 g^{-1}, which was greater than 409 $m^2.g^{-1}$ and 289 m^2 g^{-1} for the samples activated by H_2SO_4, H_3PO_4, respectively. Also, the sample activated by $ZnCl_2$ exhibited higher adsorption capacity on mercury.

Similarly, in a study by Wang et al. (2011) H_3PO_4 was less effective than $ZnCl_2$ in preparation of activated SBA inside the microwave reactor. The mesoporous SBA prepared from H_3PO_4 acquired S_{BET} of 290.6 m^2 g^{-1} while in the case of the $ZnCl_2$ surface area mounted to 377.1 m^2 g^{-1}. The impregnation rations were chosen 1:2 and 1:1.5 (weight of activating agent/weight of raw material) for $ZnCl_2$ and H_3PO_4, respectively.

Generally, it is believed that acidic activators, acts as a dehydration agent and tar formation suppressant. Acidic reagents primarily increase porosity by interacting with oxygen functional groups to catalyze the dehydration and dehydrogenation reactions (Wang et al. 2011). The resulting charring and aromatization of the carbon skeleton give rise to the development in the pore structure. Also, it is deduced that the porosity created in the carbon structure is the result of the $ZnCl_2$ left in the particles after removal by intense washing (Ahmadpour and Do 1996).

Other types of activators such as alkali and alkaline earth metal-containing substances were also utilized for the activating sludge under thermal conversion. Stüber et al. (2011) physically mixed a secondary sludge with the K_2CO_3 at the ratio of 1:1 (weigh mass). Activation was conducted in a tubular furnace at 800 °C for 60 min followed by washing with R/O water to remove the activation by-products. Resulting dried SBA acquired surface area of 442 m^2 g^{-1}. Gómez-Pacheco et al. (2012) reported the optimal condition of; temperature equals700 °C, impregnation ration of 1:1 (weight of NaOH/weight of sludge) and dwell time of 3 hours to obtain SBA with the BET surface area of 139 m^2 g^{-1}. Also, Zou et al. (2013) impregnated a carbonized acid-treated secondary sludge with NaOH at the weight ratio of 1:1 (dry mass). The activation temperature was varied between 500-1000 °C. The highest surface area and pore volume of 346.5 m^2 g^{-1} and 0.46 cm^3 g^{-1} were respectively obtained at the temperature of 600 °C.

Effect of chemical activator concentration is crucial in the preparation of the SBA with well-developed textural properties. Rio et al. (2005a) varied the concentration of H_2SO_4 solution from 1 M to 3 M which is equal to the mass ratio of 0.5–1.5 (w_{H2SO4} / w_{sludge}). They concluded when experiments are carried out with a high impregnation ratio, the increase in temperature allows S_{BET} to be increased. The optimal S_{BET} was obtained 352 m^2 g^{-1} at the carbonization temperature of 700 °C for 145 min. Contrarily, Mahapatra et al. (2012) investigated three different concentrations of $ZnCl_2$ solution between 1-3 N. Activator solution at 2 N concentration exhibited the highest adsorption capacity of Iodine. Similarly, Lu and Lau (1996) found that at both 550 °C and 850 °C temperatures, the microporosity was higher at a $ZnCl_2$ concentration of 3 M than at 5 M. High amount of $ZnCl_2$ deteriorated the micropore structure of SBA due to excessive carbonization. In a study by Ren et al. (2012) secondary sludge was impregnated with different concentrations of $ZnCl_2$ solutions from 5% to 30% (w/w). The optimum condition was reported at the weight ratio of 20%. Also, Hwang et al. (2008) studied the effect of concentration of chemical activators including KOH and NaOH on the SBAs' surface area. It was concluded increasing the concentration of both activators beyond certain values could demolish the pore walls. The negative impact of a very concentrated activator in carbon adsorbent was also reported for other organic precursors such as sugar cane bagasse and sunflower seed hull activated with $ZnCl_2$ (Liou 2010). It can be inferred that the use of a very concentrated activating agent does not necessarily have a positive effect on the development of higher surface areas. Plus, higher concentrations of the activator will not have economic justification due to its high cost.

2.8.7. Activation with potassium hydroxide

Activation with KOH resulted in SBAs with superior textural properties in comparison to the other chemical agents. Ros et al. (2006) prepared SBA in two-step heating treatment with different activating agents including KOH, NaOH, H_3PO_4, and CO_2. Although the two latter activators were reported non-effective the alkali salts produced SBAs with well-developed surface areas. In the case of alkali salts, the temperature of carbonization and activation was selected 700 °C. Furthermore, they investigated different methods of mixing including physical (powder and ground KOH) as well as wet impregnation with alkali salts. Physical mixing with powder KOH at the mass ratio of 3:1 (w_{KOH}/w_{sludg}) was the most effective method which prepared SBA with the surface area and micropore volume of 1686 m^2 g^{-1} and 0.64 cm^3 g^{-1}, respectively. Lower mass ratios of activator/sludge including 2:1 and 1:1 resulted in SBAs with lower surface areas of 853 $m^2.g^{-1}$ and 1061 $m^2.g^{-1}$. In another study conducted with the same researchers (Lillo-Ródenas et al. 2008), they further confirmed the effectiveness of physical activation with ground KOH for the production of SBA derived from different types of sludge. Biological sludge from three different wastewater treatment facilities were examined. At the mixing ratio of 1:1 (w/w), SBAs with the surface area of 1058 m^2 g^{-1}, 1301 m^2 g^{-1}, and 1882 m^2 g^{-1} were prepared through two-step heating treatment at 700 °C. Physical mixing of the KOH with other carbon sources including rice husk (Fu et al. 2019), extracted sawdust waste (Wang et al. 2010), anthracite (Lillo-Ródenas et al. 2001), and coal (Ahmadpour and Do 1996) showed a strong effect in pore development of resulting activated carbonaceous materials.

Although the pre-pyrolyzed precursor is more favorable in the manufacture of activated carbon as compared to direct chemical activation, KOH is a strong base that supports single-step activation as well (Hui and Zaini 2015). In a study by Monsalvo et al. (2011) single step KOH activation was employed to produce the SBA. In their work, two mass ratios of 1:1 and 3:1 of ground lentil KOH/sludge and two temperatures of 400 °C and 750 °C were tested. At the maximum temperature and dwell time of 30 min, SBAs with surface areas of 950 m^2 g^{-1} and 1832 m^2 g^{-1} were produced by mixing ratio of 1:1 and 3:1, respectively. This method of mixing and activation was also successful in preparing carbon adsorbent derived from other carbon precursors such as cane (Singh et al. 2017).

Single-step activation by solid KOH is an approach that significantly reduces the time and efforts involved in the whole carbon preparation process. Furthermore, high porosity could be achieved with this technique concluding it could be a suitable method for the production of activated carbon materials at the industrial scale (Lillo-Ródenaset al. 2001).

2.8.7.1. Mechanism of activation with KOH

The mechanism of KOH activation includes several simultaneous/consecutive reactions which optimally occurred above 700 °C. It is postulated KOH dehydration and formation of potassium carbonate are thermodynamically possible at 300 °C and ambient temperature (Di Blasi et al. 2009):

$$2KOH \rightarrow K_2O + H_2O \tag{2-1}$$

$$K_2O + CO_2 \rightarrow K_2CO_3 \tag{2-2}$$

Furthermore, the alkali activator is molten at 360 °C without decomposition. The reaction between activator and carbon occurred via a solid-liquid redox reaction according to Di Blasi et al. (2009);

$$4KOH + C \rightarrow K_2O + K_2CO_3 \tag{2-3}$$

The release of CO and CO_2 could be attributed to the potassium carbonate decomposition which is initiated at 450 °C in the presence of carbon source. At 600 °C the KOH is thoroughly consumed (Singh et al. 2017b). As the temperature exceeds 700 °C K_2CO_3 significantly decompose to into CO_2 and K_2O and the metallic potassium is formed (Di Blasi et al. 2009)

$$K_2O + H_2 \rightarrow 2K + H_2O \tag{2-4}$$

$$K_2O + C \rightarrow 2K + CO \tag{2-5}$$

The formation of activated carbons with high porosity is attributed to the above-mentioned reactions of depolymerisation, dehydration, and the evolution of gases in carbon occurring during the process of activation. Moreover, the as-prepared metallic potassium efficiently intercalating into the carbon lattices of the carbon matrix during the activation, results in the expansion of the carbon lattices and subsequent acid washing is inevitable to produce highly porous carbon materials. Figure 2.10 exhibited activation mechanism by the penetration of metallic K into the carbon lattices.

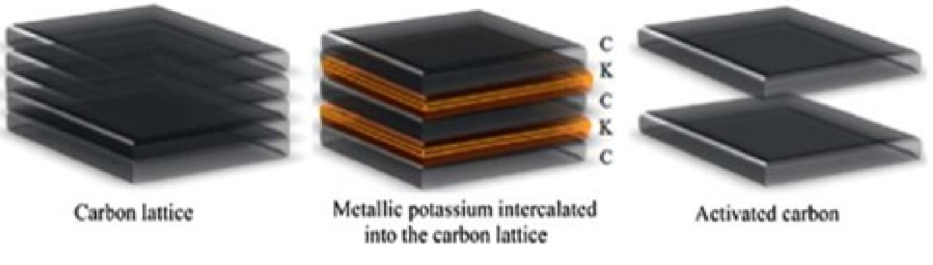


Figure 2.10 Activation mechanism by the penetration of metallic K into the carbon lattices, the expansion of the lattices by the intercalated metallic K, and the removal of the intercalated K from the carbon matrix (Wang et al. 2012)

2.8.7.2. Post-treatment of the KOH activated SBA

It is expected that most of the potassium and its relevant by-products remained inside the carbon matrix and block the pores after pyrolysis. Therefore, it is required to wash out these residues from the carbonaceous product. Ahmadpour and Do (1996) indicated at higher concentration of chemical activators including KOH and $ZnCl_2$ the effect of acid washing could be more pronounced. (Lozano-Castello et al. 2001) reported unwashed carbon product prepared from KOH activation of anthracite doesn't show any nitrogen adsorption, i.e. no development of porosity. Whereas product washed with 5M hydrochloric acid exhibited higher nitrogen gas adsorption than water washed sample. Similarly, Monsalvo et al. (2011) confirmed adsorption capacity of KOH activated SBA was four times lower when the SBA was washed with water in comparison to the SBA washed by 5M HCl.

2.8.8. Co-processing of sludge with other carbonaceous material

According to several studies, the textural properties of the SBA could be ameliorated through the mixing of the sludge with relatively higher carbon content materials. The carbon-rich materials not only add additional porosity but also will provide a reducing environment via providing carbon element in the solid-state reactions (Kante et al. 2008).

Seredych and Bandosz (2007) indicated co-processing of the secondary sludge with industrial oil sludge caused a significant increase in the nitrogen uptake suggesting the synergetic effect during pyrolysis. The heating of the mixture at a high temperature of 950 °C resulted in a 100% increase in the volume of micropores, compared to the adsorbents derived from individual sludge.

Velghe et al. (2012) found that the adsorbent attained from the mixture of sewage sludge and filter cake (mass ratio 85g/15g) exhibited higher BET surface area (60 m^2 g^{-1}) than sewage sludge-based adsorbents (15 m^2 g^{-1}).

Adsorbent derived from a blend of metal sludge and spent car oil mixture acquired 50% more volume of microporosity in comparison to the products prepared from sludge (Kante et al. 2008). The waste oil precursor provides the active carbonaceous phase which is not merely responsible for the development of micropores but also contributes to the formation of new active surface chemistry on the adsorbent.

With the aid of electron microscopic images, Xu et al. (2017) indicated the adsorbent derived from a mixture of sludge and hazelnut shell acquired numerous cavities relative to the insufficient pore structure of the adsorbent prepared from sole sludge.

The results of corn cob addition into the secondary sludge revealed enhancement of textural properties in the KOH activated SBA (Wu et al. 2013). The surface area and microporosity of SBA increased from 287 m^2 g^{-1} to 591 m^2 g^{-1} and 5% to 48%, respectively. Furthermore, corn cob addition led to a decrease in the oxygenated functional group involving –OH, –NH and C=O functionalities on the surface of the carbonaceous adsorbent.

The experiment conducted by Tay et al. (2001) revealed the addition of coconut husk to the secondary sludge could enhance the microporosity of the SBA up to 40%. In their study co-activation of coconut husk and secondary sludge at the mass ratio of 1:2 ($w_{\text{carbon source}}/w_{\text{sludge}}$) with 5M $ZnCl_2$ resulted in the SBA with the maximum BET surface area of 867.61 m^2 g^{-1}.

In order to increase the carbon content, corn straw was added to the secondary sludge precursor. The raw materials were mixed with different concentrations of KOH solution. At the mass ratio of 3:7:6 (sludge/straw/activator) resulting sludge straw-based activated carbon obtained maximum S_{BET} value and pore volume of 689.64 $m^2.g^{-1}$ and 0.73 $cm^3.g^{-1}$, respectively (Zeng et al. 2018).

Li et al. (2016) investigated co-activation of corn stalk as a rich carbon source with secondary sludge. SBA with the BET surface area of 475 m^2 g^{-1} could be obtained by 5M $ZnCl_2$ while BET value increased to the 769 m^2 g^{-1} after 25% (weight basis) corn stalk addition.

Contrarily, some of the researchers reported the antagonist effect of biomass addition to the porosity of the sludge-based adsorbent. Bamboo sawdust addition to the sludge decreased the surface area of resulting carbon material prepared at the temperature of 400 °C and 500 °C (Jin et al. 2017). The formation of tars derived from sawdust decomposition in those temperatures caused the blockage of pores. Huang et al. (2017) studied the co-pyrolysis of the secondary sludge with two different biomass including softwood sawdust as well as rice straw. The authors found the biomass increased the contents of organic matters of the SBA while it is reduced the surface area and pore volume of SBA. They recommended the application of appropriate activators in order to ameliorate the textural characteristics of SBA.

In conclusion, co-pyrolysis of the sewage sludge with the carbonaceous biomass is a novel approach which is still under development. Particularly, efforts should be made to assess the co-pyrolysis of sludge and various biomasses for the production of high-quality carbonaceous adsorbents. In spite of that, co-pyrolysis is a more advantageous approach in waste management since not only the sludge's disposal problem could be solved, but also secondary organic waste containing higher carbon content could be recycled to a valorized material.

2.8.9. Adsorption of EOMs with SBA

The number of studies that investigated secondary sludge-based adsorbent for the EOM removal is scarce. In one of the primary works, Yao et al. (2013) produced SBA from various wastewater sludge samples. The prepared mesoporous SBAs from carbonization of precursor exhibited efficient adsorptive removal of an antibiotic (more than 80%).

Nielsen et al. (2015) prepared carbonaceous adsorbents from secondary sludge, fish waste and their homogenized mixtures (90:10, 75:25, or 50:50) at two temperatures (650 and 950 °C). The adsorbents were successful in removing the CBZ from the aqueous solution. An addition of a small amount of the fish waste to sludge increased the content of the carbon phase which provided hydrophobicity in micropores and contributed to the favorable dispersion of the inorganic phase. In their later work (Nielsen and Bandosz 2016) similar adsorbents were tested to remove the SMX from aqueous solution. Although the prepared materials exhibited low surface areas (21 m^2 g^{-1} to 101 m^2 g^{-1}) and pore volume, the SMX was adsorbed by the waste derived materials. The authors stated the adsorption of SMX mostly was governed by surface chemistry including acid-base reactions.

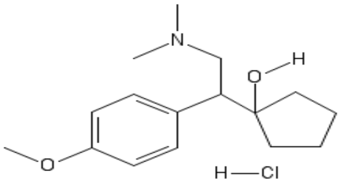
3. Materials and Methods

3.1. Chemical and materials

The following materials were applied into the tests: chromafil syringe filters (glass fiber/polyester, 1/0.45 µm, 25 mm) were purchased from Sorbtech Company, U.S. Latex-free disposable syringes (60 mL and 10 mL), amber glass bottles, 125 mL amber jars, HDPE bottles, and proclaim dishes were obtained from Fisher Scientific.

A number of chemicals were used in the present investigation. The potassium hydroxide (KOH powder, technical grade) was purchased from Sigma Aldrich. Hydrochloric acid (HCl (37%)), sodium hydroxide (NaOH) and potassium nitrate (KNO_3) were purchased from Fisher Scientific. The Venlafaxine hydrochloride standard (CAS# 99300-78-4) was obtained from TCI America. Table 3-1 shows the chemical formula, structure, molecular weight, and water solubility of this compound.

Table 3.1 Physicochemical properties of the venlafaxine chloride

Chemical formula	Structure	MW (g mol^{-1})	S_w (mg L^{-1})
$C_{17}H_{27}NO_2.HCl$		313.87	572000

A type of commercially available granular activated carbon, derived from coconut shells, was used as reference in this study to compare with the produced sludge-based adsorbents. Previously to its use, the activated carbon was washed with deionized water to remove fines and dried at 105 °C overnight. Hereafter, commercial activated carbon was named CGAC.

3.2. Sampling procedure

A WWTP with an activated sludge system was selected as the case study in this research. The WWTP was located in the City of Saint Catherine, Quebec, Canada. Treated effluent and stabilized biological sludge, used in this research, were all collected from this particular WWTP.

More details on the study area as well as the sampling procedure are described in the subsequent sub-chapters.

3.2.1. Description of study area

3.2.1.1. WWTP's general specifications

The selected WWTP serves five municipalities and also various nearby service industries (circa 240,000 equivalent inhabitants). Hence, the COD load to the treatment plant is approximately 50% of municipal origin and 50% of industrial origin.

The WWTP employs conventional activated sludge treatment consisting of the following compartments: automatic screening (two bar racks), grit and grease removal (2 units), four premixing ponds, four aeration basins, and clarifiers (3 units). The average hydraulic retention time (HRT) of the plant is 24 hours. The WWTP discharges its effluent at the mean flow of 60,000 m^3 day^{-1} to the Saint Lawrence River (SLR). At the time of sampling, the plant was working in its normal condition which was assessed by analyzing general wastewater effluent quality parameters.

Furthermore, in this particular treatment plant, the secondary sludge is thickened by gravity where a type of anionic polymer, as well as ferric sulfate, was also added as coagulants. Afterward, it is stabilized anaerobically and dewatered by centrifuge. Finally, the treated secondary sludge was loaded on the truck to be either disposed of in the landfill or incinerated. The production of biosolids (treated sludge) in this plant is approximately 10 tonnes per day.

3.2.2.2. Characteristics of the WWTP's recipient surface water

The main flow of the Saint Lawrence River, with the mean annual flow rate of 9780 m^3 s^{-1}, reaches the upstream of WWTP's outfall through the Lachine rapids located just after the Saint Louis Lake. The length and width of the rapids is 6.8 km and 1 km, respectively. The water velocity reaches up to 3 m s^{-1} in this zone. Two drinking water plant intakes are located in the upstream of the rapids.

In the downstream of the WWTP's outfall, the river directs to the massive water basin with a surface area of approximately 53 km^2 and a depth of less than 4 m. Water velocity is dramatically reduced to 0.3 m s^{-1}. Based on the mean annual flow of the SLR the water residence time in the basin was determined as approximately 6 h. The basin exhibits semi-lacustrine ecology. Two drinking water plant intakes and a recreational activity center are also located in this area. There were no other point sources of pollution and also entering tributaries between the sampling sites and WWTP effluent.

3.2.2. Collection and preservation of WWTP's effluent and surface water samples

In order to investigate the EOMs' concentrations in a wastewater treatment plant effluent and the associated receiving surface water, intensive sampling campaigns were undertaken on three consecutive days in September 2018.

3.2.2.1. Collection of water samples in the Saint Lawrence River

Surface water sampling stations were strategically chosen based on their ease of access and position in relation to WWTP outfall. Two points in the downstream and one point in the upstream of WWTPs outfall in the SLR were selected. The location of each sampling station in the river is demonstrated in Figure 3.1. The samples were collected in time of relatively low flow of the SLR, between 8500 and 9000 $m^3 s^{-1}$, and in the days without precipitation.

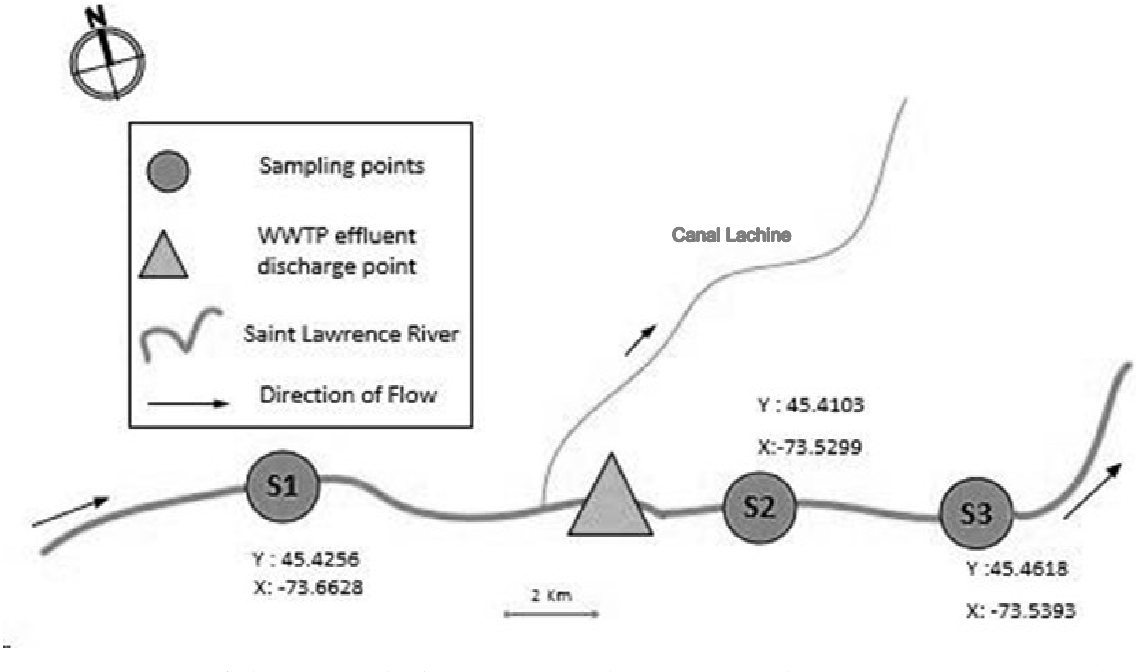


Figure 3.1 Locations of the WWTP discharge and sampling points in the Sainte Lawrence River (X and Y geographical coordination)

12-h time proportional composite samples were collected manually in each sampling site in the river. To this end, hourly grab samples were collected with the aid of 1000 mL HDPE container attached to the DWK life science grab sampler. The grab sampler was deployed inside the water in desired distance localized by GPS from the shoreline. At the specific depth of water, the rubber stopper is raised from the bottle mouth and sample was collected. Subsequently, a 50 mL aliquot of each grab sample was filtered by Chromafil syringe filter in the field. It was previously confirmed the fiber glass and polyester filters showed the least adsorption of multiclass micropollutants including pharmaceuticals, hormones, and herbicides (Darwano et al. 2014). The filtrate added to an amber glass bottle. The composite filtrate and unfiltered grab samples were stored in a cool box at the temperature 4°C. In the absence of photolysis, for the surface water samples sterilized by 0.45 µm filters and kept at cool temperature 4°C, there was no degradation observed for multiclass trace organic micropollutants consisting of pharmaceuticals, hormones and herbicides (Cormier et al. 2015). At the end of each sampling campaign, after arriving to the laboratory, the unfiltered surface water samples were homogenized in a 10 L HDPE container. It is noteworthy, blank samples were also collected at each sampling location. The blank samples mimicked the sampling and pretreatment procedure to monitor the likelihood of artifacts introduction during sample collection.

3.2.2.2. Collection of wastewater effluent sample

24-h time proportional composite wastewater effluent samples were collected for three consecutive days (i.e. 3 samples) using ISCO refrigerated autosampler. After every 24 hours, the sampling process was ceased and 50 mL aliquot was collected and filtered immediately by Chromafil syringe microfilter. The filtrate was kept in a 50 mL amber pre-cleaned glass bottle inside the cooler. Furthermore, the rest of the unfiltered composite sample was transferred to a HDPE container and kept at the temperature 4°C. Blank samples were also collected in the place.

3.2.3. Analysis of the environmental samples

3.2.3.1. Name and characteristics of targeted EOMs in surface water and wastewater effluent

Thirty compounds were totally targeted in both water and wastewater samples. The target analytes covered multi-class of EOMs including ten compounds belong to the frequently prescribed classes of PhACs (anti-inflammatories, anticonvulsants, antidepressants, beta blockers, opioid analgesics) and six pharmaceutical metabolite compounds, eleven synthetic and natural hormones (natural and synthetic estrogens, progestogen, androgens), a stimulant, herbicides and transformation products. These compounds possessed different chemical structures and physicochemical characteristics able to affect their transport and fate in both water and wastewater matrices. The names and classes of compounds beside their partition coefficient (Log K_{ow}), dissociation constant (pK_a) were tabulated in Table 3.2. The selected compounds have been frequently detected in the wastewater stream and aquatic terrestrial. Furthermore, low removal efficiencies have been observed for many of them in the conventional WWTPs (section 2.3).

3.2.3.2. Analysis of target compounds in environmental samples

The selected compounds were analyzed by automated solid-phase extraction coupled to liquid chromatography tandem mass spectrometry (on-line SPE LC-MS/MS). In this method, the extraction, purification, and detection steps are integrated into one instrument. A similar analytical methodology was used by Ouarda et al. (2019). In brief, the preconcentration was performed using the EQuan (Thermo Fisher Scientific, Waltham, Massachusetts) system. This system is based on column switching between the SPE cartridge (Hypersil Gold C18, from Thermo Scientific) and chromatographic columns (C18 column). Water and methanol are used both for pre-concentration and elution steps. The ionization of the selected compounds was achieved by electrospray ionization (ESI) interface in positive and negative selection mode. The triple quadrupole mass spectrometer (TSQ Quantiva from Thermo Scientific) was operated in selected reaction monitoring (SRM) mode for the detection of transitions at their respective m/z ratios. Quantification of compounds was performed using a standard addition calibration with linear regression and isotopically-labelled internal standards for river water and effluent samples. In this particular analytical methodology, the limit of detection is of the order of low ng L^{-1} for all compounds.

Table 3.2 List of tested micropollutants and their class, octanol-water partition coefficient (Log Kow) and disassociation constant (pKa)

Compound	Abbreviation	Class	Chemical formula	Log $\mathbf{K_{ow}}$	$\mathbf{pK_a}$
Pharmaceuticals and Metabolites					
Ibuprofen	IBU	Anti-inflammatory	$C_{13}H_{18}O_2$	3.97	4.9
2-Hydroxy ibuprofen	2OH-IBU	Metabolite	$C_{13}H_{18}O_3$	2.41	4.63
Diclofenac	DCF	Anti-inflammatory	$C_{14}H_{11}Cl_2NO_2$	4.51	4.2
4-Hydroxy Diclofenac	4OH-DCF	Metabolite	$C_{14}H_{11}Cl_2NO_3$	3.7	-
Hydromorphone	HDR	Opioid analgesic	$C_{17}H_{19}NO_3$	-	-
Sulfamethoxazole	SMX	Antibiotic	$C_{10}H_{11}N_3O_3S$	0.89	5.7
4-Nitroso Sulfamethoxazole	4N- SMX	Metabolite	$C_{10}H_9N_3O_4S$	-	-
Clarithromycin	CLT	Antibiotic	$C_{38}H_{69}O_{13}$	3.16	8.99
Amoxicillin	AMX	Antibiotic	$C_{16}H_{19}N_3O_5S$	0	2.8, 7.2
Carbamazepine	CBZ	Anticonvulsant	$C_{15}H_{12}N_2O$	2.67	13.96
10,11-dihydro-10,11-dihydroxycarbamazepine	CBZ-DiOH	Metabolite	$C_{15}H_{12}N_2O_2$	0.81	-
Acebutolol	ACB	Beta Blocker	$C_{18}H_{28}N_2O_4$	1.7	9.57
Venlafaxine	VEN	Antidepressant	$C_{17}H_{27}NO_2$	2.91	9.33
Desvenlafaxine	DVEN	Metabolite	$C_{16}H_{25}NO_2$	2.26	9.74
Fluoxetine	FLX	Antidepressant	$C_{16}H_{18}F_3NO$	4.09	8.7
Norfluoxetine	NFLX	Metabolite	$C_{16}H_{16}F_3NO$	-	9.1
Stimulant					
Caffeine	CAF	Stimulant	$C_8H_{10}N_4O_2$	0.07	10.4
Hormones					
Estradiol	E_2	Estrogen	$C_{18}H_{24}O_2$	4.01	10.3
Ethinylestradiol	EE2	Synthetic Estrogen	$C_{20}H_{24}O_2$	4.32	10.33
Estrone	E_1	Estrogen	$C_{18}H_{22}O_2$	3.69	10.33
Estriol	E_3	Estrogen	$C_{18}H_{24}O_3$	2.94	10.13
Mestranol	MEE2	Estrogen	$C_{21}H_{26}O_2$	4.67	-
Testosterone	TES	Androgen	$C_{19}H_{28}O_2$	3.47	-0.88

Progesterone	PROG	Progestogen	$C_{21}H_{30}O_2$	4.04	-
Medroxyprogesterone (MPROG)	MPROG	Progestogen	$C_{22}H_{32}O_3$	3.50	-
Altrenogest	ALNG	Progestogen	$C_{21}H_{26}O_2$	-	-
Norethisdrone	NORE	Progestogen	$C_{20}H_{26}O_2$	2.97	17.59
Norgestrel	NGT	Progestogen	$C_{21}H_{28}O_2$	-	-
Herbicide					
Atrazine	ATZ	Herbicide	$C_8H_{14}ClN_5$	2.61	1.7
Desethylatrazine	DEA	Metabolite	$C_6H_{10}ClN_5$	1.51	1.65

The values of the compounds properties extracted from the following references:
(Comtois-Marotte et al. 2017).
Chemspider database.
Drugbank database.

3.2.3.3. Mass loading of EOMs in the WWTP effluent

Mass loading of the different organic micropollutants was calculated by multiplying the individual concentration of each chemical found in wastewater by the mean flow rate of the WWTP effluent. Afterward, the mass loading of each EOM was normalized by the population equivalent served by the WWTP using equation (Paíga et al. 2016):

$$\text{Normalized mass load (mg/day/1000 inhabitants)} = \frac{\text{mass load}\left(\frac{\text{mg}}{\text{day}}\right)}{\text{Population served by WWTP}} \times 1000 \qquad (3\text{-}1)$$

Total mass loading of all organic micropollutants for each day of sampling was calculated by the total of all contaminants mass loads for each separate day.

3.2.3.4. Measurement of general water and wastewater quality parameters

The water and wastewater physicochemical parameters were measured by subsampling from the unfiltered composite samples. HACH TNT Plus^{TM} vial tests were utilized to measure the quality parameters such as COD, total nitrogen, nitrate, total Kjeldahl nitrogen, and so forth. Dissolved oxygen and temperature were measured at the field with the aid of DO/Temperature probe (Thermo Scientific™ Orion™ RDO™). Oxidation-Reduction Potential (ORP) and pH were measured by multiparameter meter (Oakton).

3.3. Production of new sludge-based adsorbent

3.3.1. Sampling of the precursors for new sludge-based adsorbent

The stabilized/dewatered sludge was collected inside the WWTP at the place where it was loaded onto the trucks. The sludge was transferred into the HDPE buckets and kept at the temperature of 4°C.

Furthermore, wood residue samples were collected from a wood mill located in the City of Mirabel, Quebec, Canada. Two types of wood residue from softwood and hardwood species were sampled.

3.3.2. Pretreatment of the precursors

All primary materials including sludge, softwood and hardwood residues were dried inside the oven at 105 ℃ up to constant weight. Following the drying of the precursors, the sludge and wood residues were ground and sieved to 0.3-1.0 mm and 1.0-1.7 mm particle sizes, respectively. Hereafter sludge, hardwood, and softwood samples were denoted to SS, HW and SW, respectively.

3.3.3. Characterization of primary materials

3.3.3.1. Proximate analysis of precursors

Proximate analysis of the raw materials was conducted according to American Society for Testing and Materials (ASTM) D1762-84 to determine their volatile matter and ash content. The amount of fixed carbon was determined as the remaining fraction after ash and volatile matter determination (on a dry basis). The moisture content of the samples was determined by weighing the samples before and after drying at 105 ^{0}C.

3.3.3.2. Elemental analysis of sludge

In order to measure the heavy metals concentrations in the raw sludge sample, acid digestion experiment based on the standard US EPA 3050B (US Environmental Protection Agency, 1996) was conducted. In this particular method, 0.5 gram (dry weight) of sludge was digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). The final digested samples were filtered by 0.45 µm syringe filters. The metal content was examined by inductively coupled plasma mass spectroscopy (ICP-MS) (Agilent Technologies 7700 Series ICP-MS).

3.3.3.3. Thermogravimetric analysis

To study the thermal behaviour of secondary sludge and wood residues thermogravimetric analysis (TGA) were conducted by a thermal analyzer (Thermal Analysis Q500, American) under a nitrogen flow rate of 100 mL min^{-1}. Each sample was heated from 30 °C to 1000 °C at the constant heating rate of 10 ^{0}C min^{-1}. Differential thermogravimetric (DTG) data were produced by using the bundled software (TRIOS Software, TA instruments) with the analyzer.

Furthermore, the interaction between secondary sludge and softwood residue under two different SS:SW mass ratios was investigated by DTG analysis. For this puropose, mixtures of 90:10 and 75:25 (%w:w) of SS and SW were prepared. The same heating procedure was applied to mixture samples. The comparison of experimental and theoretical data from DTG plot was made under two different blend ratios. The theoretical data for the blend sample was obtained based on the following equation (Xu. et al. 2017) :

$$DTG\ \% = x\ DTG_{ss} + y\ DTG_{sw} \tag{3-2}$$

Where x and y are the blend ratio and DTG_{ss} and DTG_{sw} are thermal decomposition rate of sludge and softwood during solo-pyrolysis process at the temperature, respectively.

3.3.4. Pyrolysis of the precursors

All sludge-based carbon adsorbents in this study were prepared via a single-step carbonization-activation. High temperature tubular furnace (MTI,OTF-1200X-III) was used to conduct the pyrolysis of samples. The experiments were conducted in the NanoQAM laboratory at the UQAM.

SS granules were physically mixed with powder KOH at the ratio of 1:1 (weight terms). It should be emphasized that the blending is done in the absence of water. The mixture was added to crucibles and inserted into the furnace. Nitrogen gas flow was adjusted to 2 L min^{-1} and continuously passed through the furnace. The sample was heating up to 750 ℃ at the heating rate of 10 ℃ min^{-1}. Holding time at the maximum temperature was 60 min. After the heating treatment, the resulting material was washed with HCl (3 M) to remove any activator residues. Subsequently, it was washed with a sufficient amount of distilled water. The final product was dried overnight inside an oven at 105 ℃.

In order to investigate the effect of wood addition to the resulting carbon product, two types of wood waste comprising of softwood and hardwood waste were added at the 50% (w/w%) to the sludge. Therefore two separate precursors comprising of mixtures of SS:HW and SS:SW were prepared. KOH powder was added to the mixture at a similar ration to the sludge. Same heating and post treatment, as above mentioned, were applied to these samples. Table 3.3 presents the characteristics of prepared blends and heating procedures.

Table 3.3 Characteristics of prepared mixtures of feedstocks and heating procedure

Type of mixture	Activator	Mixing ratio (Sludge:Wood:KOH)	Final temperature	Heating rate	Holding time
Sludge/hardwood (SS:HW)	KOH	2:1:2	750 °C	10 °C min^{-1}	60 min
Sludge/softwood (SS:SW)	KOH	2:1:2	750 °C	10 °C min^{-1}	60 min

The yield of the resulting products was calculated based on the following equation:

$$Y\% = \frac{w_p}{w_i} \times 100 \tag{3-3}$$

where Y is the yield (in %), w_p is the final weight of dried resulting carbon material and w_i is the primary weight of the dried organic feedstock.

3.3.5. Characterization of adsorbents

3.3.5.1. Textural characterization of adsorbents

Textural characteristics were determined by nitrogen adsorption at -196 °C using an automatic adsorption instrument (Micromeritics, TriStar 3000). Prior to nitrogen gas adsorption analyses, carbonaceous products were degassed for overnight at 120 °C to ensure that all the moisture and gaseous elements have been removed.

Specific surface area was calculated from the isotherm using the Brunauer–Emmett–Teller (BET) equation (Barrett et al. 1951). Total pore volume (V_t) was determined by using nitrogen vapor adsorption data in the last point of the isotherm. The volume of micropores (V_{mic}), and mean micropore width (W_0) were obtained from the Dubinin-Astakhov (DA) equation (Dubinin 1975). Mesopores volume (V_{mac}) was calculated from the difference of total pore volume and micropore volume.

3.3.5.2. Scanning electron microscopy

Scanning electron microscopy (SEM) analysis was carried out to visualize the surface morphology of new sludge-based adsorbents. SEM analysis of samples was recorded using a Philips XL30 microscope.

3.3.5.3. Determination of the point of zero charge (pH_{pzc}) of adsorbents

pH_{pzc} was determined according to the method described by Baccar et al. (2012). To measure pH_{pzc}, 0.05 g of the carbon adsorbent was shaken inside the 25 mL of KNO_3 solution (0.1 M) for 24 h, at different pH. The pH of the solution was adjusted by HCl and NaOH solutions. The final pH of the solution was measured after 24 h shaking at room temperature. A high precision pH meter equipped with a combined glass electrode was used (Accumot, AB2000). The $pH_{final} - pH_{initial}$ value was plotted versus the initial pH value.

3.3.5.4. Infrared spectroscopy of prepared new adsorbents

Infrared spectroscopic measurements of prepared new SBAs were done by means of Nicolet 6700 FTIR spectrometer using the attenuated total reflectance method (ATR). FTIR-ATR was obtained using diamond crystal as the internal reflection element. A blank spectrum was obtained each time before the samples were processed for the correction of background noise.

3.4. Performance evaluation

In this step, the performance of the produced new sludge-based adsorbents, as well as commercial activated carbon, was evaluated through batch sorption experiments. To this end, sorption of venlafaxine (VEN) from aqueous solution onto sludge-based adsorbents and CGAC was firstly investigated. Then, the sorption capability of two adsorbents including SS:HW product and CGAC was studied in the real secondary effluent samples.

For the adsorption process, the prepared carbon materials were screened to the fraction of a diameter between 0.3 mm and 0.5 mm. All the adsorbents were kept inside the desiccator until their use.

3.4.1. Adsorption of VEN from aqueous solution

All solutions were prepared with ultrapure water obtained from Milli-Q water purification systems. The adsorption experiments were carried out within 125 mL amber glass jars on the reciprocating- orbital shaker (Thermolyn Aros 160) at the constant rotating speed of 250 rpm. Moreover, blank samples were essayed to make sure there is no loss of analytes during the experiment.

The amount of VEN adsorbed per gram of adsorbent (q) was calculated by using the following equation:

$$q = \frac{(C_0 - C_t)}{m} V \qquad (3\text{-}4)$$

Also, the removal efficiency was calculated by using the below equation:

$$\%RE = 1 - \frac{C_t}{C_0} \qquad (3\text{-}5)$$

where q_t (mg g^{-1}) is the amount of VEN adsorbed at time t, C_0 is the VEN initial concentration (mg L^{-1}), C_t (mg L^{-1}) is VEN concentration at time t, V is the volume (L) of the adsorbate solution and m (g) is the mass of dried carbon adsorbent.

3.4.1.1. Measurement of VEN concentration in the aqueous samples

The concentrations of VEN reside in the samples were measured by UV-vis spectrophotometer (Thermofischer, Evolution 201). The maximum absorbance wavelength of the VEN was obtained 224 nm which was in agreement with the previous research work (Karani and Pingale 2009).

The calibration curve was constructed based on Beer-Lambert's law. According to Beer-Lambert's law, there is a linear relationship between solute concentration and absorbance. Blank sample and different analyte concentrations ranging from 1 mg L^{-1} to 30 mg L^{-1} were prepared. The quartz cells with 1 cm path length were used. The absorbance of each concentration was measured at the maximum absorbance wavelength. Then, the chart of absorbance versus concentration was automatically drawn by the software (Thermo Scientific™ INSIGHT™2) interfaced with the instrument.

3.4.1.2. Effect of contact time

The effect of contact time was evaluated for two adsorbents; the mixture of SS:HW product and CGAC. The dose of the adsorbent in the case of CGAC was 0.4 g L^{-1} at the initial VEN concentration of 10 mg L^{-1} (volume of 50 mL). In the case of the SS:HW adsorbent two different initial concentrations of VEN (10 and 30 mg L^{-1}) were considered. The SS:HW adsorbent was added to the 60 mL of VEN solutions at the dose of 0.083 g L^{-1}. The time started when agitation began and samples were taken at specific time intervals and immediately filtered with 0.45 µm syringe filter.

It is noteworthy to say the dosage of the adsorbent was selected so to be able to properly measure the remaining concentration of adsorbate in solution and, simultaneously, to have a significant adsorption percentage.

3.4.1.3. Adsorption kinetic modelling

The adsorption kinetic was evaluated by the three kinetic models; pseudo-first order (PSF) (Calisto et al. 2015), pseudo-second order (PSO) (Calisto et al. 2015), and Elovich (Álvarez-Torrellas et al. 2016a) according to the following equations, respectively;

$$q_t = q_e\,(1 - e^{-k_1 t}) \tag{3-6}$$

$$q_t = \frac{q_e^2 k_2\, t}{(1 + q_e k_2\, t)} \tag{3-7}$$

$$q_t = \beta \ln(\alpha\, \beta\, t) \tag{3-8}$$

with t (h) representing the adsorbent/solution contact time, q_t (mg g^{-1}) the amount of solute adsorbed by mass unit of adsorbent at time t, q_e the amount of solute adsorbed when the equilibrium is attained (mg g^{-1}), k_1 (h^{-1}) and k_2 (mg g^{-1} h) the pseudo-first and pseudo-second order rate constant, respectively. α (mg g^{-1} h^{-1}) is the initial adsorption rate, and β (g mg^{-1}) is related to the extent of surface coverage and activation energy for chemisorption.

Square root of reduced chi-squared (SD), and correlation coefficient R^2 were employed to evaluate the best fit kinetic model. SD can be described as (Bergmann and Machado 2015):

$$SD = \sqrt{\left(\frac{1}{n_p - p}\right) \sum_{i}^{n} (q_{i\,exp} - q_{i\,model})^2} \tag{3-9}$$

where $q_{i\ model}$ is each value of q predicted by the fitted model, $q_{i\ exp}$ is each value of q measured experimentally, and p is the number of parameters of the fitted model.

3.4.1.4. Comparison of the sorption capability of the new adsorbents

To evaluate the removal efficiency of VEN by produced sludge-based adsorbents, 5 mg of each prepared carbon was added to 50 mL of VEN solutions (initial concentration of 10 mg L^{-1}). After the contact time of 48 h the residual concentration of VEN in the solutions was measured. The removal efficiency was calculated based on equation 3.5.

3.4.1.5. Adsorption isotherms

Equilibrium adsorption studies of the SS:HW product were carried out keeping the adsorbent doses constant (5 mg), and varying the VEN initial concentrations (10–30 mg L^{-1}). Samples were taken at the equilibrium time determined from the kinetic study. In the case of CGAC, the initial concentration of VEN was kept constant at 10 mg L^{-1} and adsorbent dosage was varied from 0.1 to 0.6 g L^{-1}. The concentration of VEN remaining in solution at equilibrium (C_e) was determined, and the uptake (q_e) was calculated using Eq. (2)

For the isotherm modeling, two famous isotherm models, namely the Freundlich (Fan et al. 2016), and Langmuir (Fan et al. 2016) were applied to the obtained equilibrium data. The linearized forms of the isotherm equations are as follows:

Freundlich

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \tag{3-10}$$

Langmuir

$$\frac{C_e}{q_e} = \frac{1}{q_m\, k_L} + \frac{1}{q_m}\, C_e \tag{3-11}$$

where C_e (mg L^{-1}) is the equilibrium concentration, q_e (mg g^{-1}) is the adsorption capacity at equilibrium time. If the adsorption follows the Freundlich equation, a plot of $\ln q_e$ versus $\ln C_e$ should be a straight line; k_f (L mg^{-1}) and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. Similarly, from a plot of C_e/q_e against C_e, q_m (mg

g^{-1}) represents the maximum adsorption capacity of the solids phase and k_L (L mg^{-1}) which is the energy constant related to the heat of adsorption could be obtained.

The separation factor, R_L, is an essential characteristic of the Langmuir isotherm. It was used in this experiment to assess the adsorption process. R_L can be described as (Nazari et al. 2016):

$$R_L = \frac{1}{1+\ k_L C_0} \tag{3-12}$$

Where R_L represents the separation factor, k_L (L mg^{-1}) is Langmuir constant and C_0 (mg L^{-1}) is the initial concentration of adsorbate.

3.4.2. Adsorptive performance of the new sludge-based adsorbent and CGAC in a real secondary effluent

In order to evaluate the adsorptive performance of SS:HW product in the real matrix with the presence of background organic matters as well as cocktail of EOMs, batch adsorption experiments were conducted. To be assured venlafaxine was present in the medium, the effluent sample was spiked by 1 mg L^{-1} stock solution of venlafaxine prepared in DI water, to the concentration of 1 μg L^{-1}.

Different weights of SS:HW product (2, 5, 15, 30 mg) were added to the effluent samples. Also, to assess the CGAC performance in the same experimental condition, a dosage of 0.033 g L^{-1} of the commercial carbon was added to the real effluent sample. The volume of the solutions was 60 mL. Moreover, a blank sample, i.e. without any adsorbent, was also considered in this set of the experiment in order to study any analytes loss during the batch adsorption experiment. Samples were shaken for 48 h contact time at the room temperature inside the amber glass jars. Finally, samples were filtered on the vacuum with 0.45 μm fibre glass membrane.

The initial and residual concentrations of venlafaxine and other EOMs present in the secondary effluent were measured by the on-line SPE LC-MS/MS instrument using the same analytical methodology employed for the environmental samples.

4. Results and Discussion

4.1. Occurrence of EOMs in the environmental samples

In the present section, the concentrations of detected EOMs in the WWTP's effluent and its associated recipient surface water were reported.

4.1.1. Concentrations of EOMs in the WWTP's effluent

Out of thirty compounds tested, sixteen compounds were observed in the WWTP's wastewater effluent. The detected compounds were present in the wastewater effluent at 100% frequency over three days of sampling. Table 4.1 illustrated the concentrations of detected EOMs in the WWTP's outfall on each day of sampling.

Table 4.1 Concentration (ng L^{-1}) of contaminants in the WWTP's effluent

Compound's name	Mean Concentration		
	September 13, 2018	September 14, 2018	September 15, 2018
Ibuprofen	15.4	18.4	22.7
2-Hydroxy Ibuprofen	512	969	1362
Diclofenac	370	491	578
4-Hydroxy Diclofenac	12.7	25.8	40.4
Sulfamethoxazole	161	201	257
Clarithromycin	39.4	35.1	38.5
Carbamazepine	230	268	394
2-Hydroxy Carbamazepine	760	751	869
Acebutolol	44	35.3	45.9
Venlafaxine	673	713	810
Desvenlafaxine	1141	1229	1484
Fluoxetine	2.5	2.9	3.1
Caffeine	50.2	52.1	117
Estrone	26.1	16.1	40.1
Atrazine	18.4	19.6	20.9
Desethylatrazine	29.4	26.8	32.3

Mainly pharmaceutical active compounds or their metabolites were present in the WWTP's effluent. Based on the therapeutic classes of pharmaceuticals, analgesics, and their hydroxylated metabolites, two classes of antibiotics (sulfonamides, and macrolides), three psychiatric drugs (antidepressants, anticonvulsants) and their respective metabolites, and an anti-hypertension drug were detected in the wastewater effluent. Caffeine was also present in the wastewater effluent. Furthermore, among ten tested hormones in this study; estrone was the sole hormone available in the soluble form in the effluent. Herbicides including atrazine and its main transformation product were also detected in the wastewater effluent over three days of sample collection.

Interestingly, the contribution of metabolite compounds in the wastewater effluent was significant. Four out of six tested metabolite compounds were present in the effluent. The metabolites of IBU, CBZ, VEN drugs were observed at higher magnitudes than the parent compounds. All these metabolite compounds could be also regenerated in the biological works in the WWTPs (Ebele et al. 2017; Boix et al. 2016; Jelic et al. 2012). The transformation product of ATZ was also present at higher concentrations than the ATZ in the wastewater effluent.

By using equation 3-1, the total mass loading of EOMs imposed from WWTPs to the associated receiving surface water was calculated. This value was increased from 1113 mg/day/1000 inhabitants on the first day to 1315 and 1632 mg/day/1000 inhabitants on the subsequent days of sampling. The measured total mass loads in the present study were comparable with previous works conducted in Europe where the total mass loads were not exceeded 2317 mg/day/1000 in the effluents (Paíga et al. 2016; Papageorgiou et al. 2016). The results indicated mass loads of EOMs are continuously discharging to the Saint Lawrence River through the WWTP's wastewater effluent.

4.1.2. Concentration of EOMs in the Saint Lawrence River

Different classes of micropollutants were also observed in the SLR. The concentrations of detected compounds in each sampling station are shown in Table 4.2.

Pharmaceutical compounds and their metabolites were the most prevalent EOMs in the SLR. Herbicides and the stimulant were also observed in the river water. None of the tested hormones were detected in the samples collected from the river. Except for ACB, the rest of the detected EOMs were present at the 100% frequency alongside the SLR.

Table 4.2 Concentrations (ng L^{-1}) of micropollutants in the Saint Lawrence River

Compound	Name of sampling sites		
	Site 1 (S1)	Site 2 (S2)	Site 3 (S3)
Ibuprofen	3.64	4.40	4.27
2-Hydroxy Ibuprofen	330	710	713
Carbamazepine	1.85	1.83	2.31
2-Hydroxy Carbamazepine	6.01	11.5	10.3
Venlafaxine	3.08	1.15	2.06
Desvenlafaxine	3.71	1.89	3.28
Caffeine	31.3	27.9	28.6
Atrazine	16.7	55.0	24.9
Desethylatrazine	16.2	67.2	216
Acebutolol	n.d	n.d	3.77

n.d not detected

Same as the wastewater effluent the pharmaceutical metabolite compounds were present at higher levels than parent compounds in the surface water. This is also in agreement with the previous studies. For example, by comparing total concentrations of 50 and 19 pharmaceutical parents and metabolite compounds, respectively, in the Ebro river basin in Spain, López-Serna et al. (2012) revealed the overall contribution of metabolites is remarkable representing as an average 30–50% of the total pharmaceutical load (parent compounds+ metabolites).

The presence of 2OH-IBU is significantly more pronounced than IBU in the river. In the farthest downstream point of sampling, 2OH-IBU was present at the concentrations of *circa* 150 times more than IBU. The significant higher concentration of 2OH-IBU could be justified when the ratio of this compound to its respective parent in the WWTP's outfall reached up to 67.5 on the last sampling day. Furthermore, 2OH-IBU was reported as a transformation product from the IBU biodegradation in recipient surface waters (Boix et al. 2016; Ferrando-Climent et al. 2012).

To the best of author knowledge, this is the first time the occurrence of CBZ-DiOH was reported in the SLR. The concentration of CBZ-DiOH was five times higher than its respective parent compound in the downstream of the WWTP outfall to the SLR. It is in agreement with the approximately twice higher concentration of CBZ-DiOH than CBZ in the Otonabe River, ON (Miao and Metcalfe 2003).

The concentration of DVEN was measured slightly higher than the VEN in all three sampling stations in the SLR. DVEN was previously reported at the concentrations of 68.7 ng L^{-1} and 21 ng L^{-1} in the water samples collected from a WWTP effluent plume in the SLR in September and July 2007, which were higher than VEN detected at the concentration of 45.9 ng L^{-1} and 12.9 ng L^{-1} at the same time, respectively (Lajeunesse et al. 2008).

The DEA concentrations reached 10 times higher than its parent compounds, ATZ, at the third sampling station in the SLR. This result is consistent with the DEAs' concentrations of 479 ng L^{-1} and 20 ng L^{-1} in the SLR and Des Prairies Rivers, respectively. The concentrations were 10 times higher than the ATZ in those two sources of drinking water in Montreal (Garcia-Ac et al. 2009). The occurrence of ATZ and its transformation product can be explained by its intense application in agricultural fields in the US and Canada resulting in cumulative agricultural load in SLR (Garcia-Ac et al. 2009).

CAF and CBZ fairly showed conservative behaviour alongside the SLR. CAF was previously proposed as a promising indicator of recent urban fecal contamination and CBZ as a good indicator of cumulative persistence compounds (Daneshvar et al. 2012). Previously, the concentrations of CBZ and CAF were measured at 3.8 ng L^{-1} and 65 ng L^{-1} in the SLR, respectively, which was in agreement with the present study (Daneshvar et al. 2012).

ACB is the only compound detected in one sampling station downstream of the WWTP's outfall. The data on the occurrence of ACB in surface water around Canada is scarce. Based on the author's knowledge it is the first time the concentration of this beta blocker was reported in the Saint Lawrence River. In a stream highly affected by a primary WWTP's discharge, in the province of Newfoundland and Labrador, two beta-blocker persistent samples, such as metoprolol and sotalol, were found as far as 17 km downstream from the WWTP (Brun et al. 2006). These results confirmed the occurrence of beta-blockers needs more investigation in the aquatic terrestrial of Canada.

4.1.3. Selecting VEN as the target compound

Higher numbers and concentrations of EOMs were observed in the WWTP's effluent in comparison to the river. This may confirm that the WWTP effluent is the source of the EOM's emission. Through WWTP's outfall, the total mass load of 4060 mg/day per 1000 inhabitants of micropollutants was discharged into Saint Lawrence River over three days. Psychiatric drugs, as well as their respective metabolite compounds including VEN, DVEN, FLX, CBZ, and CBZ-DiOH, contributed with 61.65 % of the total mass load indicating their remarkable prevalence in the WWTP's wastewater effluent.

Among the psychiatric parent compounds, VEN was observed at the highest concentrations in the wastewater effluent. The results were in accordance with the previous research works that reported concentrations of VEN at the highest level among the other class of psychiatric drugs (Paíga et al. 2016; Lajeunesse et al. 2012; Metcalfe et al. 2010). Moreover, VEN was also present with 100% frequency alongside the SLR. This may suggest its persistency in the surface water (Metcalfe et al. 2010).

Furthermore, the presence of VEN in aquatic terrestrial can impose negative impacts on non-target aquatic organisms. For example, adult male fathead minnows exposures to the VEN (305 ng L^{-1} and 1104 ng L^{-1}) resulted in mortality (Schultz et al. 2011). Chronic, aqueous exposure of zebrafish to environmentally relevant concentrations of VEN decreased reproductive outputs and influence kidney tubule morphology (Galus et al. 2013). Also, this contaminant was previously observed in the brain tissue of the fish species exposed to the WWTP's effluent revealing its bioaccumulation tendency (Schultz et al. 2010).

As a consequence, it is required to inhibit the further emission of VEN from the selected WWTP into receiving Saint Lawrence River. Thus, this compound was chosen as the target contaminant for the next phases of present work where the removal of VEN from aqueous solution was investigated.

4.2. Production of new sludge-based adsorbents

4.2.1. Characterization of primary materials

The properties of the sludge and wood residues are indicated in Table 4.3. Among the raw precursors, sewage sludge has significant higher ash content. The higher ash content of the sludge suggested the high content of inorganic specimens in this sample (Singh et al. 2017a). The concentrations of heavy metals in secondary sludge were also listed in the Table 4.3.

Table 4.3 Properties of the primary materials and concentrations of heavy metals in the sludge

	Sewage sludge	Hardwood residue	Softwood residue
Component	-	Sapindaceae (Maple wood)	Pinaceae (Fir and spruce wood)
Water content (%)	63.2	5.4	27
Volatile matter* (%)	68.9	91.9	88.8
Ash content* (%)	27.4	0.1	0.5
Fixed carbon* (%)	3.7	8.0	10.7
pH	7.2	-	-
Heavy metal element (mg kg^{-1})			
Cr	27.05		
Mn	310.36		
Ni	22.78		
Cu	210.58		
Zn	869.12		
As	3.34		
Cd	1.17		
Pb	54.59		
Fe	75.95×10^2		
Al	16.20×10^3		

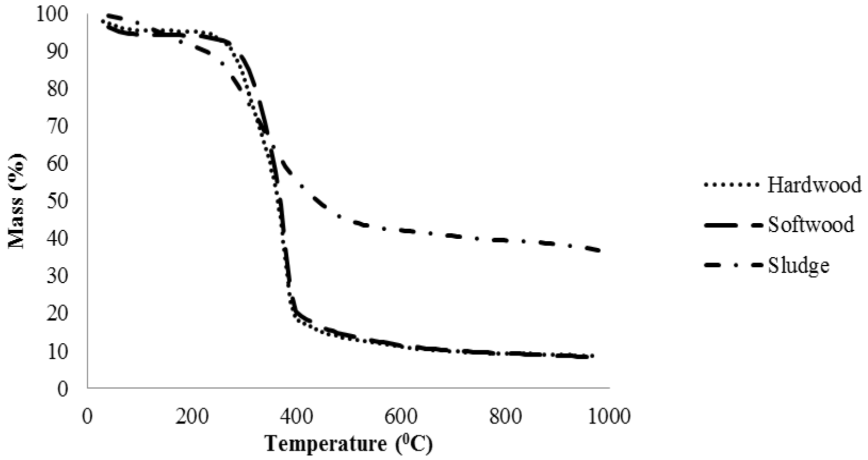
* Dry basis (%)

As can be seen, the two wood samples were mainly composed of volatile matter indicating their higher organic content. Both wood residues contained more fixed carbon as well. According to

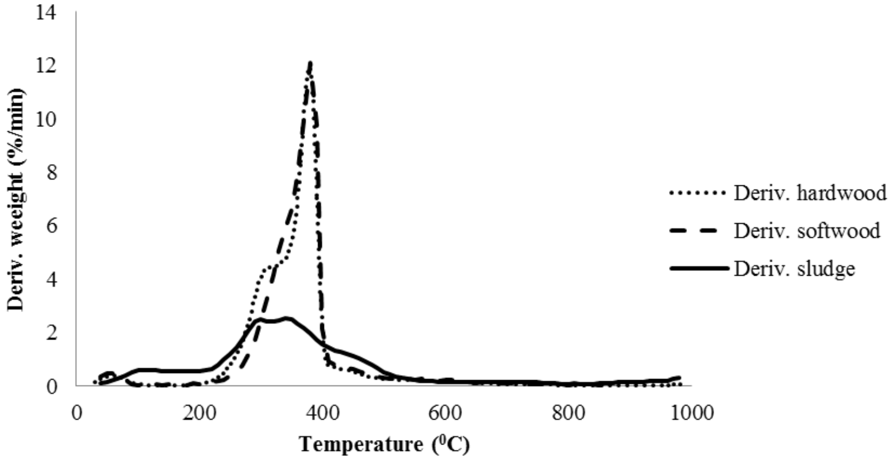
Singh et al. (2017a) fixed carbon is, strictly speaking, not pure carbon but simply dry mass that is not volatile matter nor ash, and therefore dominated by fused aromatic carbon structures.

4.2.1.1. Thermal behavior of precursors

The TG and DTG analysis of each precursor are depicted in Figure 4.1. The total mass loss of sewage sludge in the course of thermal decomposition is lower than that of two wood residues as shown in Figure 4.1 a. The final mass yield in the case of sludge was 37.9% which for the HW and SW samples was reduced to 10.9 and 11.4%, respectively. The lower mass loss of SS is in accordance with its higher ash content (Wang et al. 2016a).



a



b

Figure 4.1. a) TG and b) DTG profiles of individual raw precursors

Given the obtained DTG curves the maximum rate of mass loss of wood residues is approximately four times higher than the SS sample which could be confirmed by significant volatile matter contents in wood residues. The results are in agreement with another study (Zhu et al. 2015) that reported the pyrolysis of sludge and pine sawdust.

Mass loss regions were identified from the DTG curves. The main decomposition of SS during the pyrolysis process was in the temperature range of 200–600 °C (Magdziarz and Werle 2014). According to Magdziarz and Werle (2014) the highest mass loss is caused mainly by the decomposition of carbohydrates and lipids. Consecutively, the decomposition of inorganic matters, for example, calcium carbonate is occurred in the SS up to 1000 °C (Huang et al. 2017). While the sludge exhibited continues mass loss, both wood residues showed an abrupt mass loss in the 200-400 °C temperature range. Thermal degradation of hemicellulose and cellulose in biomass has been reported to occur at 220–315 °C and at 315–400 °C, respectively (Jin et al. 2017).

4.2.1.2. Thermal decomposition of the mixture of sludge and softwood residues

During co-pyrolysis, there may be some interactive effects between two waste samples which could accelerate or inhibit the process of thermal decomposition. Figure 4.2 compared the DTG rates obtained from thermal decomposition of mixture samples (including different ratios of SS and SW) with the DTG rates derived from the individual decompositions of SS and SW. The thermal behaviors of blended samples are similar to that of SS rather than that of SW. Similar behavior was observed in the thermal analysis of sludge and hazelnut shell (Xu et al. 2017).

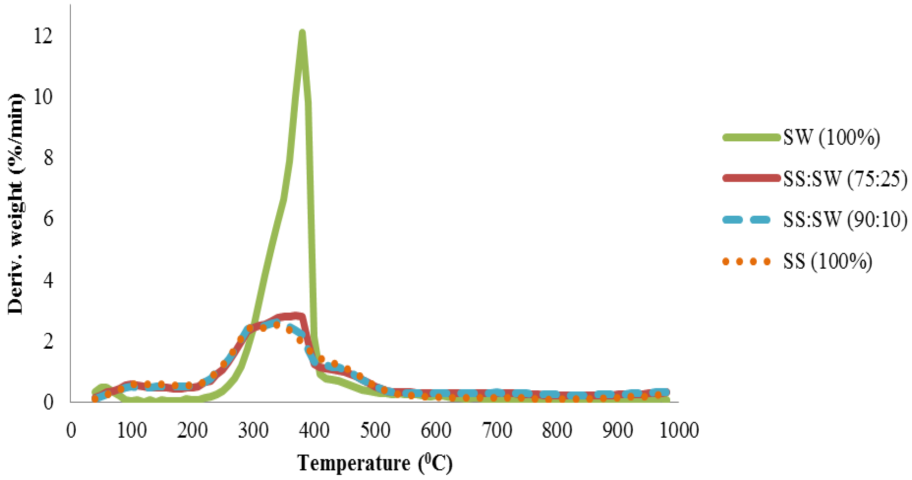


Figure 4.2 Comparison of the DTG curves of the mixture of softwood and sludge with the sole precursor

An increase in the SW weight percentage from 10% to 25% in the mixtures slightly increased mass loss of these samples because SW contains more volatile matter than SS (Xu et al. 2017)

Figure 4.3 compares the DTG rates obtained from experiments with the theoretical values determined through equation 3-2. Experimental DTG rates were measured fewer than the calculated rates in both blend rations. Increasing the softwood percentage augmented that discrepancy. Hence, no synergetic effect between these two waste samples is expected in their co-carbonization. The same behavior was observed in the blend of dewatered sewage sludge and pine sawdust (Zhu et al. 2015).

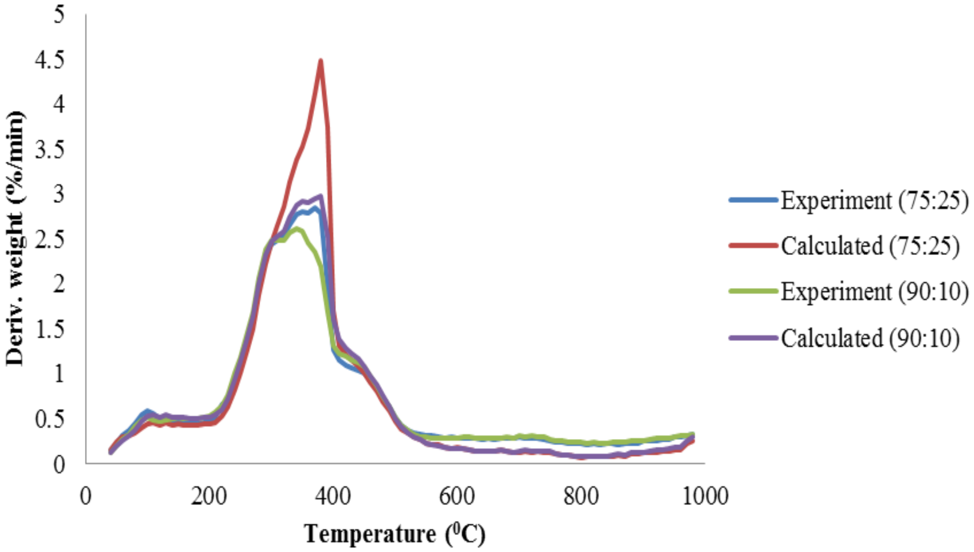


Figure 4.3 Comparison of experimental and theoretical DTG curves for two blend ratios (wt.%) of softwood (SW) and sludge (SS)

Inhibitive interaction occurred in the temperature range of 280-400 °C where the wood residue is mostly decomposed. Xu et al. (2017) attributed this behavior to two reasons: i) lignocellulosic materials exhibited low thermal conductivity, therefore, increasing the weight of wood residue may inhibit the thermal transfer; ii) wood waste has higher volatile content than SS, while temperature increases, the accumulation of wood residue could block the pore structure and decelerate several polymerization and condensation reactions.

Huang et al. (2017) indicated pyrolysis of the blend of sludge and fir sawdust at 500 °C caused reduction of textural properties. The surface area and micropore volume of the resulting carbon material were lower than the adsorbent obtained from sole sludge carbonized at the same temperature. The authors recommended investigating the appropriate catalysis to promote the textural properties of the mixture. Similarly, Jin et al. (2017) indicated the co-pyrolysis of sludge and bamboo sawdust up to 500 °C resulted in adsorbents with a lower specific area in comparison to the sole sludge pyrolysis. It could be attributed to the formation of tars resulted from bamboo sawdust thermal decomposition.

Therefore, the results suggested for acquiring sludge-based adsorbent with well-developed textural properties it is needed to employ suitable activator. Regarding the thermal behavior of primary materials and previous research works on the pyrolysis of sludge, a methodology (section 3.3.4) based on KOH activation for the production of SBA was proposed. The following section illustrates the outcomes associated with the produced SBAs.

4.2.2. Characterization of adsorbents

4.2.2.1. Textural properties of the new products and commercial activated carbon

The nitrogen gas adsorption-desorption isotherms of adsorbents derived from sludge, the mixture of sludge and wood residues, and commercial activated carbon are presented in Figure 4.4.

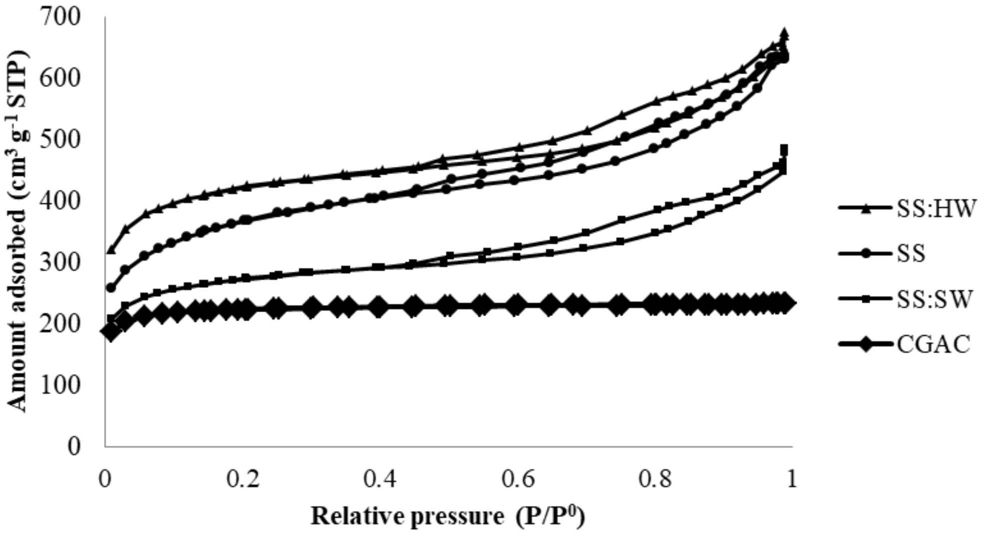


Figure 4.4 Nitrogen gas adsorption-desorption isotherms for prepared new sludge-based adsorbents and commercial activated carbon

The carbonaceous products presented higher adsorption capacities than the CGAC. According to the International Union of Pure and Applied Chemistry (IUPAC) classification (Thommes et al.

2015), sludge-based carbons possessed type IV isotherm with H4 loop hysteresis indicating its micro-mesoporous texture. CGAC was displayed as a type I isotherm showing its essential microporous nature since it presented a marked knee in the low relative pressure region, and a horizontal plateau in the multilayer, indicating a low external surface and the absence of significant mesoporosity (Mestre et al. 2011).

Table 4.4 presents textural and morphological properties and also the yields of resulting products and commercial activated carbon. The results indicated the single-step activation with solid KOH could be an effective methodology to produce the carbon adsorbent with high surface area and developed porosity from both sole sludge and mixture precursors.

KOH can react with carbon atoms at high temperatures (600– 900 °C) and form metallic K as well as K_2CO_3, CO, and H_2. The potassium compounds formed in the course of the process are efficiently intercalated into the carbon matrix and their subsequent removal using acid wash results in the highly porous carbon structure accompanied by a high specific surface area (Singh et al. 2017b; Li et al. 2016).

Table 4.4 Textural properties of produced new sludge-based adsorbents and commercial activated carbon and the yield of carbon products

Sample	S_{BET} (m^2 g^{-1})	V_t (cm^3 g^{-1})	W_p (nm)	V_{mic} (cm^3 g^{-1})	W_0 (nm)	V_{mic}/V_t	V_{meso} (cm^3 g^{-1})	Yield (%)
SS	1320	0.96	2.9	0.55	1.71	0.57	0.41	10%
SS:SW	999	0.69	2.7	0.41	1.65	0.59	0.28	17%
SS:HW	1565	0.99	2.5	0.73	1.64	0.73	0.26	16%
CGAC	870	0.36	1.7	0.32	1.86	0.88	0.04	-

W_p = average pore width, assumed cylindrical shape pore, $W_p = 4V_{total}/S_{BET}$

The mixture of HW and SS acquired the highest specific surface area and total pore volume relative to the other samples. In comparison to the SS adsorbent addition of hardwood resulted in an increase in the degree of microporosity and volume of micropores up to 16% and 32%, respectively. The addition of wood led to a more microporous carbon structure since the degree of microporosity was also slightly increased in the case of SS:SW adsorbent. This could suggest the effect of biomass addition in the development of microporosity. Similar findings have been highlighted in other studies where addition of carbon-rich biomass such as corn cobs, industrial oil sludge, and coconut husk to the sewage sludge have led to an increase in microporosity of the matrix (Wu et al. 2013; Seredych and Bandosz 2007; Tay et al. 2001).

Furthermore, in comparison to the sole sludge activation, the yields of final products were increased by 6% and 7% with the addition of hardwood and softwood residues, respectively. The higher fixed carbon content of wood residues could justify the increase in the yield of carbonaceous adsorbents prepared from the mixtures. Same results were reported for the co-activation of rice husk and oily sludge with solid KOH where the yield of the product prepared from the mixture of feedstocks was 15.9%, although, the yield of oily sludge and rice husk derived products were measured 4.5% and 8.3%, respectively (Wang et al. 2018).

4.2.2.1.1. Comparison of the new adsorbents with the previous studies

Table 4.5 summarizes the experimental conditions as well as the surface area of the sludge-based adsorbents derived from activation of sole secondary sludge as well as co-activation of the secondary sludge and biomass in previous research work.

Table 4.5 Properties of sludge-based adsorbents and heating conditions reported in the previous research works

Precursor	Activator	Mixing ratio	Pre-treatment	Activation temperature (°C)	Holding time (min)	Post-treatment	S_{BET} (m^2 g^{-1})	Ref
SS:HW	KOH (mixture)	2:1:2 w_{sludge}:$w_{biomass}$:w_{KOH}	-	750	60	HCl (3M)	1565	Present study
SS	KOH (mixture)	1:1 w_{KOH}:w_{sludge}	-	750	60	HCl (3M)	1320	Present study
SS:SW	KOH (mixture)	2:1:2 w_{sludge}:$w_{biomass}$:w_{KOH}	-	750	60	HCl (3M)	999	Present study
Sludge/corn straw	KOH (impregnation)	3:7:6 w_{sludge}:$w_{biomass}$:w_{KOH}	-	750	60	HCl (3M)	689	(Zeng et al. 2017)
Sludge/corn stalk	$ZnCl_2$ (impregnation)	-	-	600	60	HCl (3M)	769	(Li, et al 2016)
Sludge/corn cob	KOH (impregnation)	2:1 w_{KOH}:w_{sludge}	Carbonization at 550°C	800	90	-	591	(Wu et al. 2013)
Sludge/ coconut husk	$ZnCl_2$ (impregnation)	-	-	500	120	HCl (3M)	867	(Tay, J. H et al. 2001)
Sludge	KOH (mixture)	3:1 w_{KOH}:w_{sludge}	Carbonization At 700°C	700	60	HCl (5M)	1301	(Lillo-Ródenas et al. 2008)

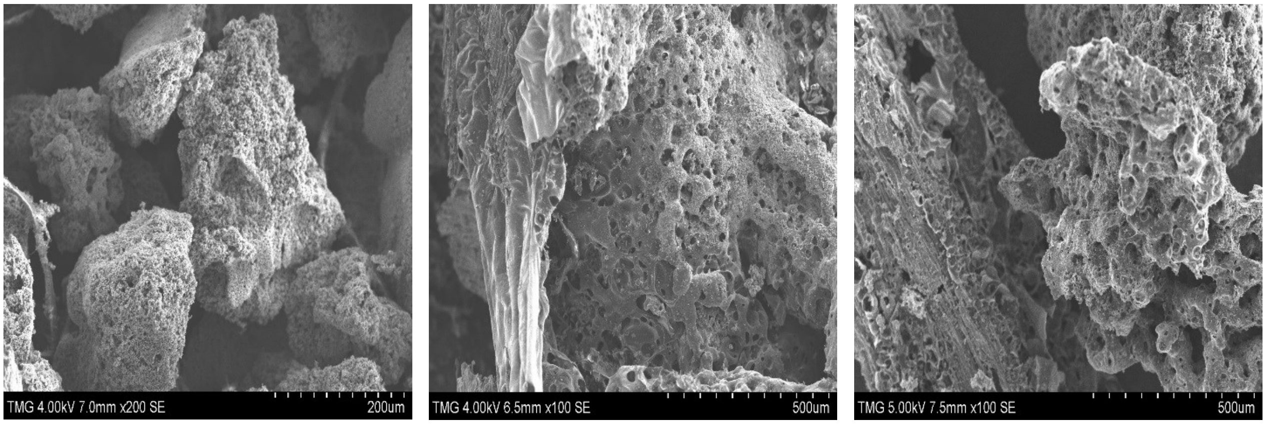
Sludge	KOH (mixture)	3:1 $w_{KOH}:w_{sludge}$	-	750	30	HCl (5M)	1832	(Monsalvo et al. 2011)
Sludge	KOH (mixture)	3:1 $w_{KOH}:w_{sludge}$	Carbonization at 700°C	700	60	HCl (5M)	1686	(Ros et al. 2006)

While the experimental condition of the present work is comparable with the previous studies, the prepared SBAs derived from the mixture of sludge and wood waste acquired higher surface areas in comparison to the previously reported SBAs derived from the mixture of sludge with other biomasses.

Furthermore, the textural properties of SS:HW product is comparable with previous studies in which higher surface area of sludge-based adsorbents were prepared by KOH activation of sole sludge. Maximum surface areas of 1832 m^2 g^{-1} and 1686 m^2 g^{-1} was previously reported for the secondary sludge-based adsorbent in two studies (Monsalvo et al. 2011; Ros et al. 2006). However, in those studies, sole sludge was either carbonized prior to the activation by KOH (i.e. two steps pyrolysis) or mixed with three times more activator. In the present work, co-processing of hardwood waste with the sludge in a single step activation process could be more advantageous since it involves shorter processing time, and lower energy and chemical consumption. In addition, as a result of co-processing of two waste larger amount of waste than the previous work was transformed into the value-added materials.

4.2.2.2. Surface morphology of the new sludge-based adsorbents

The SEM technique is employed to observe the surface morphology of the sludge-based carbon adsorbents. Figure 4.5 illustrated the micrograph of the prepared new adsorbents.



a b c

Figure 4.5 Micrograph of new sludge-based adsorbents a) SS, b) SS:SW, and c) SS:HW

The SEM micrographs of the prepared adsorbents confirmed their porous structure which could be attributed to the aggressive attack of the reagent during activation. However, the microstructure of the samples was completely different; the SS adsorbent had a distinct fluffy shape while SS:HW and SS:SW revealed a composite structure and irregular pores. More SEM micrographs are also provided in the appendix of this manuscript.

4.2.2.3. FTIR-ATR analysis of the produced new adsorbents

FTIR analysis could show a qualitative difference in the surface functional group between the resulting solid matrices. Figure 4.6 presents the FTIR-ATR spectrum of the prepared carbon products.

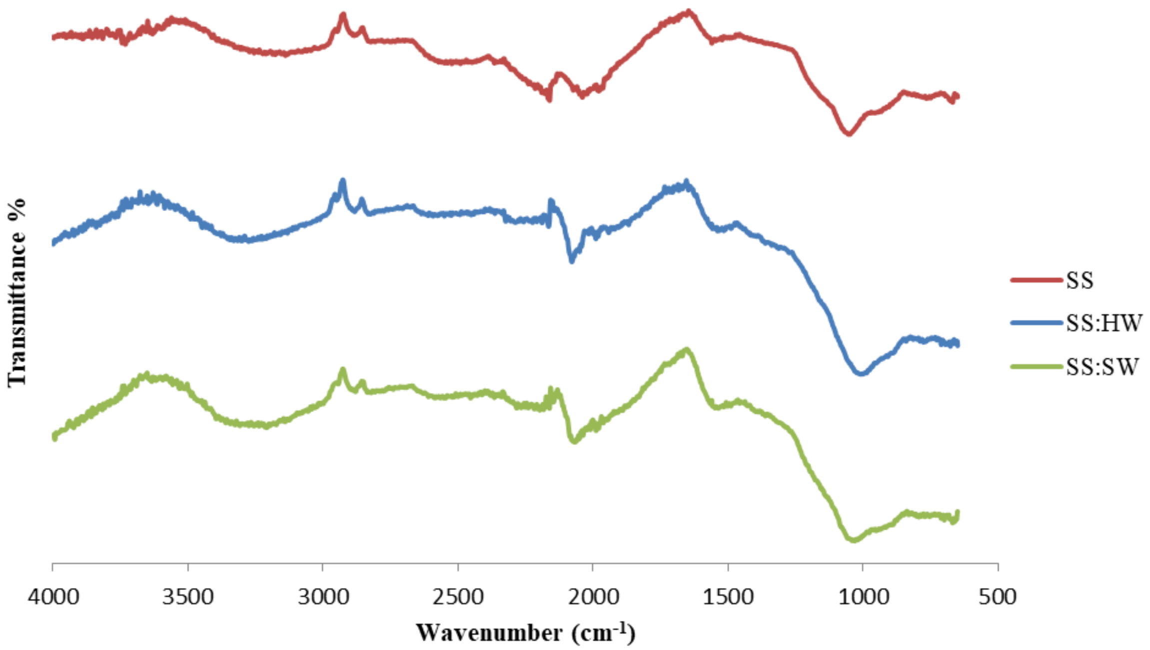


Figure 4.6 FTIR-ATR spectra of the materials prepared from sludge (SS), mixture of sludge and hardwood (SS:HW), and mixture of sludge and softwood (SS:SW)

The prominent broad band between 3100-3600 cm^{-1} representing the stretching vibration of hydrogen-bonded hydroxyl groups present in alcohols, phenols, and carboxylic acids (Gomez et al. 2009). The bands between 3600-3700 cm^{-1} region (stretching of internal bonded OH group) for the sludge-derived adsorbent can be attributed to minerals as also indicated by the high ash content of the sludge (Figueiredo et al. 2018). The near-absence band at the 2880 cm^{-1} for all products can be ascribed to the presence of saturated aliphatic groups (–CH). The stronger bands located at about 1550 cm^{-1} that can be assigned to skeletal C=C stretching vibration in aromatic rings. The introduction of wood residues to the sludge led to creation of more aliphatic and aromatic carbon structures in the final products. The absorption peacks between 2000 and 2200 cm^{-1}, can be linked to the cyano groups (C≡N), cumulated double bond (–N=C=N–) and similar species (such as isocyanides) indicating incorporation of nitrogen to carbon structure (Kante et al. 2008). The wide band at around 1050 cm^{-1} is common to sludge-based adsorbents, and may be attributed to the presence of C–O stretching vibration of alcoholic, phenolic and carboxylic groups (Lin et al. 2012). It can also be assigned to Si–O–Si and Si–O–C groups (Smith et al. 2012) which would indicate the contribution of minerals in the formation of sludge-based materials. The spectral 680-900 cm^{-1} band could be associated with the presence of aromatic groups, as well as Si–C and Si–O vibration of inorganic materials, in the products (Zielińska et al. 2015).

4.2.2.4. Determination of pH_{pzc} of adsorbents

The point zero charge (pH_{pzc}) is the pH in which the net surface charge of the carbon adsorbent is neutral (Moreno-Castilla 2004). It also provides an indication of acidity and basicity of the carbon surface (Mestre et al. 2014).

The pH_{final} –$pH_{initial}$ value was plotted versus the initial pH value in Figure 4.7. The point of intersection of the resulting curve with the axis of abscissas resulted in the pH_{pzc}. Therefore, this value was measured 7.0, 6.7, 6.0, and 5.0 for the CGAC, SS, SS:HW, and SS:SW, respectively.

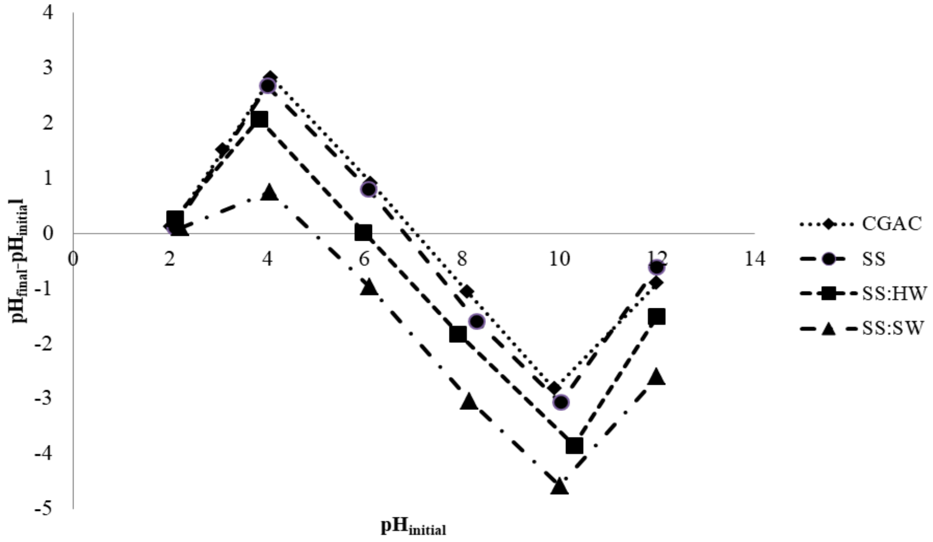


Figure 4.7 Point of zero charge of the new sludge-based adsorbents and commercial carbon

Given the pH_{pzc} value of the samples, the acidity of the prepared carbon materials was in the following order of SS:SW>SS:HW>SS indicating the strength of the surface acidity was increased after wood addition.

The increase in the acidity of the mixture adsorbents could be linked to the enhancement of the IR absorption bands assigned to the acidic oxygenated functionalities such as alcoholic and phenolic groups after wood addition. Wu et al. (2013) reported changes in the oxygenated functional groups and correlated them to a change in the acidity of sludge-based adsorbents after the addition of biomass.

These results confirmed that addition of woody biomass to the sludge not only changed the porosity and surface area of the adsorbents but also altered the surface chemistry of the resulting products.

4.3. Performance evaluation

4.3.1. Effect of contact time in sorption of VEN from aqueous solution

An adsorption process, especially that was performed on porous adsorbent requires some time to achieve the equilibrium state (Bedia et al. 2018). As can be seen in Figures 4.8 a, and 4.8 b, adsorption of VEN involves an initial faster stage and a more gradual occupation of active sites until the adsorption reaches equilibrium where no more adsorbate is further removed from the solution. Based on the obtained data it was concluded that 48 h-contact time was enough to reach equilibrium for sorption of VEN by SS:HW and CGAC.

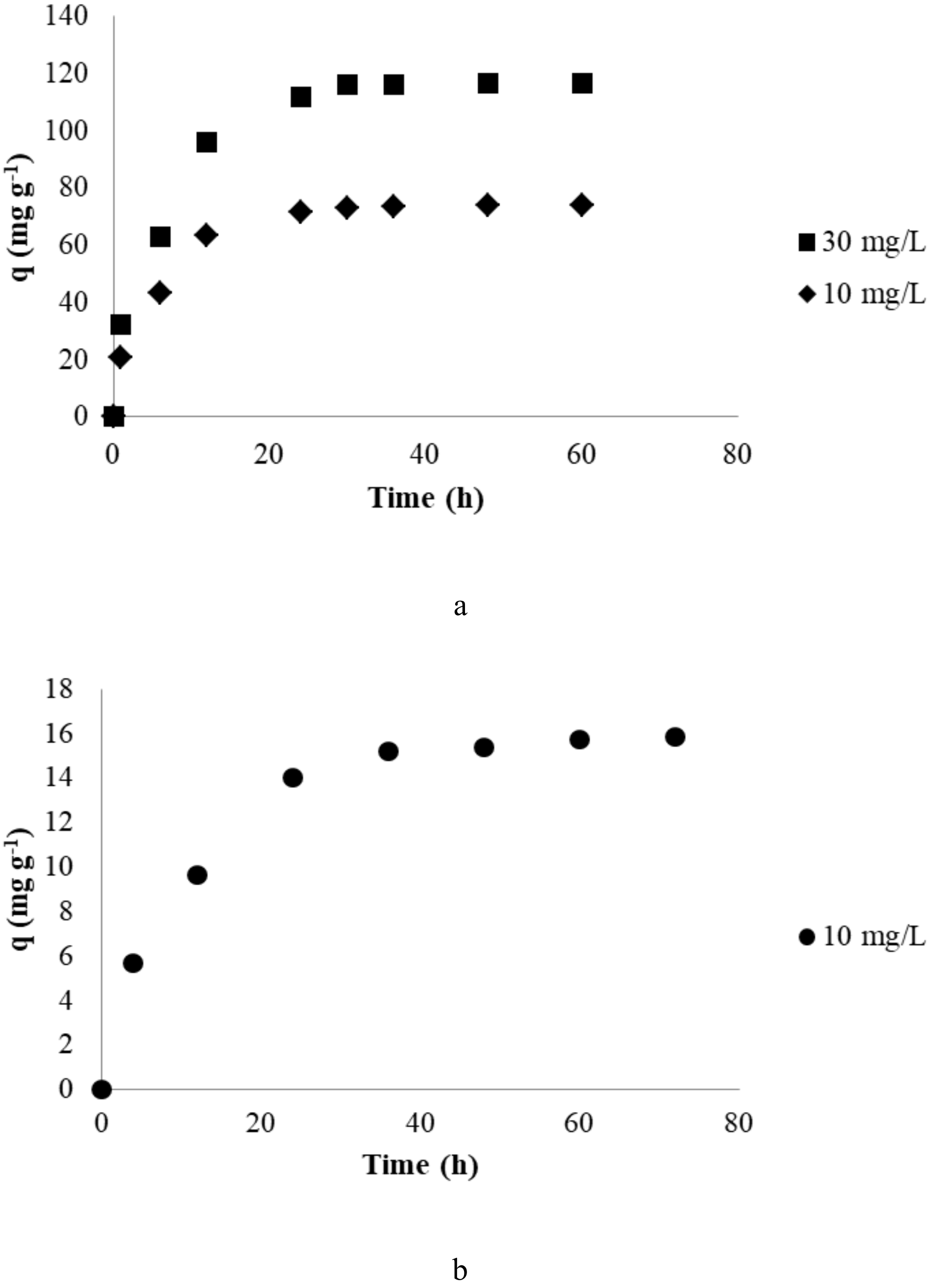


Figure 4.8 Effect of contact time on adsorption of VEN onto a) SS:HW (initial concentrations: 10 and 30 mg L^{-1}, the dosage of adsorbent: 0.083 g L^{-1}) and b) CGAC (initial concentration 10 mg L^{-1}, dosage of adsorbent: 0.4 g L^{-1}).

4.3.2. Kinetic modeling of VEN sorption

The results of kinetic data analysis are summarized in Table 4.6. The best fit model is the one with the lowest value of SD and the one with a closer amount of R^2 to unity (Bergmann and Machado 2015).

Table 4.6 Kinetic data predicted by pseudo-first order (PFO), pseudo-second order (PSO) and Elovich models for adsorption of VEN to SS:HW product and commercial carbon

Adsorbent	Initial Conc.	q_{exp}	PFO				PSO				Elovich			
			k_1	q_e	R^2	SD	k_2	q_e	R^2	SD	α	β	R^2	SD
SS:HW	10	73.86	0.168	73.42	0.9938	3.74	3×10^{-3}	80.82	0.9947	3.05	0.345	14.07	0.9891	4.32
	30	116.57	0.147	116.3	0.9916	6.51	1×10^{-3}	129.59	0.9926	5.81	0.179	22.81	0.9754	6.99
CGAC	10	15.39	0.089	15.75	0.9973	0.48	5×10^{-3}	18.39	0.9960	0.53	0.338	3.73	0.9913	0.83

Initial concentration (mg L^{-1}), q_e represents the amount of solute adsorbed at equilibrium (mg g^{-1}), k_1 (h^{-1}) and k_2 (mg g^{-1} h^{-1}) the pseudo- first and pseudo-second order rate constant, respectively. α (mg g^{-1} h^{-1}) is the initial adsorption rate, and β (g mg^{-1}) is adsorption coefficient.

Statistical analysis showed the PSO as the best model fitted to the experimental data for the adsorption of VEN onto SS:HW. It is noteworthy, the correlation coefficient R^2 for both PFO and PSO are quite close to the unity (>0.99) also the value of estimated adsorption capacity by PFO is very close to the experimental value (q_{exp}). Hence, both models considered reasonably describe the experimental data. The same behaviour was reported for adsorption of other PhACs to the carbonaceous adsorbents (Jaria et al. 2019; Álvarez-Torrellas et al. 2016a; Jaria et al. 2015). Given the statistical analysis and value of predicted adsorption capacity, the experimental data were well fitted to the PFO kinetic model in the case of CGAC.

In the case of SS:HW the rate constants k_1 and k_2 were decreased with increasing the initial VEN concentration, which reveals the fact that it is faster for an adsorption system with VEN at lower initial concentrations to reach equilibrium The rate constant of Elovich model also confirmed that. The similar behaviour was also reported for the adsorption of pharmaceutical compounds such as ibuprofen on activated carbon (Mondal, Bobde et al. 2016; Mestre et al. 2007). The adsorption capacity was increased by increasing the initial concentration. This is related to the driving force of concentration gradients to overcome the mass transfer resistance of adsorbate between aqueous and adsorbent which has been increased by increasing the initial VEN concentrations (Hadi et al. 2015). Furthermore, higher initial adsorbate concentrations results in more collision between the adsorbent particles and VEN molecules leading to the enhancement of adsorption capacity (Hadi et al. 2015).

4.3.3. Comparison of the sorption capability of adsorbents

The three prepared sludge-based carbon materials along with the CGAC were assayed as adsorbents of VEN from aqueous solution (Figure 4.9). The adsorbent performance decreased in the order of: SS:HW>SS>SS:SW>CGAC. Considering the textural properties of carbon materials, the prepared sludge-based adsorbents acquired higher surface areas with well-developed networks of micro-mesoporosities in comparison to the strictly microporous CGAC. The presence of an adequate network of mesopores in the structures of SBAs allows the adsorbate molecules to access the inner micropores (Jaria et al. 2019 and Baccar et al. 2012). This may remarkably enhance the sorption capability of the SBAs relative to the CGAC.

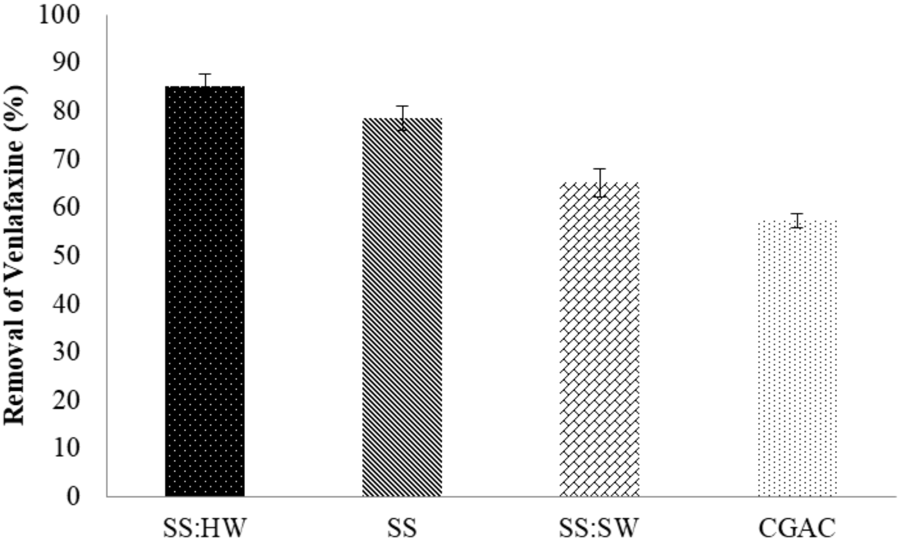
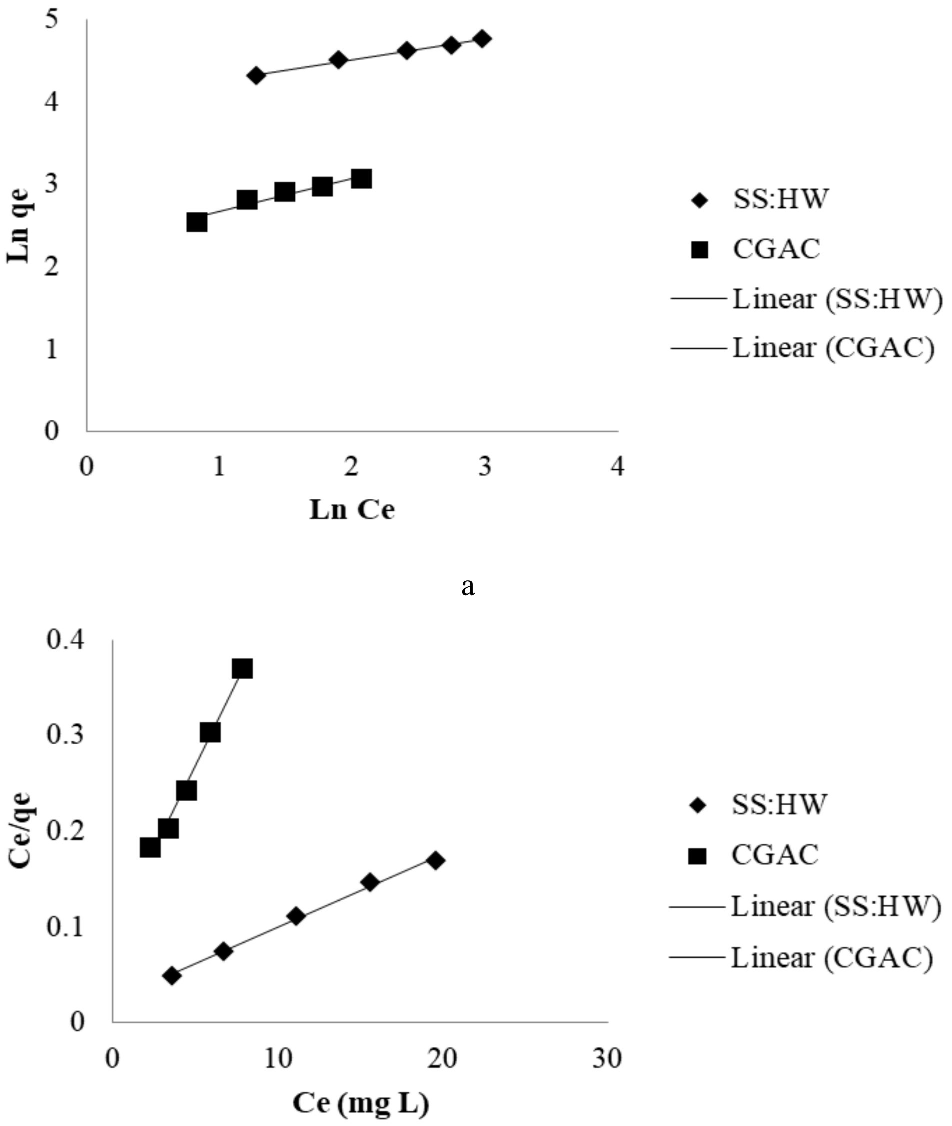


Figure 4.9 Removal efficiencies of studied adsorbents assayed for VEN removal (volume of solution 50 mL, contact time 48 h, mass of produced carbon materials and CGAC was 5 mg and 20 mg, respectively), number of samples=3

Furthermore, the role of chemical interaction between the adsorbate and SBAs may be involved in the sorption process. The functional groups on the surface of prepared materials are potential binding sites for the VEN molecule. FTIR analysis confirmed the presence of oxygenated functional groups on the surface of the prepared SBAs. Moreover, given the VEN structure, three hydrogen bond acceptors are present (Calisto et al 2015) which could interact with the surface of SBAs. In addition, the π-π electron donor-acceptor (EDA) interaction has been proposed for the sorption of aromatic structure pharmaceutical onto carbon solids (Spessato et al. 2019; Chen et al. 2017). The benzene ring of VEN molecules can play as a π-electron acceptor and the aromatic moieties and electron-rich OH group of SBAs are strong electron donors resulting in π-π electron donor-acceptor (EDA) interaction.

4.3.4. Adsorption isotherms

Adsorption isotherm study provides fundamental physiochemical data to assess the adsorption capacities of adsorbents, one of the most important criteria in selecting a suitable adsorbent. In the present study, experimental data were fitted to Langmuir, Freundlich isotherm models (Figure 4.10).



a

b

Figure 4.10 Experimental data of adsorption isotherm and fitting of a) Freundlich, b) Langmuir

The parameters obtained from those two models were shown in Table 4.7. Given to the correlation coefficient, R^2, the comparison of tested models for the description of equilibrium adsorption isotherms on both adsorbents is as follows: Langmuir> Freundlich.

The Freundlich adsorption model is used to describe the multi-layer adsorption process on heterogeneous solid surfaces. In this model, the favorability of VEN adsorption onto prepared carbons can be concluded from the values of parameter *n*. The value *n*>1 represents a favourable condition. For both adsorbent *n* was measured higher than 1 indicating the adsorption process

Table 4.7 Equilibrium isotherms constants for adsorption of VEN onto SS:HW and CGAC adsorbents

Adsorbent	Freundlich			Langmuir		
	K_f (L mg^{-1})	n	R^2	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2
SS:HW	54.55	3.96	0.9879	131.57	0.33	0.9963
CGAC	9.57	2.46	0.9322	28.57	0.37	0.9915

was favourable. The *n* value for SS:HW adsorbent is higher than CGAC leading to the conclusion SS:HW is more efficient in VEN adsorption.

The best fitting for experimental data was achieved by Langmuir (R^2>0.99) which is valid for monolayer adsorption within the adsorbent surface with a uniform distribution of energy level. In the case of the SS:HW adsorbent the value of the separation factor (R_L) obtained from different initial concentrations of VEN is depicted in Figure 4.11.

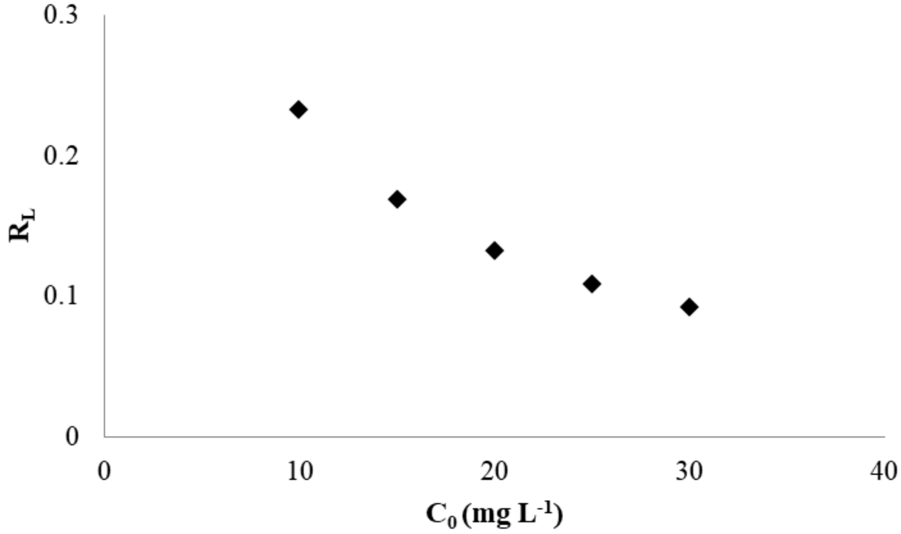


Figure 4.11 Plot of the separation factor (R_L) versus VEN initial concentration.

If $R_L = 0$, the adsorption is irreversible, if $0<R_L<1$ it is favorable, if $R_L=1$ it is linear and if $R_L>1$ it is unfavorable. The measured values of R_L are less than 1 showing the suitability of SS:HW adsorbent in sorption of VEN. With increasing initial concentration, R_L approached to the zero and adsorption reaction desire to irreversibility.

Based on the Langmuir isotherm the maximum adsorption capacity of venlafaxine onto the SS:HW product was higher than that of CGAC as well as previously reported values of different adsorbent materials. The maximum adsorption capacities of different adsorbents are listed in Table 4.8.

Table 4.8 Comparison of maximum adsorption capacity of VEN on various adsorbent and their respective surface area

Adsorbent	q_{max} (mg g^{-1})	Surface area (m^2 g^{-1})	Ref
SS:HW	131.57	1565	Present study
CGAC	28.57	870	Present study
Expanded vermiculite	3.9	9	(Silva et al. 2018a)
Vermiculite	5.8	21	(Silva et al. 2018a)
Acid-base treated vermiculite	33	45	(Silva et al. 2018a)
Base treated vermiculite	6.3	18	(Silva et al. 2018a)
Paper mill sludge-based carbon	8.5	209.12	(Calisto et al. 2015)
Commercial activated carbon (PBFG4)	42.6	848.22	(Calisto et al. 2015)

In the case of SS:HW adsorbent, high regression coefficients (R^2>0.98) of both isotherms were obtained. According to Tan and Sen (2019) this could basically suggest sorption of VEN molecules takes place on the heterogeneous adsorbent's active sites (Freundlich adsorption) after completion of the monolayer (Langmuir adsorption) adsorption.

4.3.5. Adsorptive performance in the real wastewater effluent sample

As Table 4.9 shows ten EOMs including different therapeutic classes of PhACs such as non-steroidal anti-inflammatory drugs (DCF), psychiatric drugs (VEN and CBZ), antibiotics (SMX and CLT), and beta-blockers (ACB), as well as stimulants (CAF), a pharmaceutical metabolite compound (DVEN), herbicides (ATZ), and its transformation product (DEA) were present in the wastewater effluent sample.

The concentrations of compounds in the blank sample indicated no significant losses of adsorbates were occurred during the batch experiment. Hence, the decrease in the EOMs concentrations were all attributed to the sorption by adsorbents.

Table 4.9 Concentration (ng L^{-1}) of detected pharmaceutical compounds before and after batch adsorption experiment

Compound	Initial concentration	Final concentration					
			Mass of SS:HW adsorbent				Mass of CGAC
		Blank	2 mg	5 mg	15 mg	30 mg	2 mg
CAF	53.0	49.6	n.d	n.d	n.d	n.d	37.7
ACB	51.8	49	n.d	n.d	n.d	n.d	27.4
VEN	1993	2091	198	97.2	42	21	2123
DVEN	2186	2058	876	250	18.4	4.2	2116
SMX	180	170	n.d	n.d	n.d	n.d	n.d
ATZ	18.4	20.3	3.8	2.8	n.d	n.d	14
DEA	21.4	23.7	n.d	n.d	n.d	n.d	n.d
CBZ	635	619	40.2	14.1	n.d	n.d	442
DCF	500	494	83.9	23.7	n.d	n.d	419
CLT	27.4	26.1	9.9	3.6	n.d	n.d	30.6

Blank: without adsorbent, n.d: not detected

According to equation 3-1 total mass loading of EOMs in the spiked effluent was measured 1535.56 mg/day/1000 inhabitants. After treatment by the lowest dosage of SS:HW product this value dropped to 328.16 mg/day/1000 equaling more than 78% efficiency. At the highest dosage of produced sludge-based adsorbent total mass loading of EOMs was significantly declined to the quite negligible amount of 6.84 mg/day/1000 inhabitants. CGAC was ineffective to reduce the mass load of EOMs since this measure was reduced merely 8% in the case of commercial activated carbon.

Venlafaxine was removed effectively by the SS:HW product from wastewater effluent. Given Table 4.9 at the lowest dosage of SS:HW (30 mg L^{-1}), the antidepressant was removed by 90% while CGAC failed to adsorb VEN from the effluent sample. The removal percentage of SS:HW product was also comparable with the study (Alves et al,. 2018) which reported 79% removal of VEN with a dosage of 20 mg L^{-1} of a chemically activated commercial carbon in a secondary effluent sample after 48 h contact time.

The same behaviour was observed for the VEN metabolite and CLT. The 2 mg of adsorbent prepared from the mixture of sludge and hardwood was able to remove almost 59.9% and 63.8 % of the DVEN and CLT from the effluent sample whereas CGAC failed to do so. The psychiatric drug, CBZ, was removed 93% by the lowest dosage of SS:HW adsorbent while CGAC at the same dosage of adsorbent adsorbed only 30% of the CBZ. SS:HW adsorbent was able to adsorb 79.3%, and 83.2%, of ATZ, and DCF respectively at the lowest dosage, while these values dropped to 24%, and 16%, respectively, in the case of CGAC.

Four compounds including CAF, ACB, SMX, and DEA were not detected in the samples after adsorption with the SS:HW adsorbent. Similarly, SMX and DEA were not detected in the case of CGAC. However, CAF and ACB removal efficiency with CGAC were obtained 28.8% and 47.1%, respectively.

Increasing the mass of SS:HW adsorbent increased the removal efficiencies which could be attributed to the availability of more active sites on the adsorbent surface to adsorb contaminants. At the two highest masses of SS:HW adsorbent all of the listed EOMs in Table 4.9 were completely removed with the exception of VEN and DVEN whose concentration decreased by 97% and 99%, respectively.

Despite the presence of the background organic compounds and competitive sorption of salutes in a complex matrix such a secondary effluent, the results revealed the highly enriched micro-mesopores carbonaceous adsorbent prepared from the mixture of sewage sludge and hardwood residue exhibited satisfactory adsorptive performance for different micropollutants involving multiclass of pharmaceuticals, metabolite compounds, herbicides, and transformation products.

The outstanding performance of SS:HW sludge-based adsorbent could reduce effectively the mass load of EOM discharging from the WWTP's outfall. Therefore, such a carbon adsorbent could be utilized as a suitable alternative for the commercially available activated carbons in tertiary treatments of the wastewater treatment industry.

5. Conclusions and Future Work

Chapter 5 summarizes the general conclusions from the obtained results. Furthermore, the research contribution, future developments and recommendations are also included.

5.1. Conclusions

1- Sixteen out of thirty tested EOMs were observed at the concentrations ranging from a few ng L^{-1} to $\mu g\ L^{-1}$ in the wastewater effluent of the targeted WWTP. The detected chemicals belong to different classes of compounds including pharmaceutical compounds, their respective metabolites, hormones as well as herbicides and transformation products. The results revealed the present conventional biological treatment inside the WWTP is ineffective in removing the EOMs. Hence, mass loads of micropollutants are continuously discharged to the Saint Lawrence River. Psychiatric drugs and their associated metabolites possess almost 62% of the mass loads of detected micropollutants in the wastewater effluent. Furthermore, ten out of thirty compounds were also detected in the Saint Lawrence River. The same classes of chemicals except hormones were present in the river. While all contaminants except for herbicides were observed at the higher magnitudes in the treated wastewater than the surface water, the distribution pattern was almost the same in which the metabolite and transformation products compounds were at the higher levels than the parent compounds.

2- Wasted sewage sludge and wood chips additives found to be adequate primary compounds for the production of new adsorptive materials (SBA). The developed production method showed that single-step activation process with potassium hydroxide can be suitable for producing new SBA from a mixture of sludge and wood residues. The resulting new sludge-based adsorbents exhibited a high surface area with a well-developed pore structure. In comparison with the adsorbent derived from sole secondary sludge, co-activation of sludge and hardwood residues exhibited a synergic effect; the surface area was increased from 1320 $m^2\ g^{-1}$ to 1565 $m^2\ g^{-1}$ and degree of microporosity was raised 16%. Also, the strength of the surface acidity and yield of products were increased after wood addition.

3- Sorption of Venlafaxine (VEN) from aqueous solution onto the new SBAs was remarkably more favorable than the commercial granular activated carbon (CGAC). While the maximum sorption capacity of VEN onto the mixture of sludge and hardwood (SS:HW) adsorbent was measured 131.5 mg g^{-1} from the Langmuir isotherm in the case of CGAC this value significantly dipped to 28.57 mg g^{-1}. The maximum sorption capacity of SS:HW was also exceptionally higher than the previously reported values in the literature. Furthermore, significant higher removal efficiencies for the new SBAs derived from sole sludge as well as the mixture of sludge: softwood was also observed in comparison to the CGAC.

4- Performance of the SS:HW product was verified in real WWTP effluent, containing a variety of EOMs, TOC, and traces of metals. Multi-class of EOMs was successfully removed by the SS:HW product form wastewater effluent samples. For instance, VEN was removed with 90% efficiency at the lowest dosage of SS:HW, 33 mg L^{-1}. The same dosage of CGAC failed to do so. Furthermore, mass loads of the detected EOMs in the wastewater effluent sample was decreased 78% with the lowest dosage of SS:HW. Mass load of EOMs reduced more than 99% at the maximum dosage of SS:HW which was 0.5 g L^{-1}. The results showed the pore enriched SS:HW adsorbent could be a suitable alternative for the commercial activated carbons in the wastewater treatment plants.

5.2. Contributions

This study permitted to understand the contribution of pharmaceutical metabolite compounds in the wastewater effluent and Saint Lawrence River could be more pronounced than the drug's parent compounds. Hence, it is required to attribute more attention to the occurrence of these xenobiotics in the waste streams and Canadian aquatic terrestrial.

It was found that hardwood residue addition to the secondary sludge could enhance the textural properties of the produced sludge-based adsorbent. Single-step activation of that particular mixture with the solid KOH showed to be an effective methodology to produce highly micro and mesoporous carbon adsorbent. The produced new carbon material possessed remarkable sorption capacity for the removal of micropollutants. Hence, such a methodology could be an effective alternative waste management technique particularly in Canada where both types of waste are generated in large amounts.

5.3. Future work

Optimization of the proposed thermal methodology regarding the final temperature, residence time, and activator dosage can be investigated.

Furthermore, a sorption column study of the venlafaxine from aqueous solution with the sludge-based adsorbent is recommended. Also, the column study could be done for the real wastewater effluent at the pilot scale.

Regeneration of the exhausted adsorbents can be assessed which could reduce the cost of treatment. However, a life cycle assessment supposes to be conducted in order to assess the sustainability of the regeneration considering the fact that the new adsorptive material is produced from waste.

Reference

Abegglen, C., and Siegrist, H. (2012). "Micropolluants dans les eaux usées urbaines." *Etapes De Traitement Supplémentaire Dans Les Stations D'Épuration. Swiss Federal Office for the Environment, Connaissance De L'Environnement,* 1214 87.

Afonso-Olivares, C., Čadková, T., Sosa-Ferrera, Z., Santana-Rodríguez, J., and Nováková, L. (2017). "Simplified solid-phase extraction procedure combined with liquid chromatography tandem–mass spectrometry for multiresidue assessment of pharmaceutical compounds in environmental liquid samples." *Journal of Chromatography A,* 1487 54-63.

Agrafioti, E., Bouras, G., Kalderis, D., and Diamadopoulos, E. (2013). "Biochar production by sewage sludge pyrolysis." *J.Anal.Appl.Pyrolysis,* 101 72-78.

Ahmadpour, A., and Do, D. (1996). "The preparation of active carbons from coal by chemical and physical activation." *Carbon,* 34(4), 471-479.

Akhtar, J., Amin, N. A. S., and Shahzad, K. (2016). "A review on removal of pharmaceuticals from water by adsorption." *Desalination and Water Treatment,* 57(27), 12842-12860.

Álvarez-Torrellas, S., Muñoz, M., Zazo, J., Casas, J., and García, J. (2016a). "Synthesis of high surface area carbon adsorbents prepared from pine sawdust-Onopordum acanthium L. for nonsteroidal anti-inflammatory drugs adsorption." *J.Environ.Manage.,* 183 294-305.

Álvarez-Torrellas, S., Rodríguez, A., Ovejero, G., and García, J. (2016b). "Comparative adsorption performance of ibuprofen and tetracycline from aqueous solution by carbonaceous materials." *Chem.Eng.J.,* 283 936-947.

Alves, T. C., Cabrera-Codony, A., Barceló, D., Rodriguez-Mozaz, S., Pinheiro, A., and Gonzalez-Olmos, R. (2018). "Influencing factors on the removal of pharmaceuticals from water with micro-grain activated carbon." *Water Res.,* 144 402-412.

Andrási, N., Molnár, B., Dobos, B., Vasanits-Zsigrai, A., Záray, G., and Molnár-Perl, I. (2013). "Determination of steroids in the dissolved and in the suspended phases of wastewater and Danube River samples by gas chromatography, tandem mass spectrometry." *Talanta,* 115 367-373.

Azaïs, A., Mendret, J., Gassara, S., Petit, E., Deratani, A., and Brosillon, S. (2014). "Nanofiltration for wastewater reuse: counteractive effects of fouling and matrice on the rejection of pharmaceutical active compounds." *Separation and Purification Technology,* 133 313-327.

Azargohar, R., and Dalai, A. (2008). "Steam and KOH activation of biochar: Experimental and modeling studies." *Microporous and Mesoporous Materials,* 110(2-3), 413-421.

Baccar, R., Sarrà, M., Bouzid, J., Feki, M., and Blánquez, P. (2012). "Removal of pharmaceutical compounds by activated carbon prepared from agricultural by-product." *Chem.Eng.J.,* 211 310-317.

Bagreev, A., Bandosz, T. J., and Locke, D. C. (2001). "Pore structure and surface chemistry of adsorbents obtained by pyrolysis of sewage sludge-derived fertilizer." *Carbon,* 39(13), 1971-1979.

Bansal, R. C., and Goyal, M. (2005). *Activated carbon adsorption.* CRC press, .

Barrett, E. P., Joyner, L. G., and Halenda, P. P. (1951). "The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms." *J.Am.Chem.Soc.,* 73(1), 373-380.

Bayen, S., Estrada, E. S., Juhel, G., Kit, L. W., and Kelly, B. C. (2016). "Pharmaceutically active compounds and endocrine disrupting chemicals in water, sediments and mollusks in mangrove ecosystems from Singapore." *Mar.Pollut.Bull.,* 109(2), 716-722.

Bedia, J., Peñas-Garzón, M., Gómez-Avilés, A., Rodriguez, J. J., and Belver, C. (2018). "A review on the synthesis and characterization of biomass-derived carbons for adsorption of emerging contaminants from water." *C—Journal of Carbon Research,* 4(4), 63.

Bergmann, C. P., and Machado, F. M. (2015). *Carbon nanomaterials as adsorbents for environmental and biological applications.* Springer, .

Bo, L., Gao, N., Liu, J., and Gao, B. (2016). "The competitive adsorption of pharmaceuticals on granular activated carbon in secondary effluent." *Desalination and Water Treatment,* 57(36), 17023-17029.

Boehler, M., Zwickenpflug, B., Hollender, J., Ternes, T., Joss, A., and Siegrist, H. (2012). "Removal of micropollutants in municipal wastewater treatment plants by powder-activated carbon." *Water Science and Technology,* 66(10), 2115-2121.

Boix, C., Ibáñez, M., Sancho, J. V., Parsons, J. R., de Voogt, P., and Hernández, F. (2016). "Biotransformation of pharmaceuticals in surface water and during waste water treatment: Identification and occurrence of transformation products." *J.Hazard.Mater.,* 302 175-187.

Bonvin, F., Omlin, J., Rutler, R., Schweizer, W. B., Alaimo, P. J., Strathmann, T. J., McNeill, K., and Kohn, T. (2012). "Direct photolysis of human metabolites of the antibiotic sulfamethoxazole: evidence for abiotic back-transformation." *Environ.Sci.Technol.,* 47(13), 6746-6755.

Bosch, H., Kleerebezem, G., and Mars, P. (1976). "Activated carbon from activated sludge." *Journal (Water Pollution Control Federation),* 551-561.

Bridgwater, A. V. (2012). "Review of fast pyrolysis of biomass and product upgrading." *Biomass Bioenergy,* 38 68-94.

Brun, G. L., Bernier, M., Losier, R., Doe, K., Jackman, P., and Lee, H. (2006). "Pharmaceutically active compounds in Atlantic Canadian sewage treatment plant effluents and receiving waters, and potential for environmental effects as measured by acute and chronic aquatic toxicity." *Environmental Toxicology and Chemistry: An International Journal,* 25(8), 2163-2176.

Buttiglieri, G., Migliorisi, L., and Malpei, F. (2011). "Adsorption and removal at low atrazine concentration in an MBR pilot plant." *Water Science and Technology,* 63(7), 1334-1340.

Cabrita, I., Ruiz, B., Mestre, A. S., Fonseca, I. M., Carvalho, A. P., and Ania, C. O. (2010). "Removal of an analgesic using activated carbons prepared from urban and industrial residues." *Chem.Eng.J.,* 163(3), 249-255.

Calisto, V., Ferreira, C. I., Oliveira, J. A., Otero, M., and Esteves, V. I. (2015). "Adsorptive removal of pharmaceuticals from water by commercial and waste-based carbons." *J.Environ.Manage.,* 152 83-90.

Campo, J., Masiá, A., Blasco, C., and Picó, Y. (2013). "Occurrence and removal efficiency of pesticides in sewage treatment plants of four Mediterranean River Basins." *J.Hazard.Mater.,* 263 146-157.

Cardenas, M. A. R., Ali, I., Lai, F. Y., Dawes, L., Thier, R., and Rajapakse, J. (2016). "Removal of micropollutants through a biological wastewater treatment plant in a subtropical climate, Queensland-Australia." *Journal of Environmental Health Science and Engineering,* 14(1), 14.

Castiglioni, S., Bagnati, R., Fanelli, R., Pomati, F., Calamari, D., and Zuccato, E. (2006). "Removal of pharmaceuticals in sewage treatment plants in Italy." *Environ.Sci.Technol.,* 40(1), 357-363.

CCME, A. (2010). "Review of the Current Canadian Legislative Framework for Wastewater Biosolids." *Canadian Council of Ministers of the Environment (CCMC),* .

Celiz, M. D., Pérez, S., Barceló, D., and Aga, D. S. (2009). "Trace analysis of polar pharmaceuticals in wastewater by LC-MS-MS: Comparison of membrane bioreactor and activated sludge systems." *J.Chromatogr.Sci.,* 47(1), 19-25.

Chamy, R. (2013). *Biodegradation: life of science.* BoD–Books on Demand, .

Chen, D., Xie, S., Chen, C., Quan, H., Hua, L., Luo, X., and Guo, L. (2017). "Activated biochar derived from pomelo peel as a high-capacity sorbent for removal of carbamazepine from aqueous solution." *RSC Advances,* 7(87), 54969-54979.

Chen, X., Jeyaseelan, S., and Graham, N. (2002). "Physical and chemical properties study of the activated carbon made from sewage sludge." *Waste Manage.,* 22(7), 755-760.

Chemspider database, http://www.chemspider.com/ (accessed 20.07.2018)

Cleuvers, M. (2003). "Aquatic ecotoxicity of pharmaceuticals including the assessment of combination effects." *Toxicol.Lett.,* 142(3), 185-194.

Comeau, F., Surette, C., Brun, G., and Losier, R. (2008). "The occurrence of acidic drugs and caffeine in sewage effluents and receiving waters from three coastal watersheds in Atlantic Canada." *Sci.Total Environ.,* 396(2-3), 132-146.

Comtois-Marotte, S., Chappuis, T., Duy, S. V., Gilbert, N., Lajeunesse, A., Taktek, S., Desrosiers, M., Veilleux, É, and Sauvé, S. (2017). "Analysis of emerging contaminants in water and solid samples using high resolution mass spectrometry with a Q Exactive orbital ion trap and estrogenic activity with YES-assay." *Chemosphere,* 166 400-411.

Cormier, G., Barbeau, B., Arp, H. P. H., and Sauvé, S. (2015). "The degradation behaviour of nine diverse contaminants in urban surface water and wastewater prior to water treatment." *Environmental Science: Processes & Impacts,* 17(12), 2051-2065.

Cruz-Morató, C., Lucas, D., Llorca, M., Rodriguez-Mozaz, S., Gorga, M., Petrovic, M., Barceló, D., Vicent, T., Sarrà, M., and Marco-Urrea, E. (2014). "Hospital wastewater treatment by fungal bioreactor: removal efficiency for pharmaceuticals and endocrine disruptor compounds." *Sci.Total Environ.,* 493 365-376.

Daneshvar, A., Aboulfadl, K., Viglino, L., Broséus, R., Sauvé, S., Madoux-Humery, A., Weyhenmeyer, G. A., and Prévost, M. (2012). "Evaluating pharmaceuticals and caffeine as indicators of fecal contamination in drinking water sources of the Greater Montreal region." *Chemosphere,* 88(1), 131-139.

Darwano, H., Duy, S. V., and Sauvé, S. (2014). "A new protocol for the analysis of pharmaceuticals, pesticides, and hormones in sediments and suspended particulate matter from rivers and municipal wastewaters." *Arch.Environ.Contam.Toxicol.,* 66(4), 582-593.

De Ridder, D. J., Verberk, J., Heijman, S. G., Amy, G. L., and Van Dijk, J. C. (2012). "Zeolites for nitrosamine and pharmaceutical removal from demineralised and surface water: mechanisms and efficacy." *Separation and Purification Technology,* 89 71-77.

De Ridder, D., Verliefde, A., Heijman, S., Verberk, J., Rietveld, L., Van Der Aa, L., Amy, G., and Van Dijk, J. (2011). "Influence of natural organic matter on equilibrium adsorption of neutral and charged pharmaceuticals onto activated carbon." *Water Science and Technology,* 63(3), 416-423.

Devi, P., and Saroha, A. K. (2017). "Utilization of sludge based adsorbents for the removal of various pollutants: A review." *Sci.Total Environ.,* 578 16-33.

Di Blasi, C., Galgano, A., and Branca, C. (2009). "Effects of potassium hydroxide impregnation on wood pyrolysis." *Energy Fuels,* 23(2), 1045-1054.

Drugbank database; http://www.drugbank.ca/ (accessed 20.07.2018)

Dubinin, M. i. (1975). "Physical adsorption of gases and vapors in micropores." *Progress in surface and membrane science,* Elsevier, 1-70.

Ebele, A. J., Abdallah, M. A., and Harrad, S. (2017). "Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment." *Emerging Contaminants,* 3(1), 1-16.

Fan, S., Tang, J., Wang, Y., Li, H., Zhang, H., Tang, J., Wang, Z., and Li, X. (2016). "Biochar prepared from co-pyrolysis of municipal sewage sludge and tea waste for the adsorption of methylene blue from aqueous solutions: kinetics, isotherm, thermodynamic and mechanism." *Journal of Molecular Liquids,* 220 432-441.

Fan, Z., Wu, S., Chang, H., and Hu, J. (2011). "Behaviors of glucocorticoids, androgens and progestogens in a municipal sewage treatment plant: comparison to estrogens." *Environ.Sci.Technol.,* 45(7), 2725-2733.

Fang, S., Yu, Z., Lin, Y., Lin, Y., Fan, Y., Liao, Y., and Ma, X. (2016). "Effects of additives on the co-pyrolysis of municipal solid waste and paper sludge by using thermogravimetric analysis." *Bioresour.Technol.,* 209 265-272.

Ferrando-Climent, L., Collado, N., Buttiglieri, G., Gros, M., Rodriguez-Roda, I., Rodriguez-Mozaz, S., and Barceló, D. (2012). "Comprehensive study of ibuprofen and its metabolites in activated sludge batch experiments and aquatic environment." *Sci.Total Environ.,* 438 404-413.

Figueiredo, C., Lopes, H., Coser, T., Vale, A., Busato, J., Aguiar, N., Novotny, E., and Canellas, L. (2018). "Influence of pyrolysis temperature on chemical and physical properties of biochar from sewage sludge." *Archives of Agronomy and Soil Science,* 64(6), 881-889.

Fonts, I., Gea, G., Azuara, M., Ábrego, J., and Arauzo, J. (2012). "Sewage sludge pyrolysis for liquid production: a review." *Renewable and Sustainable Energy Reviews,* 16(5), 2781-2805.

Fuhrman, V. F., Tal, A., and Arnon, S. (2015). "Why endocrine disrupting chemicals (EDCs) challenge traditional risk assessment and how to respond." *J.Hazard.Mater.,* 286 589-611.

Fu, Y., Shen, Y., Zhang, Z., Ge, X., and Chen, M. (2019). "Activated bio-chars derived from rice husk via one-and two-step KOH-catalyzed pyrolysis for phenol adsorption." Sci.Total Environ., 646 1567-1577.

Gagné, F., Bouchard, B., André, C., Farcy, E., and Fournier, M. (2011). "Evidence of feminization in wild Elliptio complanata mussels in the receiving waters downstream of a municipal effluent outfall." *Comparative Biochemistry and Physiology Part C: Toxicology & Pharmacology,* 153(1), 99-106.

Gagnon, C., and Lajeunesse, A. (2012). "Low removal of acidic and hydrophilic pharmaceutical products by various types of municipal wastewater treatment plants." *Journal of Xenobiotics,* 2(1), e3-e3.

Gagnon, C., Lajeunesse, A., Cejka, P., Gagne, F., and Hausler, R. (2008). "Degradation of selected acidic and neutral pharmaceutical products in a primary-treated wastewater by disinfection processes." *Ozone: Science and Engineering,* 30(5), 387-392.

Galus, M., Kirischian, N., Higgins, S., Purdy, J., Chow, J., Rangaranjan, S., Li, H., Metcalfe, C., and Wilson, J. Y. (2013). "Chronic, low concentration exposure to pharmaceuticals impacts multiple organ systems in zebrafish." *Aquatic Toxicology,* 132 200-211.

Gao, P., Munir, M., and Xagoraraki, I. (2012). "Correlation of tetracycline and sulfonamide antibiotics with corresponding resistance genes and resistant bacteria in a conventional municipal wastewater treatment plant." *Sci.Total Environ.,* 421 173-183.

Garcia-Ac, A., Segura, P. A., Viglino, L., Fürtös, A., Gagnon, C., Prévost, M., and Sauvé, S. (2009). "On-line solid-phase extraction of large-volume injections coupled to liquid chromatography-tandem mass spectrometry for the quantitation and confirmation of 14 selected trace organic contaminants in drinking and surface water." *Journal of Chromatography A,* 1216(48), 8518-8527.

Giannakis, S., Hendaoui, I., Jovic, M., Grandjean, D., De Alencastro, L. F., Girault, H., and Pulgarin, C. (2017). "Solar photo-Fenton and UV/H2O2 processes against the antidepressant Venlafaxine in urban wastewaters and human urine. Intermediates formation and biodegradability assessment." *Chem.Eng.J.,* 308 492-504.

Gómez-Pacheco, C., Rivera-Utrilla, J., Sánchez-Polo, M., and López-Peñalver, J. (2012). "Optimization of the preparation process of biological sludge adsorbents for application in water treatment." *J.Hazard.Mater.,* 217 76-84.

Gomez, L. M., Kumar, A., Zhang, Y., Ryu, K., Badmaev, A., and Zhou, C. (2009). "Scalable light-induced metal to semiconductor conversion of carbon nanotubes." Nano Letters, 9(10), 3592-3598.

Gonzalez-Rey, M., and Bebianno, M. J. (2012). "Does non-steroidal anti-inflammatory (NSAID) ibuprofen induce antioxidant stress and endocrine disruption in mussel Mytilus galloprovincialis?" *Environ.Toxicol.Pharmacol.,* 33(2), 361-371.

Grandclément, C., Seyssiecq, I., Piram, A., Wong-Wah-Chung, P., Vanot, G., Tiliacos, N., Roche, N., and Doumenq, P. (2017). "From the conventional biological wastewater treatment to hybrid processes, the evaluation of organic micropollutant removal: a review." *Water Res.,* 111 297-317.

Guerra, P., Kim, M., Shah, A., Alaee, M., and Smyth, S. (2014). "Occurrence and fate of antibiotic, analgesic/anti-inflammatory, and antifungal compounds in five wastewater treatment processes." *Sci.Total Environ.,* 473 235-243.

Guillossou, R., Le Roux, J., Mailler, R., Vulliet, E., Morlay, C., Nauleau, F., Gasperi, J., and Rocher, V. (2019). "Organic micropollutants in a large wastewater treatment plant: What are the benefits of an advanced treatment by activated carbon adsorption in comparison to conventional treatment?" *Chemosphere,* 218 1050-1060.

Hadi, P., Xu, M., Ning, C., Lin, C. S. K., and McKay, G. (2015). "A critical review on preparation, characterization and utilization of sludge-derived activated carbons for wastewater treatment." *Chem.Eng.J.,* 260 895-906.

Hancock, N. T., Xu, P., Heil, D. M., Bellona, C., and Cath, T. Y. (2011). "Comprehensive bench-and pilot-scale investigation of trace organic compounds rejection by forward osmosis." *Environ.Sci.Technol.,* 45(19), 8483-8490.

Heberer, T. (2002). "Tracking persistent pharmaceutical residues from municipal sewage to drinking water." *Journal of Hydrology,* 266(3-4), 175-189.

Hernando, M. D., Mezcua, M., Fernández-Alba, A. R., and Barceló, D. (2006). "Environmental risk assessment of pharmaceutical residues in wastewater effluents, surface waters and sediments." *Talanta,* 69(2), 334-342.

Holeton, C., Chambers, P. A., and Grace, L. (2011). "Wastewater release and its impacts on Canadian waters." *Can.J.Fish.Aquat.Sci.,* 68(10), 1836-1859.

Hossain, M. K., Strezov, V., Chan, K. Y., and Nelson, P. F. (2010). "Agronomic properties of wastewater sludge biochar and bioavailability of metals in production of cherry tomato (Lycopersicon esculentum)." *Chemosphere,* 78(9), 1167-1171.

Hua, W. Y., Bennett, E. R., Maio, X., Metcalfe, C. D., and Letcher, R. J. (2006). "Seasonality effects on pharmaceuticals and s-triazine herbicides in wastewater effluent and surface water from the Canadian side of the upper Detroit River." *Environmental Toxicology and Chemistry: An International Journal,* 25(9), 2356-2365.

Huang, H., Yang, T., Lai, F., and Wu, G. (2017). "Co-pyrolysis of sewage sludge and sawdust/rice straw for the production of biochar." *J.Anal.Appl.Pyrolysis,* 125 61-68.

Huber, M. M., GÖbel, A., Joss, A., Hermann, N., LÖffler, D., McArdell, C. S., Ried, A., Siegrist, H., Ternes, T. A., and von Gunten, U. (2005). "Oxidation of pharmaceuticals during ozonation of municipal wastewater effluents: a pilot study." *Environ.Sci.Technol.,* 39(11), 4290-4299.

Hui, T. S., and Zaini, M. A. A. (2015). "Potassium hydroxide activation of activated carbon: a commentary." *Carbon Letters (Carbon Lett.),* 16(4), 275-280.

Hwang, H., Choi, W., Kim, T., Kim, J., and Oh, K. (2008). "The preparation of an adsorbent from mixtures of sewage sludge and coal-tar pitch using an alkaline hydroxide activation agent." *J.Anal.Appl.Pyrolysis,* 83(2), 220-226.

Jaria, G., Calisto, V., Gil, M. V., Otero, M., and Esteves, V. I. (2015). "Removal of fluoxetine from water by adsorbent materials produced from paper mill sludge." *J.Colloid Interface Sci.,* 448 32-40.

Jaria, G., Calisto, V., Silva, C. P., Gil, M. V., Otero, M., and Esteves, V. I. (2019). "Obtaining granular activated carbon from paper mill sludge–A challenge for application in the removal of pharmaceuticals from wastewater." *Sci.Total Environ.,* 653 393-400.

Jelic, A., Fatone, F., Di Fabio, S., Petrovic, M., Cecchi, F., and Barcelo, D. (2012). "Tracing pharmaceuticals in a municipal plant for integrated wastewater and organic solid waste treatment." *Sci.Total Environ.,* 433 352-361.

Jin, J., Wang, M., Cao, Y., Wu, S., Liang, P., Li, Y., Zhang, J., Zhang, J., Wong, M. H., and Shan, S. (2017). "Cumulative effects of bamboo sawdust addition on pyrolysis of sewage sludge: biochar properties and environmental risk from metals." *Bioresour.Technol.,* 228 218-226.

Jindarom, C., Meeyoo, V., Kitiyanan, B., Rirksomboon, T., and Rangsunvigit, P. (2007). "Surface characterization and dye adsorptive capacities of char obtained from pyrolysis/gasification of sewage sludge." *Chem.Eng.J.,* 133(1-3), 239-246.

Jung, C., Boateng, L. K., Flora, J. R., Oh, J., Braswell, M. C., Son, A., and Yoon, Y. (2015). "Competitive adsorption of selected non-steroidal anti-inflammatory drugs on activated biochars: experimental and molecular modeling study." *Chem.Eng.J.,* 264 1-9.

Kante, K., Qiu, J., Zhao, Z., Cheng, Y., and Bandosz, T. J. (2008). "Development of surface porosity and catalytic activity in metal sludge/waste oil derived adsorbents: Effect of heat treatment." *Chem.Eng.J.,* 138(1-3), 155-165.

Karani, N. A., and Pingale, P. (2009). "Analytical method development & validation of venlafaxine hydrochloride in solid dosage forms using UV spectrophotometer." *J Pharma Res,* 2 1246-1249.

Kårelid, V., Larsson, G., and Björlenius, B. (2017). "Pilot-scale removal of pharmaceuticals in municipal wastewater: Comparison of granular and powdered activated carbon treatment at three wastewater treatment plants." *J.Environ.Manage.,* 193 491-502.

Knopp, G., Prasse, C., Ternes, T. A., and Cornel, P. (2016). "Elimination of micropollutants and transformation products from a wastewater treatment plant effluent through pilot scale ozonation followed by various activated carbon and biological filters." *Water Res.,* 100 580-592.

Knudsen, F., and Pottinger, T. (1998). "Interaction of endocrine disrupting chemicals, singly and in combination, with estrogen-, androgen-, and corticosteroid-binding sites in rainbow trout (Oncorhynchus mykiss)." *Aquatic Toxicology,* 44(3), 159-170.

Köck-Schulmeyer, M., Villagrasa, M., de Alda, M. L., Céspedes-Sánchez, R., Ventura, F., and Barceló, D. (2013). "Occurrence and behavior of pesticides in wastewater treatment plants and their environmental impact." *Sci.Total Environ.,* 458 466-476.

Lajeunesse, A., Gagnon, C., and Sauvé, S. (2008). "Determination of basic antidepressants and their N-Desmethyl metabolites in raw sewage and wastewater using solid-phase extraction and liquid chromatography− tandem mass spectrometry." *Anal.Chem.,* 80(14), 5325-5333.

Lajeunesse, A., Smyth, S., Barclay, K., Sauvé, S., and Gagnon, C. (2012). "Distribution of antidepressant residues in wastewater and biosolids following different treatment processes by municipal wastewater treatment plants in Canada." *Water Res.,* 46(17), 5600-5612.

Lambropoulou, D., Evgenidou, E., Saliverou, V., Kosma, C., and Konstantinou, I. (2017). "Degradation of venlafaxine using TiO2/UV process: kinetic studies, RSM optimization, identification of transformation products and toxicity evaluation." *J.Hazard.Mater.,* 323 513-526.

Lee, H., Sarafin, K., and Peart, T. E. (2007). "Determination of β-blockers and β2-agonists in sewage by solid-phase extraction and liquid chromatography–tandem mass spectrometry." *Journal of Chromatography A,* 1148(2), 158-167.

Li, W., Yue, Q., Gao, B., Ma, Z., Li, Y., and Zhao, H. (2011). "Preparation and utilization of sludge-based activated carbon for the adsorption of dyes from aqueous solutions." *Chem.Eng.J.,* 171(1), 320-327.

Li, Y., Li, Y., Li, L., Shi, X., and Wang, Z. (2016). "Preparation and analysis of activated carbon from sewage sludge and corn stalk." *Advanced Powder Technology,* 27(2), 684-691.

Lillo-Ródenas, M. A., Ros, A., Fuente, E., Montes-Morán, M. A., Martin, M. J., and Linares-Solano, A. (2008). "Further insights into the activation process of sewage sludge-based precursors by alkaline hydroxides." *Chem.Eng.J.,* 142(2), 168-174.

Lillo-Ródenas, M., Lozano-Castelló, D., Cazorla-Amorós, D., and Linares-Solano, A. (2001). "Preparation of activated carbons from Spanish anthracite: II. Activation by NaOH." *Carbon,* 39(5), 751-759.

Lin, L., Jiang, W., and Xu, P. (2017). "Comparative study on pharmaceuticals adsorption in reclaimed water desalination concentrate using biochar: Impact of salts and organic matter." *Sci.Total Environ.,* 601 857-864.

Lin, Q., Cheng, H., and Chen, G. (2012). "Preparation and characterization of carbonaceous adsorbents from sewage sludge using a pilot-scale microwave heating equipment." *J.Anal.Appl.Pyrolysis,* 93 113-119.

Linares-Solano, A., Lillo-Rodenas, M. A., Marco Lozar, J. P., Kunowsky, M., and Romero Anaya, A. J. (2012). "NaOH and KOH for preparing activated carbons used in energy and environmental applications." .

Liou, T. (2010). "Development of mesoporous structure and high adsorption capacity of biomass-based activated carbon by phosphoric acid and zinc chloride activation." *Chem.Eng.J.,* 158(2), 129-142.

Lishman, L., Smyth, S. A., Sarafin, K., Kleywegt, S., Toito, J., Peart, T., Lee, B., Servos, M., Beland, M., and Seto, P. (2006). "Occurrence and reductions of pharmaceuticals and personal care products and estrogens by municipal wastewater treatment plants in Ontario, Canada." *Sci.Total Environ.,* 367(2-3), 544-558.

Llorca, M., Castellet-Rovira, F., Farré, M., Jaén-Gil, A., Martínez-Alonso, M., Rodríguez-Mozaz, S., Sarrà, M., and Barceló, D. (2019). "Fungal biodegradation of the N-nitrosodimethylamine precursors venlafaxine and O-desmethylvenlafaxine in water." *Environmental Pollution,* 246 346-356.

Lloret, L., Eibes, G., Feijoo, G., Moreira, M., and Lema, J. M. (2012). "Continuous biotransformation of estrogens by laccase in an enzymatic membrane reactor." *Chemical Engineering,* 27.

López-Serna, R., Petrović, M., and Barceló, D. (2012). "Occurrence and distribution of multi-class pharmaceuticals and their active metabolites and transformation products in the Ebro River basin (NE Spain)." *Sci.Total Environ.,* 440 280-289.

Lozano-Castello, D., Lillo-Rodenas, M., Cazorla-Amorós, D., and Linares-Solano, A. (2001). "Preparation of activated carbons from Spanish anthracite: I. Activation by KOH." *Carbon,* 39(5), 741-749.

Lu, H., Zhang, W., Wang, S., Zhuang, L., Yang, Y., and Qiu, R. (2013). "Characterization of sewage sludge-derived biochars from different feedstocks and pyrolysis temperatures." *J.Anal.Appl.Pyrolysis,* 102 137-143.

Luo, Y., Guo, W., Ngo, H. H., Nghiem, L. D., Hai, F. I., Zhang, J., Liang, S., and Wang, X. C. (2014). "A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment." *Sci.Total Environ.,* 473 619-641.

Lussier, M. G., Shull, J. C., and Miller, D. J. (1994). "Activated carbon from cherry stones." *Carbon,* 32(8), 1493-1498.

Magdziarz, A., and Werle, S. (2014). "Analysis of the combustion and pyrolysis of dried sewage sludge by TGA and MS." *Waste Manage.,* 34(1), 174-179.

Mahapatra, K., Ramteke, D., and Paliwal, L. (2012). "Production of activated carbon from sludge of food processing industry under controlled pyrolysis and its application for methylene blue removal." *J.Anal.Appl.Pyrolysis,* 95 79-86.

Mailler, R., Gasperi, J., Coquet, Y., Derome, C., Buleté, A., Vulliet, E., Bressy, A., Varrault, G., Chebbo, G., and Rocher, V. (2016a). "Removal of emerging micropollutants from wastewater by activated carbon adsorption: experimental study of different activated carbons and factors influencing the adsorption of micropollutants in wastewater." *Journal of Environmental Chemical Engineering,* 4(1), 1102-1109.

Mandaric, L., Celic, M., Marcé, R., and Petrovic, M. (2015). "Introduction on emerging contaminants in rivers and their environmental risk." *Emerging Contaminants in River Ecosystems,* Springer, 3-25.

Marsh, H., and Rodríguez-Reinoso, F. (2000). *Sciences of carbon materials.* Universidad de Alicante, .

Martin, M., Serra, E., Ros, A., Balaguer, M., and Rigola, M. (2004). "Carbonaceous adsorbents from sewage sludge and their application in a combined activated sludge-powdered activated carbon (AS-PAC) treatment." *Carbon,* 42(7), 1389-1394.

Melo-Guimarães, A., Torner-Morales, F. J., Durán-Álvarez, J. C., and Jiménez-Cisneros, B. E. (2013). "Removal and fate of emerging contaminants combining biological, flocculation and membrane treatments." *Water Science and Technology,* 67(4), 877-885.

Méndez, A., Gascó, G., Freitas, M., Siebielec, G., Stuczynski, T., and Figueiredo, J. (2005). "Preparation of carbon-based adsorbents from pyrolysis and air activation of sewage sludges." *Chem.Eng.J.,* 108(1-2), 169-177.

Mestre, A. S., Bexiga, A. S., Proença, M., Andrade, M., Pinto, M. L., Matos, I., Fonseca, I. M., and Carvalho, A. P. (2011). "Activated carbons from sisal waste by chemical activation with K2CO3: kinetics of paracetamol and ibuprofen removal from aqueous solution." *Bioresour.Technol.,* 102(17), 8253-8260.

Mestre, A. S., Pires, R. A., Aroso, I., Fernandes, E. M., Pinto, M. L., Reis, R. L., Andrade, M. A., Pires, J., Silva, S. P., and Carvalho, A. P. (2014). "Activated carbons prepared from industrial pre-treated cork: Sustainable adsorbents for pharmaceutical compounds removal." *Chem.Eng.J.,* 253 408-417.

Metcalf, L., Eddy, H. P., and Tchobanoglous, G. (1972). *Wastewater engineering: treatment, disposal, and reuse.* McGraw-Hill NewYork, .

Metcalfe, C. D., Chu, S., Judt, C., Li, H., Oakes, K. D., Servos, M. R., and Andrews, D. M. (2010). "Antidepressants and their metabolites in municipal wastewater, and downstream exposure in an urban watershed." *Environmental Toxicology and Chemistry,* 29(1), 79-89.

Miao, X., Bishay, F., Chen, M., and Metcalfe, C. D. (2004). "Occurrence of antimicrobials in the final effluents of wastewater treatment plants in Canada." *Environ.Sci.Technol.,* 38(13), 3533-3541.

Miao, X., and Metcalfe, C. D. (2003). "Determination of carbamazepine and its metabolites in aqueous samples using liquid chromatography− electrospray tandem mass spectrometry." *Anal.Chem.,* 75(15), 3731-3738.

Mohd Amin, M., Heijman, S., and Rietveld, L. (2015). "Clay-biodegradable polymer combination for pollutant removal from water." *Drinking Water Engineering & Science Discussions,* 8(2),.

Monsalvo, V. M., Mohedano, A. F., and Rodriguez, J. J. (2011). "Activated carbons from sewage sludge: application to aqueous-phase adsorption of 4-chlorophenol." *Desalination,* 277(1-3), 377-382.

Moreno-Castilla, C. (2004). "Adsorption of organic molecules from aqueous solutions on carbon materials." *Carbon,* 42(1), 83-94.

Nazari, G., Abolghasemi, H., and Esmaieli, M. (2016). "Batch adsorption of cephalexin antibiotic from aqueous solution by walnut shell-based activated carbon." *Journal of the Taiwan Institute of Chemical Engineers,* 58 357-365.

Nguyen, L. N., Hai, F. I., Price, W. E., Leusch, F. D., Roddick, F., Ngo, H. H., Guo, W., Magram, S. F., and Nghiem, L. D. (2014). "The effects of mediator and granular activated carbon addition on degradation of trace organic contaminants by an enzymatic membrane reactor." *Bioresour.Technol.,* 167 169-177.

Nielsen, L., and Bandosz, T. J. (2016). "Analysis of sulfamethoxazole and trimethoprim adsorption on sewage sludge and fish waste derived adsorbents." *Microporous and Mesoporous Materials,* 220 58-72.

Nielsen, L., Zhang, P., and Bandosz, T. J. (2015). "Adsorption of carbamazepine on sludge/fish waste derived adsorbents: Effect of surface chemistry and texture." *Chem.Eng.J.,* 267 170-181.

Noguera-Oviedo, K., and Aga, D. S. (2016). "Lessons learned from more than two decades of research on emerging contaminants in the environment." *J.Hazard.Mater.,* 316 242-251.

Ocampo-Pérez, R., Rivera-Utrilla, J., Gómez-Pacheco, C., Sánchez-Polo, M., and López-Peñalver, J. (2012). "Kinetic study of tetracycline adsorption on sludge-derived adsorbents in aqueous phase." *Chem.Eng.J.,* 213 88-96.

Otero, M., Rozada, F., Morán, A., Calvo, L., and García, A. (2009). "Removal of heavy metals from aqueous solution by sewage sludge based sorbents: competitive effects." *Desalination,* 239(1-3), 46-57.

Ouarda, Y., Bouchard, F., Azaïs, A., Vaudreuil, M., Drogui, P., Tyagi, R. D., Sauvé, S., Buelna, G., and Dubé, R. (2019). "Electrochemical treatment of real hospital wastewaters and monitoring of pharmaceutical residues by using surrogate models." *Journal of Environmental Chemical Engineering,* 7(5), 103332.

Ouarda, Y., Tiwari, B., Azaïs, A., Vaudreuil, M., Ndiaye, S. D., Drogui, P., Tyagi, R. D., Sauvé, S., Desrosiers, M., and Buelna, G. (2018). "Synthetic hospital wastewater treatment by coupling submerged membrane bioreactor and electrochemical advanced oxidation process: Kinetic study and toxicity assessment." *Chemosphere,* 193 160-169.

Paíga, P., Santos, L. H., Ramos, S., Jorge, S., Silva, J. G., and Delerue-Matos, C. (2016). "Presence of pharmaceuticals in the Lis river (Portugal): Sources, fate and seasonal variation." *Sci.Total Environ.,* 573 164-177.

Papageorgiou, M., Kosma, C., and Lambropoulou, D. (2016). "Seasonal occurrence, removal, mass loading and environmental risk assessment of 55 pharmaceuticals and personal care products in a municipal wastewater treatment plant in Central Greece." *Sci.Total Environ.,* 543 547-569.

Pastor-Villegas, J., and Durán-Valle, C. (2001). "Pore structure of chars and activated carbons prepared using carbon dioxide at different temperatures from extracted rockrose." *J.Anal.Appl.Pyrolysis,* 57(1), 1-13.

Paz-Ferreiro, J., Nieto, A., Méndez, A., Askeland, M., and Gascó, G. (2018). "Biochar from biosolids pyrolysis: A review." *International Journal of Environmental Research and Public Health,* 15(5), 956.

Pérez-Elvira, S., Diez, P. N., and Fdz-Polanco, F. (2006). "Sludge minimisation technologies." *Reviews in Environmental Science and Bio/Technology,* 5(4), 375-398.

Raghav, M., Eden, S., Mitchell, K., Witte, B., and Polle, J. (2013). "Contaminants of Emerging Concern Raise Many Questions." *Water Resources Research Center, the University of Arizona,* 1-12.

Raheem, A., Sikarwar, V. S., He, J., Dastyar, W., Dionysiou, D. D., Wang, W., and Zhao, M. (2018). "Opportunities and challenges in sustainable treatment and resource reuse of sewage sludge: a review." *Chem.Eng.J.,* 337 616-641.

Rakić, V., Rac, V., Krmar, M., Otman, O., and Auroux, A. (2015). "The adsorption of pharmaceutically active compounds from aqueous solutions onto activated carbons." *J.Hazard.Mater.,* 282 141-149.

Rawat, J., Saxena, J., and Sanwal, P. (2019). "Biochar: a sustainable approach for improving plant growth and soil properties." *Biochar-An Imperative Amendment for Soil and the Environment,* IntechOpen, .

Ren, X., Liang, B., Liu, M., Xu, X., and Cui, M. (2012). "Effects of pyrolysis temperature, time and leaf litter and powder coal ash addition on sludge-derived adsorbents for nitrogen oxide." *Bioresour.Technol.,* 125 300-304.

Rice, S. L., and Mitra, S. (2007). "Microwave-assisted solvent extraction of solid matrices and subsequent detection of pharmaceuticals and personal care products (PPCPs) using gas chromatography–mass spectrometry." *Anal.Chim.Acta,* 589(1), 125-132.

Rio, S., Faur-Brasquet, C., Le Coq, L., Courcoux, P., and Le Cloirec, P. (2005a). "Experimental design methodology for the preparation of carbonaceous sorbents from sewage sludge by chemical activation—application to air and water treatments." *Chemosphere,* 58(4), 423-437.

Rio, S., Faur-Brasquet, C., Le Coq, L., and Le Cloirec, P. (2005b). "Structure characterization and adsorption properties of pyrolyzed sewage sludge." *Environ.Sci.Technol.,* 39(11), 4249-4257.

Rio, S., Le Coq, L., Faur, C., and Le Cloirec, P. (2006). "Production of porous carbonaceous adsorbent from physical activation of sewage sludge: application to wastewater treatment." *Water Science and Technology,* 53(3), 237-244.

Rivera-Jaimes, J. A., Postigo, C., Melgoza-Alemán, R. M., Aceña, J., Barceló, D., and de Alda, M. L. (2018). "Study of pharmaceuticals in surface and wastewater from Cuernavaca, Morelos, Mexico: occurrence and environmental risk assessment." *Sci.Total Environ.,* 613 1263-1274.

Rivera-Utrilla, J., Sánchez-Polo, M., Ferro-García, M. Á, Prados-Joya, G., and Ocampo-Pérez, R. (2013). "Pharmaceuticals as emerging contaminants and their removal from water. A review." *Chemosphere,* 93(7), 1268-1287.

Rodriguez-Narvaez, O. M., Peralta-Hernandez, J. M., Goonetilleke, A., and Bandala, E. R. (2017). "Treatment technologies for emerging contaminants in water: a review." *Chem.Eng.J.,* 323 361-380.

Ros, A., Lillo-Ródenas, M., Fuente, E., Montes-Morán, M., Martín, M., and Linares-Solano, A. (2006). "High surface area materials prepared from sewage sludge-based precursors." *Chemosphere,* 65(1), 132-140.

Rozada, F., Otero, M., Morán, A., and García, A. (2008). "Adsorption of heavy metals onto sewage sludge-derived materials." *Bioresour.Technol.,* 99(14), 6332-6338.

Rúa-Gómez, P. C., Guedez, A. A., Ania, C. O., and Püttmann, W. (2012). "Upgrading of wastewater treatment plants through the use of unconventional treatment technologies: removal of lidocaine, tramadol, venlafaxine and their metabolites." *Water,* 4(3), 650-669.

Samolada, M., and Zabaniotou, A. (2014). "Comparative assessment of municipal sewage sludge incineration, gasification and pyrolysis for a sustainable sludge-to-energy management in Greece." *Waste Manage.,* 34(2), 411-420.

Saunders, L. J., Mazumder, A., and Lowe, C. J. (2016). "Pharmaceutical concentrations in screened municipal wastewaters in Victoria, British Columbia: A comparison with prescription rates and predicted concentrations." *Environmental Toxicology and Chemistry,* 35(4), 919-929.

Schultz, M. M., Furlong, E. T., Kolpin, D. W., Werner, S. L., Schoenfuss, H. L., Barber, L. B., Blazer, V. S., Norris, D. O., and Vajda, A. M. (2010). "Antidepressant pharmaceuticals in two US effluent-impacted streams: occurrence and fate in water and sediment, and selective uptake in fish neural tissue." *Environ.Sci.Technol.,* 44(6), 1918-1925.

Schultz, M. M., Painter, M. M., Bartell, S. E., Logue, A., Furlong, E. T., Werner, S. L., and Schoenfuss, H. L. (2011). "Selective uptake and biological consequences of environmentally relevant antidepressant pharmaceutical exposures on male fathead minnows." *Aquatic Toxicology,* 104(1-2), 38-47.

Segura, P. A., Gagnon, C., and Sauvé, S. (2007). "A fully automated on-line preconcentration and liquid chromatography–tandem mass spectrometry method for the analysis of anti-infectives in wastewaters." *Anal.Chim.Acta,* 604(2), 147-157.

Seredych, M., and Bandosz, T. J. (2007). "Removal of cationic and ionic dyes on industrial− municipal sludge based composite adsorbents." *Ind Eng Chem Res,* 46(6), 1786-1793.

Servos, M., Bennie, D., Burnison, B., Jurkovic, A., McInnis, R., Neheli, T., Schnell, A., Seto, P., Smyth, S., and Ternes, T. (2005). "Distribution of estrogens, 17β-estradiol and estrone, in Canadian municipal wastewater treatment plants." *Sci.Total Environ.,* 336(1-3), 155-170.

Sichel, C., Garcia, C., and Andre, K. (2011). "Feasibility studies: UV/chlorine advanced oxidation treatment for the removal of emerging contaminants." *Water Res.,* 45(19), 6371-6380.

Silva, A., Martinho, S., Stawiński, W., Węgrzyn, A., Figueiredo, S., Santos, L. H., and Freitas, O. (2018a). "Application of vermiculite-derived sustainable adsorbents for removal of venlafaxine." *Environmental Science and Pollution Research,* 25(17), 17066-17076.

Silva, A., Stawiński, W., Romacho, J., Santos, L. H., Figueiredo, S. A., Freitas, O. M., and Delerue-Matos, C. (2019). "Adsorption of Fluoxetine and Venlafaxine onto the Marine Seaweed Bifurcaria bifurcata." *Environ.Eng.Sci.,* 36(5), 573-582.

Silva, B., Costa, F., Neves, I. C., and Tavares, T. (2015). *Psychiatric pharmaceuticals as emerging contaminants in wastewater.* Springer, .

Silva, C. P., Jaria, G., Otero, M., Esteves, V. I., and Calisto, V. (2018b). "Waste-based alternative adsorbents for the remediation of pharmaceutical contaminated waters: Has a step forward already been taken?" *Bioresour.Technol.,* 250 888-901.

Singer, H., Jaus, S., Hanke, I., Lück, A., Hollender, J., and Alder, A. C. (2010). "Determination of biocides and pesticides by on-line solid phase extraction coupled with mass spectrometry and their behaviour in wastewater and surface water." *Environmental Pollution,* 158(10), 3054-3064.

Singh, B., Camps-Arbestain, M., and Lehmann, J. (2017a). *Biochar: a guide to analytical methods.* Csiro Publishing,

Singh, G., Kim, I. Y., Lakhi, K. S., Srivastava, P., Naidu, R., and Vinu, A. (2017b). "Single step synthesis of activated bio-carbons with a high surface area and their excellent CO2 adsorption capacity." *Carbon,* 116 448-455.

Sinha, S., Jhalani, A., Ravi, M., and Ray, A. (2000). "Modelling of pyrolysis in wood: a review." *SESI Journal,* 10(1), 41-62.

Sivarajasekar, N., Balasubramani, K., Mohanraj, N., Maran, J. P., Sivamani, S., Koya, P. A., and Karthik, V. (2017). "Fixed-bed adsorption of atrazine onto microwave irradiated Aegle marmelos Correa fruit shell: statistical optimization, process design and breakthrough modeling." *Journal of Molecular Liquids,* 241 823-830.

Smith, K., Fowler, G., Pullket, S., and Graham, N. D. (2009a). "Sewage sludge-based adsorbents: a review of their production, properties and use in water treatment applications." *Water Res.,* 43(10), 2569-2594.

Smith, K., Fowler, G., Pullket, S., and Graham, N. (2012). "The production of attrition resistant, sewage–sludge derived, granular activated carbon." *Separation and Purification Technology,* 98 240-248.

Smith, S. (2009b). "Organic contaminants in sewage sludge (biosolids) and their significance for agricultural recycling." *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences,* 367(1904), 4005-4041.

Sotelo, J. L., Ovejero, G., Rodríguez, A., Álvarez, S., Galán, J., and García, J. (2014a). "Competitive adsorption studies of caffeine and diclofenac aqueous solutions by activated carbon." *Chem.Eng.J.,* 240 443-453.

Spessato, L., Bedin, K. C., Cazetta, A. L., Souza, I. P., Duarte, V. A., Crespo, L. H., Silva, M. C., Pontes, R. M., and Almeida, V. C. (2019). "KOH-super activated carbon from biomass waste: Insights into the paracetamol adsorption mechanism and thermal regeneration cycles." *J.Hazard.Mater.,* 371 499-505.

Spongberg, A. L., and Witter, J. D. (2008). "Pharmaceutical compounds in the wastewater process stream in Northwest Ohio." *Sci.Total Environ.,* 397(1-3), 148-157.

Stoquart, C., Vázquez Rodríguez, G. A., Servais, P., Sauvé, S., and Barbeau, B. (2016). "Micropollutant removal potential by aged powdered activated carbon." *J.Environ.Eng.,* 142(11), 04016058.

Stüber, F., Smith, K., Mendoza, M. B., Marques, R., Fabregat, A., Bengoa, C., Font, J., Fortuny, A., Pullket, S., and Fowler, G. (2011). "Sewage sludge based carbons for catalytic wet air oxidation of phenolic compounds in batch and trickle bed reactors." *Applied Catalysis B: Environmental,* 110 81-89.

Sun, H., Hockaday, W. C., Masiello, C. A., and Zygourakis, K. (2012). "Multiple controls on the chemical and physical structure of biochars." *Ind Eng Chem Res,* 51(9), 3587-3597.

Taheran, M., Brar, S. K., Verma, M., Surampalli, R. Y., Zhang, T. C., and Valéro, J. R. (2016). "Membrane processes for removal of pharmaceutically active compounds (PhACs) from water and wastewaters." *Sci.Total Environ.,* 547 60-77.

Tan, T. C. N., and Sen, T. K. (2019). "Aqueous-phase methylene blue (MB) dye removal by mixture of eucalyptus bark (EB) biomass and kaolin clay (KC) adsorbents: kinetics, thermodynamics, and isotherm modeling." *Sep.Sci.Technol.,* 1-15.

Tay, J., Chen, X., Jeyaseelan, S., and Graham, N. (2001). "Optimising the preparation of activated carbon from digested sewage sludge and coconut husk." *Chemosphere,* 44(1), 45-51.

Ternes, T. A., Stumpf, M., Mueller, J., Haberer, K., Wilken, R., and Servos, M. (1999). "Behavior and occurrence of estrogens in municipal sewage treatment plants—I. Investigations in Germany, Canada and Brazil." *Sci.Total Environ.,* 225(1-2), 81-90.

Thomaidi, V. S., Stasinakis, A. S., Borova, V. L., and Thomaidis, N. S. (2015). "Is there a risk for the aquatic environment due to the existence of emerging organic contaminants in treated domestic wastewater? Greece as a case-study." *J.Hazard.Mater.,* 283 740-747.

Thommes, M., Kaneko, K., Neimark, A. V., Olivier, J. P., Rodriguez-Reinoso, F., Rouquerol, J., and Sing, K. S. (2015). "Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)." *Pure and Applied Chemistry,* 87(9-10), 1051-1069.

US Environmental Protection Agency (1996) Acid digestion of sediments, sludges, and soils. Method 3050 A. USEPA, Washington, DC

Vasquez, M. I., Lambrianides, A., Schneider, M., Kümmerer, K., and Fatta-Kassinos, D. (2014). "Environmental side effects of pharmaceutical cocktails: what we know and what we should know." *J.Hazard.Mater.,* 279 169-189.

Velghe, I., Carleer, R., Yperman, J., Schreurs, S., and D'Haen, J. (2012). "Characterisation of adsorbents prepared by pyrolysis of sludge and sludge/disposal filter cake mix." *Water Res.,* 46(8), 2783-2794.

Verlicchi, P., Al Aukidy, M., and Zambello, E. (2012). "Occurrence of pharmaceutical compounds in urban wastewater: removal, mass load and environmental risk after a secondary treatment—a review." *Sci.Total Environ.,* 429 123-155.

Vieno, N. M., Tuhkanen, T., and Kronberg, L. (2006). "Analysis of neutral and basic pharmaceuticals in sewage treatment plants and in recipient rivers using solid phase extraction and liquid chromatography–tandem mass spectrometry detection." *Journal of Chromatography A,* 1134(1-2), 101-111.

Vieno, N., and Sillanpää, M. (2014). "Fate of diclofenac in municipal wastewater treatment plant—a review." *Environ.Int.,* 69 28-39.

Viglino, L., Aboulfadl, K., Mahvelat, A. D., Prévost, M., and Sauvé, S. (2008). "On-line solid phase extraction and liquid chromatography/tandem mass spectrometry to quantify pharmaceuticals, pesticides and some metabolites in wastewaters, drinking, and surface waters." *Journal of Environmental Monitoring,* 10(4), 482-489.

Wang, J., and Kaskel, S. (2012). "KOH activation of carbon-based materials for energy storage." *Journal of Materials Chemistry,* 22(45), 23710-23725.

Wang, J., Sun, C., Lin, B., Huang, Q., Ma, Z., Chi, Y., and Yan, J. (2018). "Micro-and mesoporous-enriched carbon materials prepared from a mixture of petroleum-derived oily sludge and biomass." *Fuel Process Technol,* 171 140-147.

Wang, K., Zhang, Y., Qi, R., Yang, M., and Deng, R. (2006). "Effects of activated carbon surface chemistry and pore structure on adsorption of HAAs from water." *Journal of Chemical Industry and Engineering-China-,* 57(7), 1659.

Wang, R., and Liu, S. (2010). "Activated carbon from extracted sawdust waste with alkaline activation by physical mixing." *For.Prod.J.,* 60(3), 276-281.

Wang, W., Wu, Q., Li, Z., Lu, Y., Du, Y., Wang, T., Huang, N., and Hu, H. (2017). "Light-emitting diodes as an emerging UV source for UV/chlorine oxidation: carbamazepine degradation and toxicity changes." *Chem.Eng.J.,* 310 148-156.

Wang, X., Deng, S., Tan, H., Adeosun, A., Vujanović, M., Yang, F., and Duić, N. (2016a). "Synergetic effect of sewage sludge and biomass co-pyrolysis: a combined study in thermogravimetric analyzer and a fixed bed reactor." *Energy Conversion and Management,* 118 399-405.

Wang, X., Liang, X., Wang, Y., Wang, X., Liu, M., Yin, D., Xia, S., Zhao, J., and Zhang, Y. (2011). "Adsorption of Copper (II) onto activated carbons from sewage sludge by microwave-induced phosphoric acid and zinc chloride activation." *Desalination,* 278(1-3), 231-237.

Wang, X., Zhao, B., and Yang, X. (2016b). "Co-pyrolysis of microalgae and sewage sludge: biocrude assessment and char yield prediction." Energy Conversion and Management, 117 326-334.

Waqas, M., Li, G., Khan, S., Shamshad, I., Reid, B. J., Qamar, Z., and Chao, C. (2015). "Application of sewage sludge and sewage sludge biochar to reduce polycyclic aromatic hydrocarbons (PAH) and potentially toxic elements (PTE) accumulation in tomato." *Environmental Science and Pollution Research,* 22(16), 12114-12123.

Watkinson, A., Murby, E., and Costanzo, S. (2007). "Removal of antibiotics in conventional and advanced wastewater treatment: implications for environmental discharge and wastewater recycling." *Water Res.,* 41(18), 4164-4176.

Wu, C., Song, M., Jin, B., Wu, Y., and Huang, Y. (2013). "Effect of biomass addition on the surface and adsorption characterization of carbon-based adsorbents from sewage sludge." *Journal of Environmental Sciences,* 25(2), 405-412.

Xiang, Y., Fang, J., and Shang, C. (2016). "Kinetics and pathways of ibuprofen degradation by the UV/chlorine advanced oxidation process." *Water Res.,* 90 301-308.

Xu, G., Yang, X., and Spinosa, L. (2015). "Development of sludge-based adsorbents: preparation, characterization, utilization and its feasibility assessment." *J.Environ.Manage.,* 151 221-232.

Xu, X., Zhao, B., Sun, M., Chen, X., Zhang, M., Li, H., and Xu, S. (2017). "Co-pyrolysis characteristics of municipal sewage sludge and hazelnut shell by TG-DTG-MS and residue analysis." *Waste Manage.,* 62 91-100.

Yan, S., Subramanian, S. B., Tyagi, R., Surampalli, R. Y., and Zhang, T. C. (2009). "Emerging contaminants of environmental concern: source, transport, fate, and treatment." *Pract.Periodical Hazard., Toxic, Radioact.Waste Manage.,* 14(1), 2-20.

Yang, X., Flowers, R. C., Weinberg, H. S., and Singer, P. C. (2011). "Occurrence and removal of pharmaceuticals and personal care products (PPCPs) in an advanced wastewater reclamation plant." *Water Res.,* 45(16), 5218-5228.

Yao, H., Lu, J., Wu, J., Lu, Z., Wilson, P. C., and Shen, Y. (2013). "Adsorption of fluoroquinolone antibiotics by wastewater sludge biochar: role of the sludge source." *Water, Air, & Soil Pollution,* 224(1), 1370.

Yarahmadi, H., Duy, S. V., Hachad, M., Dorner, S., Sauvé, S., and Prévost, M. (2018). "Seasonal variations of steroid hormones released by wastewater treatment plants to river water and sediments: Distribution between particulate and dissolved phases." *Sci.Total Environ.,* 635 144-155.

Yoshida, H., Christensen, T. H., and Scheutz, C. (2013). "Life cycle assessment of sewage sludge management: a review." *Waste Manage.Res.,* 31(11), 1083-1101.

Zeng, F., Liao, X., Hu, H., and Liao, L. (2018). "Effect of potassium hydroxide activation in the desulfurization process of activated carbon prepared by sewage sludge and corn straw." *J.Air Waste Manage.Assoc.,* 68(3), 255-264.

Zhang, B., Xiong, S., Xiao, B., Yu, D., and Jia, X. (2011). "Mechanism of wet sewage sludge pyrolysis in a tubular furnace." *Int J Hydrogen Energy,* 36(1), 355-363.

Zhang, F., Nriagu, J. O., and Itoh, H. (2005). "Mercury removal from water using activated carbons derived from organic sewage sludge." *Water Res.,* 39(2-3), 389-395.

Zhu, X., Chen, Z., Xiao, B., Hu, Z., Hu, M., Liu, C., and Zhang, Q. (2015). "Co-pyrolysis behaviors and kinetics of sewage sludge and pine sawdust blends under non-isothermal conditions." *Journal of Thermal Analysis and Calorimetry,* 119(3), 2269-2279.

Zielińska, A., Oleszczuk, P., Charmas, B., Skubiszewska-Zięba, J., and Pasieczna-Patkowska, S. (2015). "Effect of sewage sludge properties on the biochar characteristic." *J.Anal.Appl.Pyrolysis,* 112 201-213.

Zou, J., Dai, Y., Wang, X., Ren, Z., Tian, C., Pan, K., Li, S., Abuobeidah, M., and Fu, H. (2013). "Structure and adsorption properties of sewage sludge-derived carbon with removal of inorganic impurities and high porosity." *Bioresour.Technol.,* 142 209-217.

Appendix

A1. Physicochemical water and wastewater effluent quality parameters

Table A1-1 Physicochemical wastewater effluent's parameters, the first day of sampling (September 13th, 2018)

Parameter	Dimension	Mean Value	Method	Method Range (mg L^{-1})
<u>Physical parameter</u>				
Total Solids (TS)	mg L^{-1}	682	APHA 2540 C	-
Total Volatile Solids (TVS)	mg L^{-1}	173	APHA 2540 E	-
Total Suspended Solids (TSS)	mg L^{-1}	6.85	APHA 2540 D	-
Volatile Suspended Solids (TVSS)	mg L^{-1}	6.64	APHA 2540 E	-
Fixed Suspended Solids	mg L^{-1}	0.210	Calculated	-
Oxidation Reduction Potential (ORP)	mV	-	-	-
<u>Chemical Parameters</u>				
pH	-	-	-	-
Chemical oxygen demand (COD)	mg L^{-1}	25.4	HACH- TNT820	1.00 - 40.0
Total nitrogen	mg L^{-1}	12.8	HACH-TNT 827	5 - 40
Nitrate (NO_3^{-2})	mg L^{-1}	52.8	HACH- TNT 835	1.00 - 60.00
Nitrogen associated to nitrate ($NO_3^{-2} - N$)	mg L^{-1}	12.4	HACH- TNT 835	0.23 - 13.50
Nitrite (NO_2^{-})	mg L^{-1}	0.67	HACH-TNT 839	0.05 - 2.00
Nitrogen associated to nitrite ($NO_2^{-} - N$)	mg L^{-1}	0.21	HACH-TNT 839	0.015 - 0.600
Total kjeldahl nitrogen	mg L^{-1}	0.145	Calculated	-
Phosphate (PO_4^{-3})	mg L^{-1}	2.62	HACH-TNT 843	0.15 - 4.50
Phosphorous associated to phosphate	mg L^{-1}	0.85	HACH-TNT 843	0.05 - 1.50
Sulfate (SO_4^{-2})	mg L^{-1}	95.0	HACH-TNT 865	40 - 150

Table A1-2Physicochemical wastewater effluent's parameters, the second day of sampling (September 14th, 2018)

Parameter	Dimension	Mean Value	Method	Method Range ($mg\ L^{-1}$)
Physical Parameters				
Total Solids (TS)	$mg\ L^{-1}$	673	APHA 2540 C	-
Total Volatile Solids (TVS)	$mg\ L^{-1}$	182	APHA 2540 E	-
Total Suspended Solids (TSS)	$mg\ L^{-1}$	5.15	APHA 2540 D	-
Volatile Suspended Solids (TVSS)	$mg\ L^{-1}$	4.25	APHA 2540 E	-
Fixed Suspended Solids	$mg\ L^{-1}$	0.9	Calculated	-
Oxidation Reduction Potential (ORP)	mV	-	OAKTON pH, ORP, Temperature probe	-
Chemical Parameters				
pH	-		-	-
Chemical oxygen demand (COD)	$mg\ L^{-1}$	21.7	HACH- TNT820	1.00 - 40.0
Total nitrogen	$mg\ L^{-1}$	13.7	HACH-TNT 827	5 - 40
Nitrate (NO_3^{-2})	$mg\ L^{-1}$	56.6	HACH- TNT 835	1.00 - 60.00
Nitrogen associated to nitrate ($NO_3^{-2} - N$)	$mg\ L^{-1}$	12.7	HACH- TNT 835	0.23 - 13.50
Nitrite (NO_2^{-})	$mg\ L^{-1}$	0.457	HACH-TNT 839	0.05 - 2.00
Nitrogen associated to nitrite ($NO_2^{-} - N$)	$mg\ L^{-1}$	0.139	HACH-TNT 839	0.015 - 0.600
Total kjeldahl nitrogen	$mg\ L^{-1}$	0.861	Calculated	-
Phosphate (PO_4^{-3})	$mg\ L^{-1}$	3.30	HACH-TNT 843	0.15 - 4.50
Phosphorous associated to phosphate	$mg\ L^{-1}$	1.08	HACH-TNT 843	0.05 - 1.50
Sulfate (SO_4^{-2})	$mg\ L^{-1}$	102	HACH-TNT 865	40 - 150

Table A1-3 Physicochemical wastewater effluent's parameters, the third day of sampling (September 15th, 2018)

Parameter	Dimension	Mean Value	Method	Method Range (mg L^{-1})
Physical Parameters				
Total Solids (TS)	mg L^{-1}	859	APHA 2540 C	-
Total Volatile Solids (TVS)	mg L^{-1}	170.0	APHA 2540 E	-
Total Suspended Solids (TSS)	mg L^{-1}	-	-	-
Volatile Suspended Solids (TVSS)	mg L^{-1}	-	-	-
Fixed Suspended Solids	mg L^{-1}	-	-	-
Oxidation Reduction Potential (ORP)	mV	-	-	-
Chemical Parameters				
pH	-	7.26	Measured by WWTP's pH meter	-
Chemical oxygen demand (COD)	mg L^{-1}	23.5	HACH- TNT820	1.00 - 40.0
Total nitrogen	mg L^{-1}	12.6	HACH-TNT 827	5 - 40
Nitrate (NO_3^{-2})	mg L^{-1}	45.3	HACH- TNT 835	1.00 - 60.00
Nitrogen associated to nitrate ($NO_3^{-2} - N$)	mg L^{-1}	10.2	HACH- TNT 835	0.23 - 13.50
Nitrite (NO_2^{-})	mg L^{-1}	0.920	HACH-TNT 839	0.05 - 2.00
Nitrogen associated to nitrite ($NO_2^{-} - N$)	mg L^{-1}	0.284	HACH-TNT 839	0.015 - 0.600
Total kjeldahl nitrogen	mg L^{-1}	2.12	Calculated	-
Phosphate (PO_4^{-3})	mg L^{-1}	4.36	HACH-TNT 843	0.15 - 4.50
Phosphorous associated to phosphate	mg L^{-1}	1.42	HACH-TNT 843	0.05 - 1.50
Sulfate (SO_4^{-2})	mg L^{-1}	99.0	HACH-TNT 865	40 - 150

Table A1-4 physicochemical surface water parameters, the first day of sampling (September 12th, 2018)

Parameter	Dimension	Mean Value	Method	Method Range (mg L^{-1})
Physical Parameters				
Total Solids (TS)	mg L^{-1}	318	APHA 2540 C	-
Total Volatile Solids (TVS)	mg L^{-1}	69.0	APHA 2540 E	-
Total Suspended Solids (TSS)	mg L^{-1}	2.50	APHA 2540 D	-
Volatile Suspended Solids (TVSS)	mg L^{-1}	0.930	APHA 2540 E	-
Fixed Suspended Solids	mg L^{-1}	1.50	Calculated	-
Oxidation Reduction Potential (ORP)	mV	-83.3	OAKTON pH, ORP, Temperature probe	-
Chemical Parameters				
pH	-	8.20	OAKTON pH, ORP, Temperature probe	-
Chemical oxygen demand (COD)	mg L^{-1}	14.3	HACH- TNT820	1.00 - 40.0
Nitrate (NO_3^{-2})	mg L^{-1}	1.29	HACH- TNT 835	1.00 - 60.00
Nitrogen associated to nitrate ($NO_3^{-2} - N$)	mg L^{-1}	0.301	HACH- TNT 835	0.23 - 13.50
Nitrite (NO_2^{-})	mg L^{-1}	0.071	HACH-TNT 839	0.05- 2.00
Nitrogen associated to nitrite ($NO_2^{-} - N$)	mg L^{-1}	0.022	HACH-TNT 839	0.015 - 0.600
Total kjeldahl nitrogen	mg L^{-1}	0.445	HACH-TNT880	0.0 - 16.0
Total nitrogen	mg L^{-1}	0.767	Calculated	-
Phosphate (PO_4^{-3})	mg L^{-1}	< 0.150	HACH-TNT 843	0.15 - 4.50
Phosphorous associated to phosphate	mg L^{-1}	<0.05	HACH-TNT 843	0.05 - 1.50
Sulfate (SO_4^{-2})	mg L^{-1}	<40.0	HACH-TNT 865	40 - 150

Table A1-5 physicochemical surface water parameters, the second day of sampling (September 13th, 2018)

Parameter	Dimension	Mean Value	Method	Method Range (mg L^{-1})
Physical Parameters				
Total Solids (TS)	mg L^{-1}	109	APHA 2540 C	-
Total Volatile Solids (TVS)	mg L^{-1}	36.0	APHA 2540 E	-
Total Suspended Solids (TSS)	mg L^{-1}	2.10	APHA 2540 D	-
Volatile Suspended Solids (TVSS)	mg L^{-1}	1.00	APHA 2540 E	-
Fixed Suspended Solids		1.10	Calculated	-
Oxidation Reduction Potential (ORP)	mV	-67.5	OAKTON pH, ORP, Temperature probe	-
Chemical Parameters				
pH	-	7.88	OAKTON pH, ORP, Temperature probe	-
Chemical oxygen demand (COD)	mg L^{-1}	18.9	HACH- TNT820	1.00 - 40.0
Nitrate (NO_3^{-2})	mg L^{-1}	1.78	HACH- TNT 835	1.00 - 60.00
Nitrogen associated to nitrate ($NO_3^{-2} - N$)	mg L^{-1}	0.443	HACH- TNT 835	0.23 - 13.50
Nitrite (NO_2^{-})	mg L^{-1}	0.088	HACH-TNT 839	0.05- 2.00
Nitrogen associated to nitrite ($NO_2^{-} - N$)	mg L^{-1}	0.026	HACH-TNT 839	0.015 - 0.600
Total kjeldahl nitrogen	mg L^{-1}	0.731	HACH-TNT880	0.0 - 16.0
Total nitrogen	mg L^{-1}	1.19	Calculated	-
Phosphate (PO_4^{-3})	mg L^{-1}	< 0.150	HACH-TNT 843	0.15 - 4.50
Phosphorous associated to phosphate	mg L^{-1}	<0.050	HACH-TNT 843	0.05 - 1.50
Sulfate (SO_4^{-2})	mg L^{-1}	<40.00	HACH-TNT 865	40 - 150

Table A1-6 physicochemical surface water parameters, the third day of sampling (September 14th, 2018)

Parameter	Dimension	Mean Value	Method	Method Range (mg L^{-1})
Physical Parameters				
Total Solids (TS)	mg L^{-1}	365	APHA 2540 C	-
Total Volatile Solids (TVS)	mg L^{-1}	88.0	APHA 2540 E	-
Total Suspended Solids (TSS)	mg L^{-1}	1.35	APHA 2540 D	-
Volatile Suspended Solids (TVSS)	mg L^{-1}	0.850	APHA 2540 E	-
Fixed Suspended Solids	mg L^{-1}	0.500	Calculated	-
Oxidation Reduction Potential (ORP)	mV	-113	OAKTON pH, ORP, Temperature probe	-
Chemical Parameters				
pH	-	8.50	OAKTON pH, ORP, Temperature probe	-
Chemical oxygen demand (COD)	mg L^{-1}	9.39	HACH- TNT820	1.00 - 40.0
Nitrate (NO_3^{-2})	mg L^{-1}	<1.00	HACH- TNT 835	1.00 - 60.00
Nitrogen associated to nitrate ($NO_3^{-2} - N$)	mg L^{-1}	<0.2	HACH- TNT 835	0.23 - 13.50
Nitrite (NO_2^-)	mg L^{-1}	0.56	HACH-TNT 839	0.05- 2.00
Nitrogen associated to nitrite ($NO_2^- - N$)	mg L^{-1}	0.017	HACH-TNT 839	0.015 - 0.600
Total kjeldahl nitrogen	mg L^{-1}	0.474	HACH-TNT880	0.0 - 16.0
Total nitrogen	mg L^{-1}	0.686	HACH-TNT880	-
Phosphate (PO_4^{-3})	mg L^{-1}	< 0.150	HACH-TNT 843	0.15 - 4.50
Phosphorous associated to phosphate	mg L^{-1}	<0.050	HACH-TNT 843	0.05 - 1.50
Sulfate (SO_4^{-2})	mg L^{-1}	<40.0	HACH-TNT 865	40 - 150

Table A1-7 Diurnal variation of dissolved oxygen in Sainte Lawrence River, the first sampling point (S1)

Parameters	Abbreviation	Dimension	Time of measuring				Mean value
			10h15	12h45	16h45	19h45	
Dissolved Oxygen	DO	mg L^{-1}	9.42	11.5	10.2	9.05	10.0
Temperature	T	℃	20.6	22.0	21.7	21.0	21.3

Table A1-8 Diurnal variation of dissolved oxygen in Sainte Lawrence River, the second sampling point (S2)

Parameters	Abbreviation	Dimension	Time of measuring				Mean value
			9h15	13h00	16h00	20h00	
Dissolved Oxygen	DO	mg L^{-1}	8.32	8.58	8.52	8.67	8.53
Temperature	T	℃	20.80	21.3	21.5	21.1	21.2

Table A1-9 Diurnal variation of dissolved oxygen in Sainte Lawrence River, the third sampling point (S3)

Parameters	Abbreviation	Dimension	Time of measuring				Mean value
			11h00	14h00	18h00	20h30	
Dissolved Oxygen	DO	mg L^{-1}	9.45	10.65	10.47	10.25	10.10
Temperature	T	℃	21.6	22.9	23.0	23.5	22.8

A2. Calibration curve for the venlafaxine at the maximum wavelength.

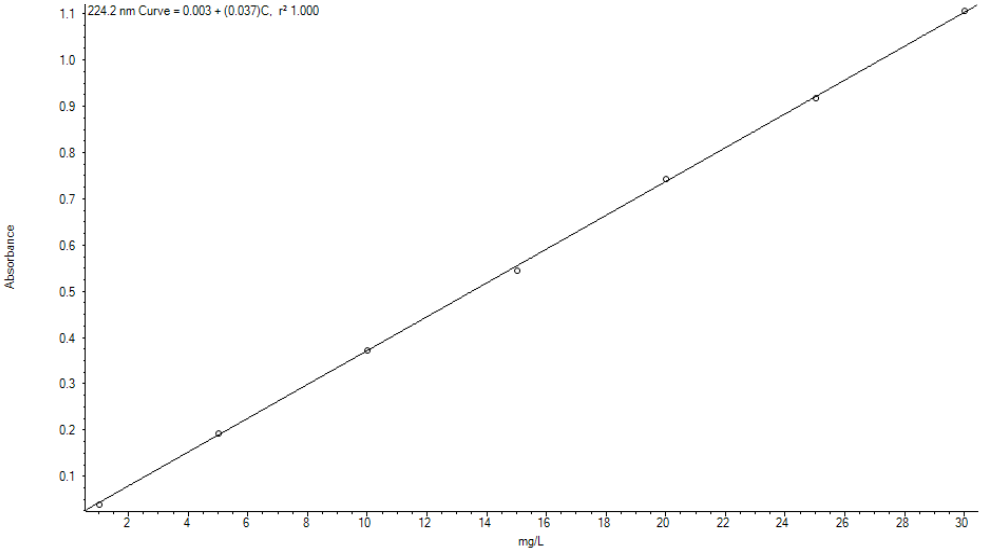
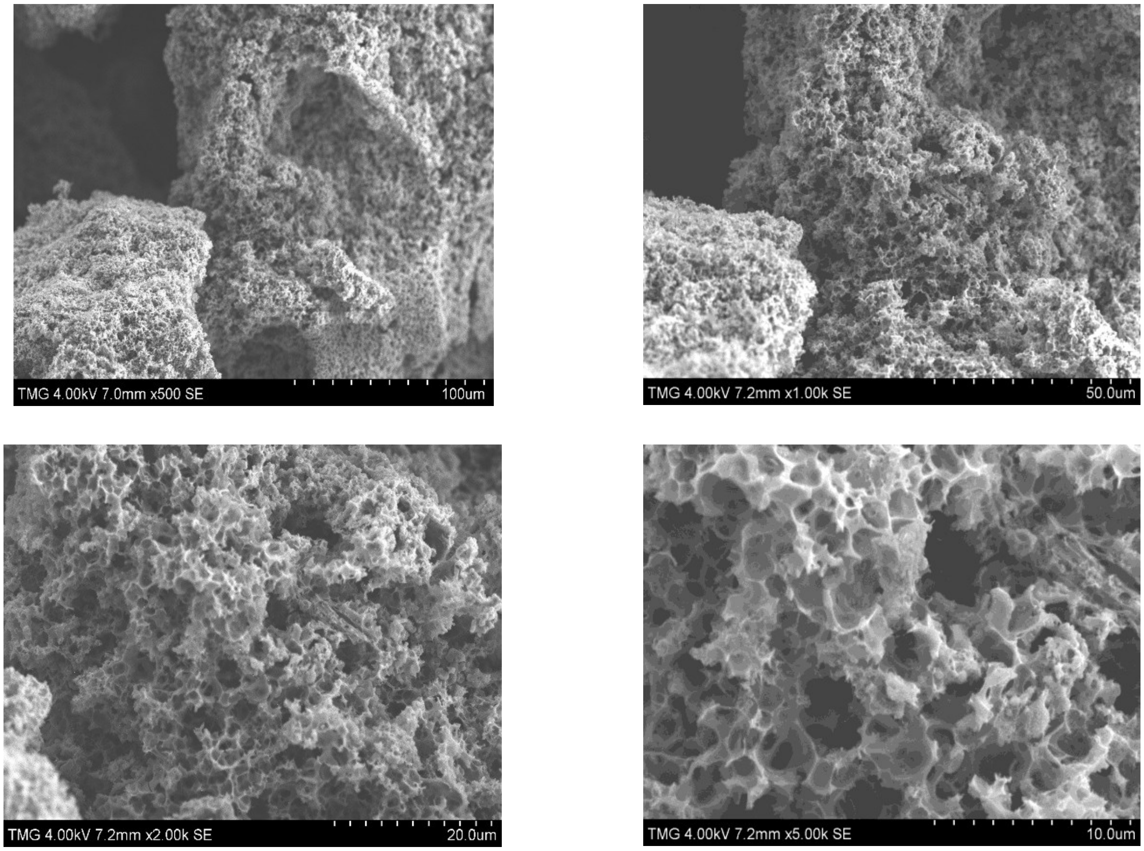
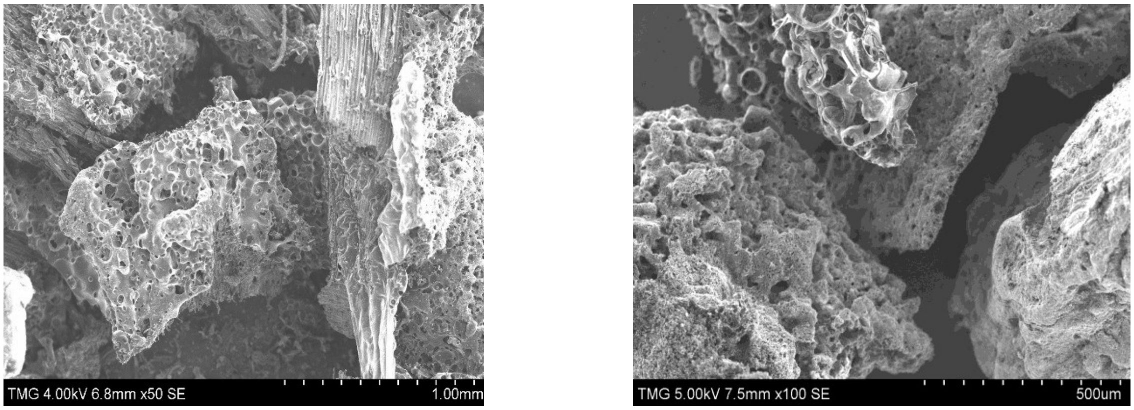


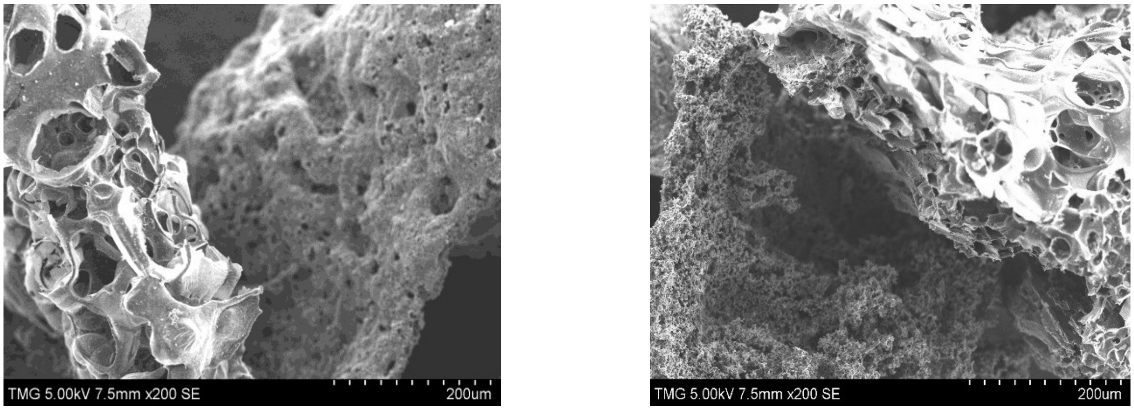
Figure A1 Calibration plot for venlafaxine

A3. Scanning electron microscopy (SEM) images of new sludge-based adsorbents

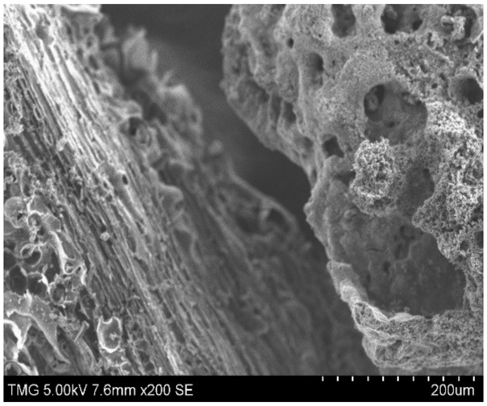


a





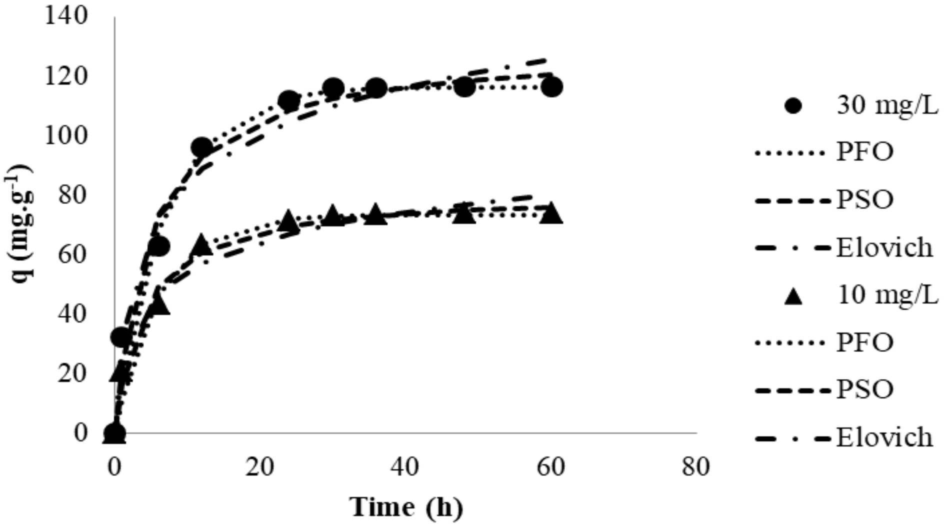
b



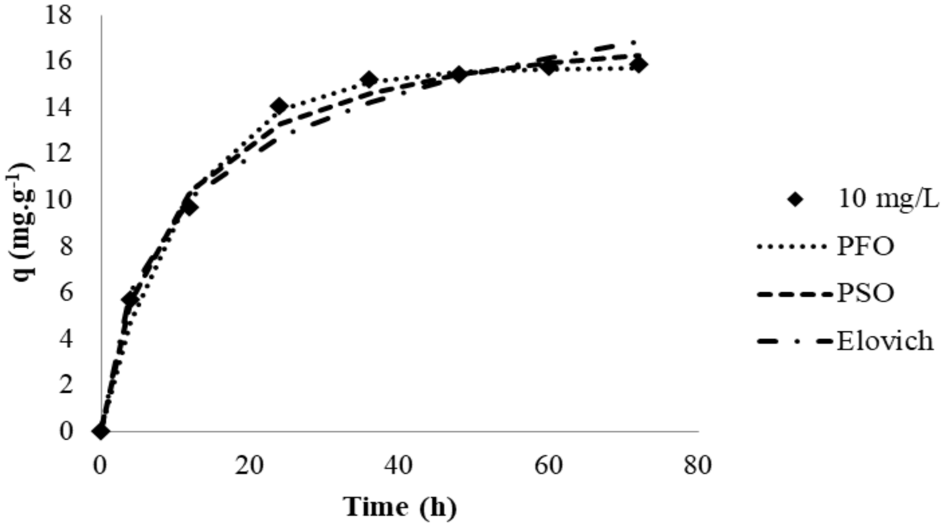
c

Figure A2 SEM images of new carbon adsorptive materials a) SS, b) SS:SW, and c) SS:HW

A4. Plots of kinetic models for the adsorption of VEN onto the selected adsorbents



a



b

Figure A3 Kinetic study of the sorption of venlafaxine onto a) SS:HW adsorbent (initial concentrations of venlafaxine: 10 and 30 mg L^{-1}, the dosage of adsorbent: 0.083 g L^{-1}), and b) CGAC (initial concentration of venlafaxine 10 mg L^{-1}, dosage of adsorbent: 0.4 g L^{-1}). PFO: pseudo-first order kinetic model, PSO: pseudo-second order kinetic model