

Electro-Adsorptive System for Removal of Pharmaceutical Products from an Aqueous Solution

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A Thesis
In the Department
of
Building, Civil, and Environmental Engineering

Presented in Partial Fulfillment of the Requirements
For the Degree of
Doctor of Philosophy (Civil Engineering) at
Concordia University
Montreal, Quebec, Canada

July 2019

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**CONCORDIA UNIVERSITY
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ABSTRACT

Electro-Adsorptive System for Removal of Pharmaceutical Products from an Aqueous Solution

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Commonly used pharmaceutical products present in sewage cannot be removed by conventional wastewater treatment plants. Therefore, they can be found in effluents discharged to aquatic systems. Endocrine disrupting compounds (EDCs) are among these releases into the environment. For example, 17α -ethynylestradiol (EE2) is a synthetic compound extensively used by the population, which is released into an environment. Thus, it can cause a negative effect on the endocrine system of aquatic biota and human.

To protect the aquatic system against an impact of EDCs comprised in the effluent, a novel system for their removal was proposed. A steroidal estrogen, EE2, was assumed to be a target compound in this investigation. Then, the objective of this study is to develop a sustainable system for EE2 removal. The methodological approach combining an adsorption with electro-kinetic phenomena has been proposed. Sustainability is supposed, based on revalorization of wasted materials and minimizing of energy use. Six phases of investigation were proposed, namely, phase 1: Manufacturing procedures; phase 2: Upgraded adsorption system; phase 3: Experimental protocol; phase 4: Electro-adsorptive system; phase 5: Electro-adsorptive system comparison; phase 6; cost-effectiveness increase and energy saving proposal. The study has been advanced, where waste generated by fisheries and forestry demonstrated already excellent materials to build an electro-adsorptive system. Application of a low direct current (DC) has also demonstrated a sufficient effectiveness of the system. In focus, to understand the partitioning of EDCs (EE2) between liquid and solid phases, eight types of adsorbents made from New Adsorptive Materials were initially used to remove EE2 from an aqueous solution. Afterward, these adsorbents were enhanced with New Adsorptive Materials (chitin) to increase EE2 removal from an aqueous solution. These adsorbents were then enhanced with New Adsorptive Materials (chitin) to increase EE2 removal from an aqueous solution.

The analytical test showed that adsorption phenomena using these types of adsorbents adequately reduces EE2 in the aquatic solution. The obtained results of the analytical test were initially sorted based on the adsorbent type: 1. Adsorbent made from New Adsorptive Material (softwood) showed 42% removal of EE2; 2. Adsorbent made from New Adsorptive Material (hardwood) showed 47% removal of EE2.

As a competitive removal capacity with cost- effectiveness increase, it was proposed to enhance the best adsorbent which was shown by the primary results using chitin. This method (adsorbent enhancement method) showed 92% EE2 removal. It was a great removal capacity, but it was still far away from the research objective. Therefore, it was proposed to establish an electrical system able to support adsorption phenomena. A combination technique was the choice. This technique was established by a combining a direct current (DC) field phenomena and adsorption phenomena (Electro-Adsorptive System). In this phase, various configurations of electrokinetic reactors were tested: 1). Electrode materials iron, aluminum, and carbon; 2) Constant voltage of 5, 10, 15, 20, 30V; 3). Time of applied electrical field from 9h to 24h; 4). Different types of synthetic adsorbents. Finally, an experimental comparison was conducted between synthetic and commercial adsorbents.

The results from the analytical tests were as follows: 1) 82 % removal of EE2 at pH between 7 to 10 using the individual formulated adsorbent from thermally treated hardwood residues (H1T1) (far from the objective with some disadvantages); 2) 99.99% removal of EE2 using the adsorbent made from chitin in electro-adsorptive system regardless electrodes types, which are a good indicator for electrode flexibility use but the disadvantage of this removal method is remaining particles of adsorbent in an aqueous solution; 3) 79% removal of EE2 using the commercial activated carbon adsorbent (CACA) made from coconut shell; 4) 99.99% removal of EE2 using the enhanced adsorbent made from NAM (H1T1)+chitin (ENAM) in electro-adsorptive system (the best method).

This study has shown the possibility of the EE2 removal by 99.99%. It is expected, that the developed system would be applied to water treatment facilities or to polish effluents before discharge into aquatic systems.

Acknowledgements

I wish to express my sincere gratitude to:

My supervisor, Prof. Maria Elektorowicz, for granting me the excellent opportunity to do this wonderful thesis entitled “Electro-Adsorptive System for Removal of Pharmaceutical Products from an Aqueous Solution” in the Department of, Building, Civil and Environmental Engineering at Concordia University. I am thankful for her patience, guidance, encouragement, and advice throughout my study period under her supervision.

I wish to sincerely thank:

1. Iraqi Higher Education and Scientific Research for granting me this opportunity to finish my study.
2. Canadian Government for ECCC project (EDF-PQ-2017 G005).
3. University of Concordia, Université du Québec à Montréal, and Université de Montréal for using their facilities.
4. Research material suppliers.
5. Professors and technical staff from inside and outside the Building, Civil, and Environmental Engineering for offering their assistance.

I wish to express my special thanks to:

The Examination Committee Members who devoted their time to the detailed review of my thesis.

I wish to express my heartfelt thanks and appreciation for the unconditional love and the source of the inspiration:

The almighty God and my parents.

I wish to express my deepest sense of gratitude and appreciation to:

My siblings and my wife for their precious comments and insightful suggestions.

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Table of symbols and abbreviations

NAM	The best formulated adsorbent among eight adsorbents (New adsorptive materials)
ENAM	Enhanced best formulated adsorbent (Enhanced New Adsorptive Material)
CACA	Commercial Activated Carbon Adsorbent
S1T1	Formulated adsorbent from softwood, particle size ≤ 1 mm, and at 600°C
S1T2	Formulated adsorbent from softwood, particle size ≤ 1 mm, and at 800°C
S2T1	Formulated adsorbent from softwood, particle size ≤ 2 mm, and at 600°C
S2T2	Formulated adsorbent from softwood, particle size ≤ 2 mm, and at 800°C
H1T1	Formulated adsorbent from hardwood, particle size ≤ 1 mm, and at 600°C
H1T2	Formulated adsorbent from hardwood, particle size ≤ 1 mm, and at 800°C
H2T1	Formulated adsorbent from hardwood, particle size ≤ 2 mm, and at 600°C
H2T2	Formulated adsorbent from hardwood, particle size ≤ 2 mm, and at 800°C
BET	Brunauer Emmett Teller
C_e & C₀	Equilibrium and initial concentrations of EE2 (mg/L)
CEC	Cation Exchange Capacity
D4	Internal standard (17 α -Ethinylestradiol-2, 4, 16, 16-d4)
DCM	Dichloromethane

$D_{i,i'}$	Distance between cities i and i'
E1	Estrone
E2	Estradiol
E3	Estriol
EE2	17 α -Ethinylestradiol
EDC	Endocrine Disrupting Chemicals
FTIR	Fourier Transform Infrared Spectroscopy
HPLC	High Pressure Liquid Chromatograph
K	Coefficient representing the change of sorption capacities
K_{oc}	Normalized organic carbon partitioning coefficient
K_{ow}	Octanol water partitioning coefficient
k_f	Measure of adsorption capacity
MC	Moisture Content
MeEE2	Mestranol
Nzvi	Nanoscale zero valent iron

PHzc	Zero charge
pK_a	Dissociation coefficient
PSA	Particle Size Assessment
q_e	Equilibrium EE2 concentration on the adsorbent (mg/g)
R_L	Dimensionless separation factor
SEM	Scanning Electron-Microscopy
TGA	Thermal Gravimetric Analysis
WWTP	Waste Water Treatment Plant
1/n	Freundlich intensity parameter, indicates the intensity of adsorptive interactions
α	Empirical parameter representing Freundlich sorption coefficient
β	Empirical parameter representing Freundlich sorption constant
γ	Empirical coefficient that characterizes the curvature of a parabola
Φ	Large positive number

Chapter 1: Introduction

1.1. Background

Pharmaceutical products, prescribed to treat medical issues in humans and animals, can be found in the sewage system. Thus, it is a primary interest of this research. EE2 (17 α -ethynylestradiol) is one of these pharmaceutical compounds, which is commonly used as a hormone replacement therapy or as a contraceptive product. Pharmaceutical products belonging to Endocrine Disrupting Compounds (EDCs) are considered global and ubiquitous problems [1]. EDCs are chemical substances which are able to cause adverse health effects in humans as well as in fish. Accordingly, EDCs have become a major focus of current research.

EDCs can negatively affect the endocrine system, including birth defects, developmental disorders, and cancerous tumors. EDCs might have a strong tendency to distribute among phases due to a weak solubility in water and their hydrophobicity [2]. EDCs can have a natural or synthetic origin, as recognized in a number of studies [1]. For example, estrone (E1), estradiol (E2), and estriol (E3) are classified as natural estrogens, while 17 α -ethynylestradiol (EE2) is classified as a synthetic estrogenic steroid, whereas, Bisphenol A (BPA) is classified as an industrial pollutant. Ecological risk study has confirmed that 17 α -ethynylestradiol (EE2) is the riskiest compounds amongst eight types of EDC. It is before these compounds: estrone (E1), estradiol (E2), estriol (E3), and bisphenol A (BPA) [3]. This research focused on EE2 as an EDC representative.

The origin of micro-pollutant contamination is predominantly a result of anthropogenic action and the aquatic environment becomes the final resting place for most of these chemical compounds [4,5,6]. EDCs are chemicals found in plasticizers, pesticides, metals, contaminants in food, personal care products, industrial chemicals, as well as natural compounds that include human hormones and their breakdown products. Mammalian and human urine excreted into wastewater are natural sources for estrone (E1) and estrogen (E2) contamination. Both domestic and industrial wastewaters contain micro-pollutants, which are not entirely removed by conventional wastewater treatment plant (WWTP) processes, therefore, are continually discharged into the aquatic environment [6,7]. Wastewater treatment plants (WWTPs) have been reported as the major source

of EDCs [8,9,10,11,12] as shown in Fig.1. Thus, EDCs need to be urgently removed from effluent to avoid adverse effects to humans, wildlife, and fish. This research proposes a new technique to remove EDC from an aqueous solution using new adsorptive materials based on waste residues.

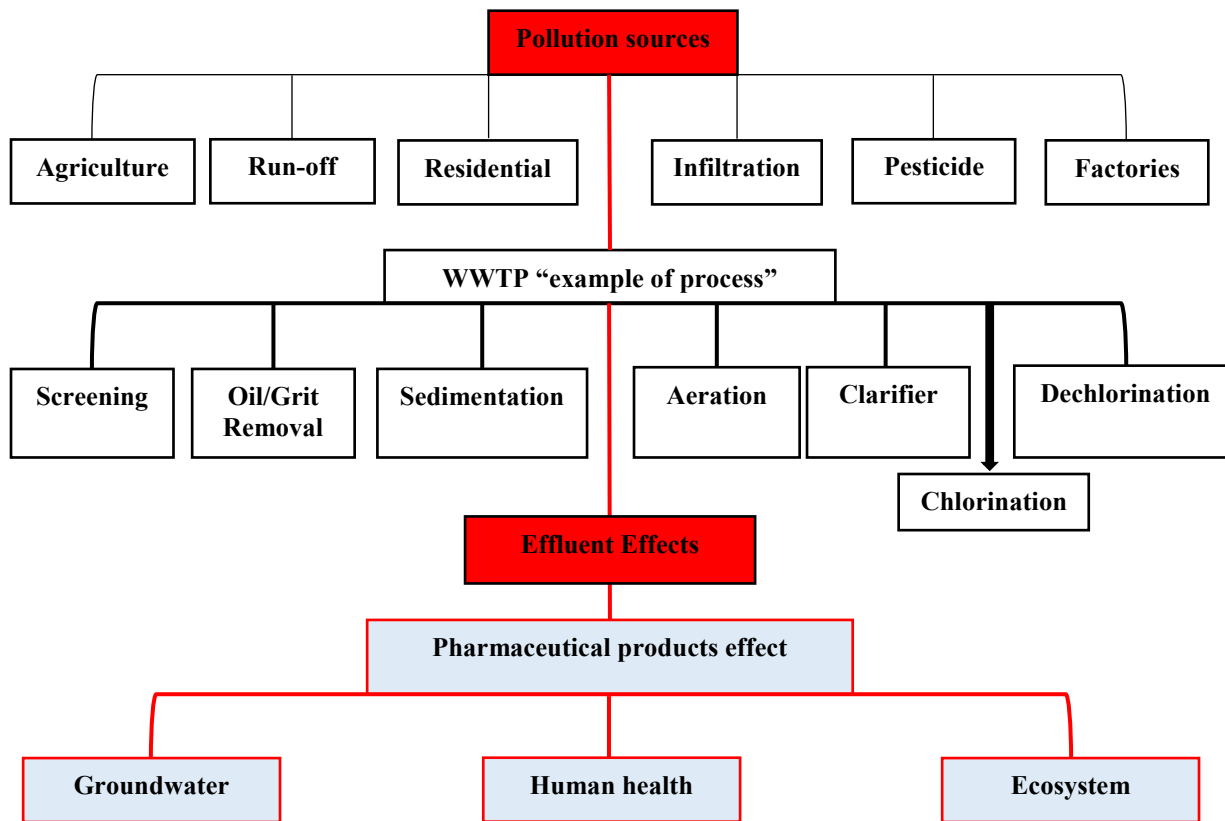


Figure 1: Potential sources and pathways of EDCs in the environment

Legend in Fig. 1 [13]:

1. **Preliminary treatment (pre-treatment):** it aims to remove coarse solids and other large materials often found in raw wastewater, such as grit removal, coarse screening, and in some cases, comminution of large objects.
 2. **Primary treatment:** it aims to remove settleable inorganic and organic solids by sedimentation, such as BOD₅ 25 to 50%, the total suspended solids (TSS) 50 to 70%, and the oil and grease 65%.
 3. **Secondary treatment:** it aims to further treat of the effluent from primary treatment to remove suspended solids and residual organics, such as colloidal organic and biodegradable dissolved matter using aerobic biological treatment processes.
 4. **Clarifier:** it is an individual treatment process employed to remove phosphorus, nitrogen, heavy metals and dissolved solids, refractory organics, and additional suspended solids.
 5. **Wastewater effluent:** it is a liquid waste or sewage discharged into a river, a lake, or the sea.
- ***Disinfection** it is the injection process of a chlorine solution (or ozone and ultra violet (UV)) at the head end of a chlorine contact basin with dosages of 5 to 15 mg/l.
- ***De-chlorination:** it is a process to remove residual chlorine (by sulfur dioxide) from disinfected wastewater before discharge into the environment.

1.2. Research questions and focuses

The endocrine disrupting compounds (EDCs) impact on environmental and public health has been a primary concern of recent years. Therefore, finding a sustainable and cost-effective system to restrain their negative impact seems to be a contemporary task of present time. To establish this study, the following scientific questions and focuses were made:

➤ Questions

- ❖ Why have endocrine disrupting compounds (EDCs) received unique attention at WWTP?
- ❖ What WWTP technologies have been proposed for EDCs removal from an aqueous solution?
- ❖ What are the physicochemical properties of EDCs, and what are their impact on the environment?

➤ Focuses

- ❖ Pharmaceutical products representative (*EE2*)
- ❖ Cost-effectiveness increase and energy saving proposal (*waste materials, models*)
- ❖ Solution sustainability (*available source of waste materials*)
- ❖ Removal capacity increase (*enhancement method and techniques combination*)

To answer these questions with making a focus, a survey of the available data has been conducted.

1.3. Motivation

Over 100,000 new chemicals have been introduced as common consumer products into an environment in recent decades. Endocrine disrupting compounds (EDCs) are among these chemicals. As yearly normal investigations conducting of chemicals worldwide, it has been found that bisphenol A (BPA) [14] to be endocrine disruptor, and top of a potent chemicals list by (the EPA in 2014) [15], a “toxic substance” by the Canadian government in 2010 [16], and most recently a “substance of very high concern” by the European Union in 2017 [17]. Endocrine disrupting compounds (EDCs) have received unique attention especially in recent years due to their toxicity in animal and human populations [18]. This is due in part to the discovery of the many risky ecological and health impacts of these chemicals, in part to commercial and industrial use of these compounds leading to greater concentrations in water resources. In fact, many suspected and known endocrine disrupting compounds (EDCs) are being found at the environmentally significant concentrations in the effluent of wastewater. A wide number of publications confirm the detection of steroids, having potential environmental risk, in treated sewage effluents, raw sewage, receiving rivers, and surface waters [19]. Subsequently, this research focuses on finding a sustainable technique for this issue because of their ubiquitous existence in the principle compounds of life, such as water, food and air.

1.4. Problem formulation

The endocrine system of the human (Fig. 2) comprises a series of glands distributed throughout the body [20]. The main function of these glands is to secrete hormones, which play an important role in maintaining homeostasis. Meanwhile, any disruption in the function of these glands may lead to adverse health effects. Most studies confirmed that an exogenous factor was the major reason which affected health. The studies also showed similarity between the structure of an endocrine disruption compound (EDC) and a hormone (for example thyroid hormone) [51].

An EDC, once in an aquatic environment, is an exogenous factor causing adverse health effects into living organisms. It affects the endocrine system due to the similarity in the structure between EDC and a hormone secreted by the glands. Figure 2 shows the similarity between EDC and thyroid hormone. Similarly, other synthetic compounds mimic natural hormones.

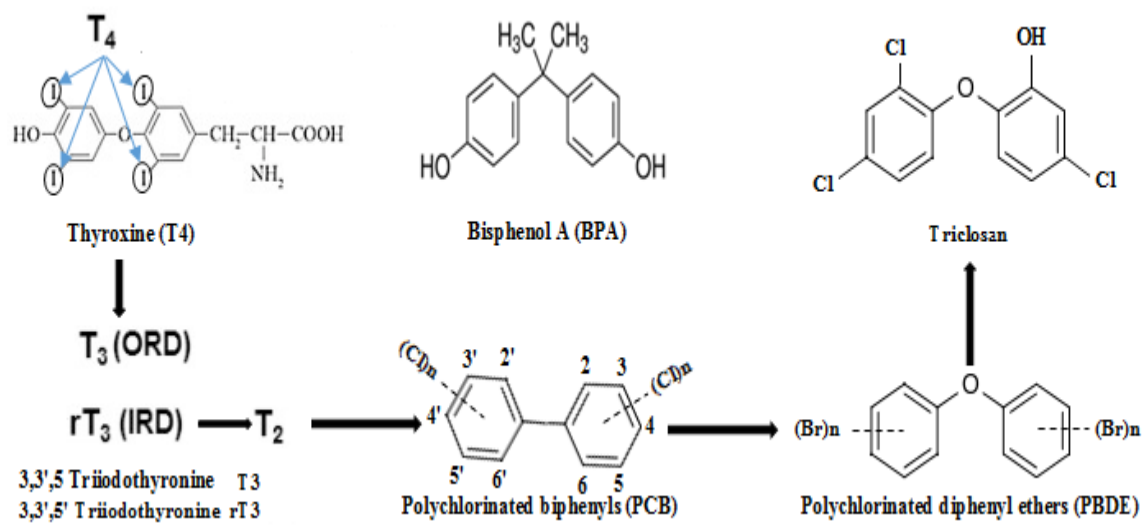
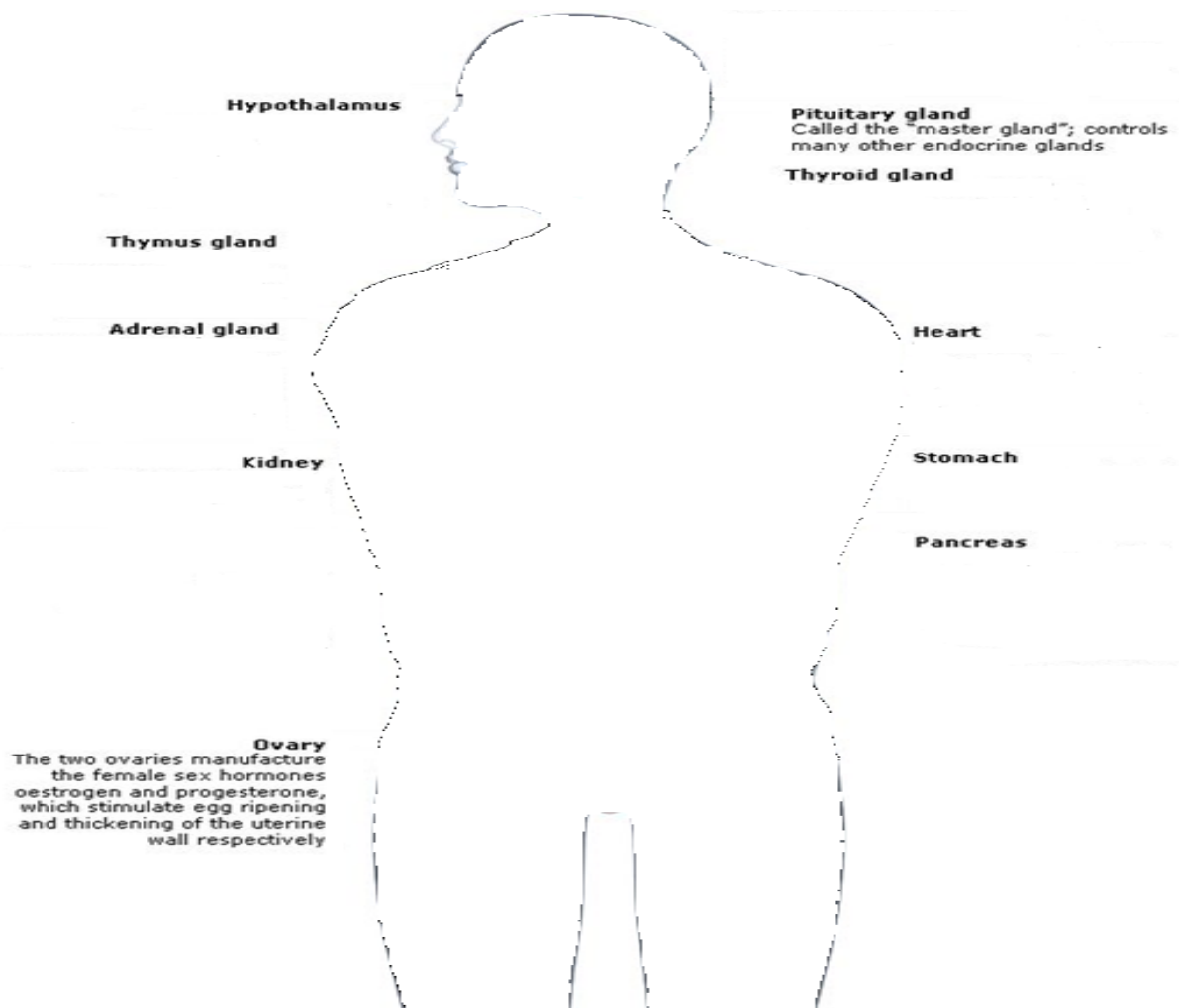


Figure 2: Major endocrine glands in the human body and structure similarity between EDC and thyroid hormone

1.5. Significance and purpose of the study

Endocrine disruptors compounds (EDCs) are water-present pollutants, which can interfere with endocrine systems at certain doses. EDCs interfere with the body's endocrine system by influencing the synthesis, release, transport, metabolism and excretion of hormone [18]. These disruptors can cause serious problems for humans, such as birth defects and developmental disorders. Some studies show that endocrine-disrupting compounds (EDCs) can cause adverse effects, even at low concentrations (from ng L^{-1} to $\mu\text{g L}^{-1}$), due to exogenous endocrine disruption in the reproductive, sexual differentiation, neurological and immune systems [21,22,23]. EDCs can comprise estrogens which might include estrone (E1), 17- β -estradiol (E2), and estriol (E3) which are predominantly female hormones, responsible for the maintenance healthy reproductive tissues, breast, skin and brain [24,25,46]. In addition, 17 α -ethynylestradiol (EE2), norethindrone, and mestranol (MeEE2) are very potent estrogenic compounds as shown by vivo [26,27] and in vitro [28,29] studies [30,31,32]. For example, EE2 maintains elevated levels of estrogen and progesterone in the blood stream and inhibit release of hormones FSH and LH by pituitary gland, thus preventing ovulation.

Equally important, water and wastewater treatment plants are not designed for removal of EDCs. Therefore, potential removal of the EDCs from water is a significant contribution to public health and environmental protection.

This study aims to investigate the potential of EDC removal from the aqueous solution at a cost-effective way. It focuses on finding a technique for removing the most potent compounds namely EE2, from the aqueous solution. It is assuming that newly developed system minimizes potential risks to environment and enhances the quality of water resources. To summarize, the following significance and purpose of this study are considered:

1. Finding sustainable system for EE2 removal from the aqueous solution.
2. Developing a removal technique of EE2 from aqueous solution by adsorption but with a novel source of material.
3. Finding an advanced engineered approach to formulate an adsorptive system.

1.6. Research objectives

It becomes an urgent need to develop a removal system of a synthetic steroidal estrogenic compound (17 α -ethynylestradiol) from the aqueous solution. The system might be the most efficient based on adsorption phenomena combined with electrokinetic phenomena. To decrease the costs of a newly developed adsorptive material, the use of waste residues was considered.

To achieve this objective, two types of waste attracted attention such as forestry waste (wood chips) and fishery waste (chitin), which are generated in large amounts in Canada. Subsequently, the following main and detailed objectives were formulated:

Objective 1: Investigating adequate components for formulated adsorbents

- 1) Finding new waste materials that have initial properties capable to be adequately transformed during the processing (e.g. wood).
- 2) Development of an advanced engineered approach to formulate a sustainable adsorptive system.
- 3) Development of the adsorption capacity, by modifying functional groups on the surface of adsorbents (enhancing the target compound adsorption using new waste materials).
- 4) Development of models for increasing a cost-effectiveness and saving an energy.

Objective 2: Study of adsorbent performance under different environmental conditions

- 1) Evaluation of the performance of the formulated adsorbents with respect to partitioning process of EE2, considering equilibrium time, the initial EE2 concentrations, and pH effect.
- 2) Evaluation of the correlation between eight formulated adsorbents with the maximum achievable partitioning of EE2 from aqueous solution, considering adsorptive material type and manufacturing conditions, such as effect of pyrolysis temperature effect and particle size.
- 3) Assessing the best isotherm models.
- 4) Evaluation of the correlation between formulated adsorbent properties with the maximum achievable partitioning of EE2 from aqueous solution, considering surface area and functional groups.
- 5) Development of a procedure to achieve maximum extraction and detection efficiencies of a low concentration of the estrogenic compound (17α -ethynylestradiol).
- 6) Development of an electrocoagulation system to achieve a maximum extraction and detection efficiencies for EE2 removal and remains of adsorbent particles.

Chapter 2: Literature review

2.1. Endocrine Disrupting Compounds (EDCs)

Endocrine Disrupting Compounds (EDCs), present in air, water, food, soil, dust, can be defined as environmental chemicals that can interfere with endocrine (hormone) systems at certain doses to cause adverse effects in humans, wildlife, and fish. Evidence for altered physiology, sexual development & function, has been shown in fish [33].

EDCs are estrogens in mixture: Estrone (E1), 17- β -estradiol (E2), and estriol (E3) are predominantly female hormones, responsible for the maintenance of the health of reproductive tissues, breast, skin and brain [34,35,46], 17 α -ethynylestradiol (EE2), norethindrone, and mestranol (MeEE2) are very potent estrogenic compounds as shown by vivo [36,37] and in vitro studies [38,39]. EE2 can maintain high levels of estrogen and progesterone in the blood stream and inhibit the release of hormones FSH and LH by the pituitary gland, thus, preventing ovulation [40]. The origin of EDC is predominantly anthropogenic action, such as mammal and human urine, pharmaceuticals, plasticizers, pesticides, and other industrial chemicals, as well as natural compounds include human hormones and their breakdown products, and the final resting place for EDC compounds is the aquatic environment [6, 41,42,43]. EDCs are negatively charged ions in an aqueous solution [44].

2.1.1. EDC Structure

Synthetic and natural hormones are extensively used for animals and humans. Estrogen is estradiol (a dialcohol), followed by estrone (a ketone). Steroid hormones are a group of biologically active compounds that are synthesized from cholesterol, a precursor of mammalian sexual steroids [45,46]. The steroid is a type of organic compound that contains a characteristic arrangement of four cycloalkane rings joined to each other, such as the sex hormones estradiol and testosterone. The steroid hormones are 18-carbon molecules with an aromatic A-ring as a distinctive part of their tetracyclic molecular framework (Fig 3). This phenolic (A-ring) is the structural component that characterizes the affinity of binding to the estrogen receptor [47,48]. The key structural

difference that distinguishes the steroid hormones from one another arises in the D-ring component of their tetracyclic ring skeleton; owing to the type and stereo-chemical arrangement of the functional groups attached to carbon-3, carbon-16 and carbon-17 positions (alcoholic (OH), phenolic (ring-OH), carboxyl (COOH), carbonyl (C=O), and amines (NH_x)).

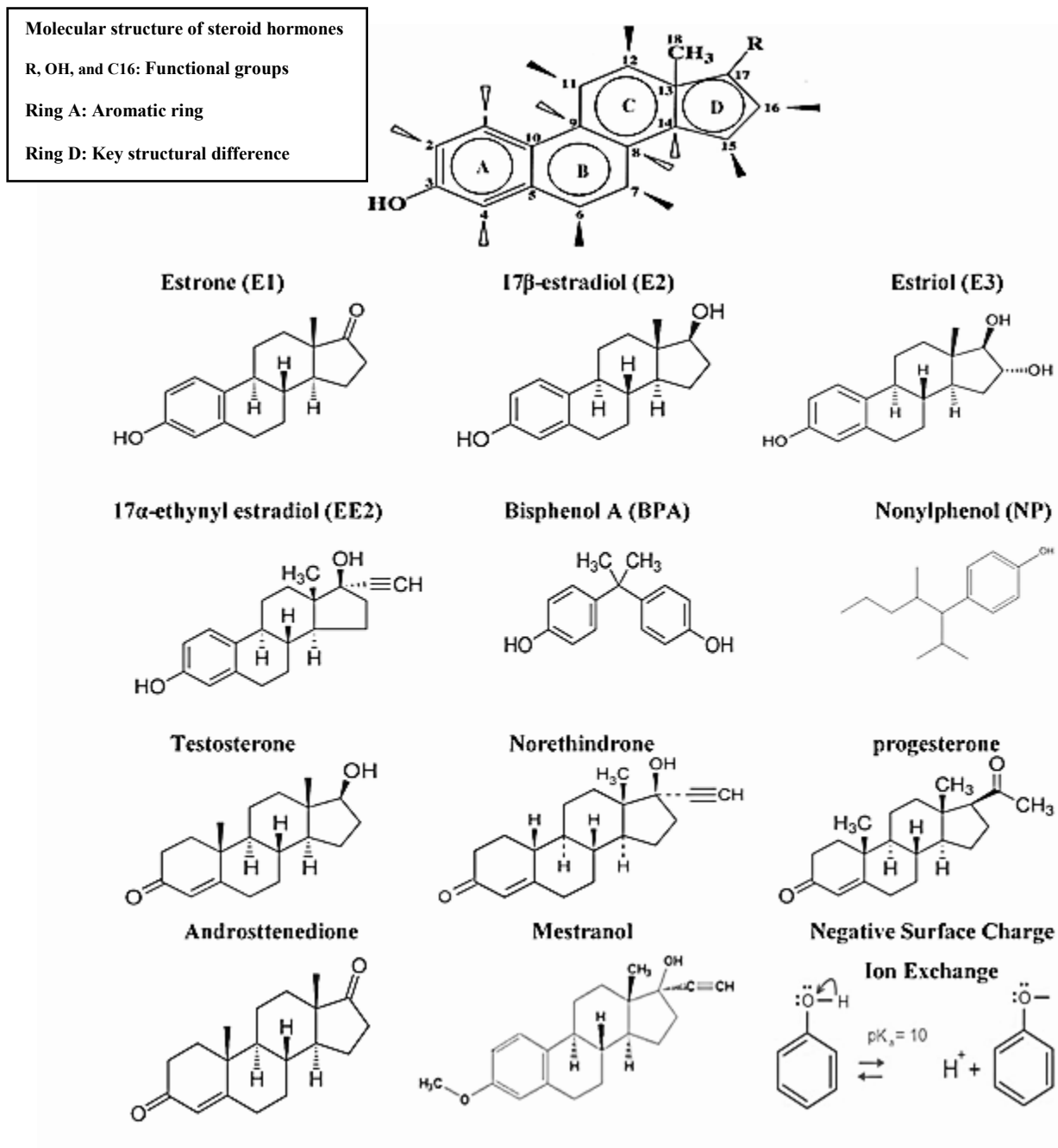


Figure 3: Molecular structure of steroid hormones

The major biosynthetic pathway for estrogen begins with cholesterol (C₂₇). Estradiol can have either a hydroxyl group at carbon-17 that points downward from the molecule (a-configuration) or a hydroxyl group that projects upward from the molecule (P configuration). Estrone differs from estradiol by the carbonyl group at carbon-17 rather than a hydroxyl group, estriol features hydroxyl groups at both carbon-16 and carbon-17 positions. Similarly, 17 α -ethynylestradiol is structurally identical to E₂, with the exception of an ethynyl substitution at carbon-17. Moreover, conjugated steroids are analogous to their parent compounds, except for a sulfate and/or glucuronide substitution at carbon-3 and/or carbon-17 [47, 48]. The group of molecules identified as endocrine disruptors is highly heterogeneous (size, shape, color, weight, distribution, etc.). This group includes synthetic compounds used as industrial solvents/ lubricants and their byproducts plastics [bisphenol A (BPA)] [49]. BPA shares some structural similarity to estradiol and binds to estrogen receptors (ER α) with weak affinity [50,51]. BPA has a strong binding affinity to the estrogen-related receptor γ and the G protein-coupled ER (GPER) [51,52,53].

2.1.2. Physicochemical properties

EDCs are relatively hydrophobic organic compounds based on their octanol-water partition coefficient (K_{ow}) values and have only one pK_a value as shown in Table 1 [1]. Estrogen has an alcohol or ketone as a functional group (should be ionic or polar to help a reaction) at the C3 and C17 positions, and a methyl group at C13. A unique aspect of estrogen biosynthesis is the conversion (catalyzed by the enzyme aromatase) of the A ring to an aromatic ring [54].

The physicochemical properties are shown in Table 1 regarding natural estrogens, namely estrone, estriol, and estradiol. They are generally considered weak acids with pK_a values ranging between 10.3 and 10.8 and steroids are relatively hydrophobic; $\log K_{ow}$ 2.8-4.7. In addition, the aqueous solubility of hydrophobic organic compounds can influence their distribution. The partitioning of estrogens between aqueous and solid phases has shown to be influenced by their aqueous solubility [55, 142]. Natural estrogens, namely estradiol, estrone and estriol have a higher water solubility of approximately 13mg/L and a low volatility. It is expected that their sorption onto materials (absorbent) is a significant factor in reducing aqueous phase concentrations.

Table 1: Physicochemical properties of the target EDCs

Ster.	Molar mass (g.mol ⁻¹)	Molar volume (gm.mol ⁻¹)	Molar density (g.cm ⁻³)	Molecule Volume (cm ⁻³)	Log K _{ow}	Log K _{oc}	pK _a	W.S. (MgL ⁻¹)	Ref.
E1	270.37	232.1 ± 3.0	1.164 ± 0.06	3.85 × 10 ⁻²²	3.13 – 3.43	3.1–3.5	10.34 ± 0.05	30	22
E2	272.38	232.6 ± 3.0	1.170 ± 0.06	3.86 × 10 ⁻²²	2.81	3.5	10.46 ± 0.03	13	22
E3	288.38	229.6 ± 3.0	1.255 ± 0.06	3.81 × 10 ⁻²²	2.81	3.5	10.38 ± 0.02	13	22
EE2	296.40	244.4 ± 3.0	1.21 ± 0.01	4.06 × 10 ⁻²²	3.67 – 4.20	3.8	10.40	4.7-19	22
BPA	228.29	199.5 ± 3.0	1.143 ± 0.06	3.31 × 10 ⁻²²	3.32		9.6 – 10.02	120	22
4tBP	150.22	154.5 ± 3.0	0.971 ± 0.06	2.57 × 10 ⁻²²	3.31	3.39	10.16	610	

2.2. Water and WWTP treatment techniques

Endocrine disrupting compounds (EDCs) are a challenge for water and wastewater treatment plants (WWTP) because they are present at very low concentrations, where the substances at much higher concentrations are competing for adsorption sites. Many separation processes such as precipitation, flocculation, and coagulation have been used for the removal of EDCs from different type of water [56,57]. EDCs may also be removed by biodegradation processes [58]. However, numerous investigations showed significant variability between the effectiveness of treatment processes [59].

Conventional biological processes, such as constructed wetlands, biofiltration, and activated sludge have shown limited removal of EDCs [56, 57]. Conventional WWTPs have been typically designed to remove the organic carbon load and nutrients (N and P) but no attention was given to the specific removal of EDCs [2]. Advanced treatment processes such as ferrate [60] free radical oxidation, photolysis, granular activated carbon, photo-catalysis, ozonation, separation, Fenton oxidation, chlorination, and membrane separation have shown more satisfactory results [56, 57, 61, 62]. Advanced oxidation processes (AOPs), such as ozonation and non-thermal plasma, have also been studied and have proven to achieve good removal of EDCs in wastewater [63,64, 65]. However, the effects of oxidation products are still not fully understood, which may delay the widespread utilization of such methods. In addition, some hybrid systems such as membrane bioreactors (MBR) followed by ultrafiltration/ nanofiltration/ reverse osmosis, flocculation followed by activated sludge and ultrafiltration can also remove EDCs efficiently from water and wastewater [56,66]. Membrane techniques, specifically reverse osmosis (RO) and nano-filtration (NF), have attracted great attention for EDCs removal in wastewater treatment [67,2], while microfiltration (MF) and ultrafiltration (UF) had limited performance due to their large pore size [68]. Chemical fouling and biofouling remain the major drawbacks of membrane application in wastewater. Some researchers have studied the adsorption of EDCs by activated carbon (AC) and found that AC is effective in removing EDCs in the lab as well as pilot and full-scale plants [69]. Operational conditions should be strictly controlled, and large amounts of AC are required in full-scale plants, therefore making this method expensive [70].

Furthermore, it is always preferable to reduce the cost involved in its treatment because the wastewater treatment is less profitable compared to other industrial sectors. The potential of bio-waste to produce a low cost adsorbent has been identified since the last decade, and many studies have been conducted to determine the efficiencies and characteristics of ACs produced from different bio-waste in a removal process of different pollutants from wastewater. Finally, given the significant research carried out and the knowledge gained so far on the fate of EDCs in the treatment process and their effects on humans and the environment, additional of treatment modules to the existing WWTPs have been proposed and investigated in the recent decade. These include biological, physical, and chemical advanced oxidation methods [69,71].

2.3. Advantages and disadvantages of water and WWTP treatment techniques

Recently, it has been assumed that slow sand filtration is an old- fashioned technique of water treatment. Therefore, it has been replaced by rapid-gravity and other high rate filtration methods. In addition, Advantages and disadvantages of EDC removal techniques were summarized in Table 2 [72,73,74,75,76,77].

Table 2: Advantages and disadvantages of EDC removal techniques

Techniques	Disadvantages	Advantages
Adsorption	Low selectivity (depending on the type of adsorbent material used).	High efficiency; Having wide pH range, ease of operations, regeneration of the adsorbent materials; low capital cost; and high metal binding capacities.
Ion exchange	Regeneration of the resin source of serious secondary pollution and high cost due to synthetic resins.	High removal efficiency; high treatment capacity; and fast kinetics.
Flocculation and coagulation	They cannot purify waste water containing heavy metals and must be followed by other purification techniques.	Removes the turbidity in addition to heavy metal removal; produced sludge with good sludge settling and dewatering characteristics
Membrane filtration absorption	Complex process; high operating cost due to membrane fouling, and low permeate flux.	High separation selectivity; low pressure requirement; small space requirement
Flotation	High initial capital cost; high operation and maintenance costs.	High metal selectivity; low operational cost; high overflow rates; low detention periods; more concentrated sludge production; and high removal efficiency.
Electrochemical techniques (or electro-dialysis)	Membrane fouling and energy consumption cause high operational cost.	High separation selectivity.
Reverse osmosis	High cost; pressure and energy are required for the good operation of this technique and not effective for the removal of smallest organic pollutant; source of waste generation.	Mostly used for the desalination of seawater; can be used for the removal of organic; inorganics and bacteria from waste water.
Photo-catalysis	Long duration time applications limited.	Simultaneously removal of organic and metal pollutants; and less harmful by-products
Chemical precipitation	Extra operational cost for sludge disposal. Not efficient for water purification with low concentration of heavy metals sludge generation	Operating conditions are simple; low cost

2.4. Advantages and disadvantages of conventional adsorbents

Advantages and disadvantages of conventional adsorbents were summarized in Table 3 [78,79,80,81,82,83, 77].

Table 3: Advantages and disadvantages of conventional adsorbents

Conventional adsorbents	Disadvantages	Advantages
Activated carbon	Low selectivity; ineffective for example for geomin and 2-methylisoborneol (2-MIB) removal; they are costly (the higher the quality the greater the cost); poor regeneration.	Mostly used by commercial system for the organic pollutants and dye removal and they have shown a good adsorption capacity; most popular for the removal of pollutant from wastewater.
Zeolites	Low adsorption capacity; low permeability; they cannot remove all dissolved and suspended organic compounds; turbidity causing substances in water adsorption mechanism on zeolite surface is complex; they absorb moisture from air causing them to lose their adsorption efficacy.	They can be used for the removal of organic; dyes inorganic (heavy metals) pollutants; low price and relatively high surface area.
Clays	Low adsorption capacity because adsorption capacity depends strongly on pH and particle size.	They are low cost natural materials; can be used for the adsorption of organic and inorganic (cationic, anionic and neutral metal species).
Siliceous materials (e.g Silica beads)	They cannot be used for pollution solutions with pH less than 8; low resistance toward alkaline solution.	They have been used due to their abundance; availability; and low cost
Bio-sorbents (e.g. Chitosan)	Chitosan cannot be used as insoluble sorbents in acidic media because they are soluble under these conditions. However, their modifications could improve their properties.	More selective than activated carbon and ion-exchange resins; they are biodegradable resources; they are effective, cheap and competitive reduce pollutants (organic and inorganic) concentrations to ppb levels.

2.5. Recent advances in applications of activated carbon from bio-waste for wastewater treatment

The adsorption method is a popular technique in reducing the amount of pollutants, which enter water bodies. Researchers have concentrated to develop activated carbons from unexpensive sources to replace costly commercial activated carbons. High carbon content in ACs synthesis makes it suitable for adsorbent production. As well, conversion of biomass to adsorbents increases its commercial value, which otherwise may require extra cost for disposal. Up to date, commercial ACs used in wastewater treatment are produced from woods, coconut shells, coals, and lignite [84, 85, 86] due to its desirable properties. Several desirable properties for ACs which enable its use in adsorption: large surface area and porosity, and together with surface chemistry which react with specific functional groups in molecules (Fig. 4).

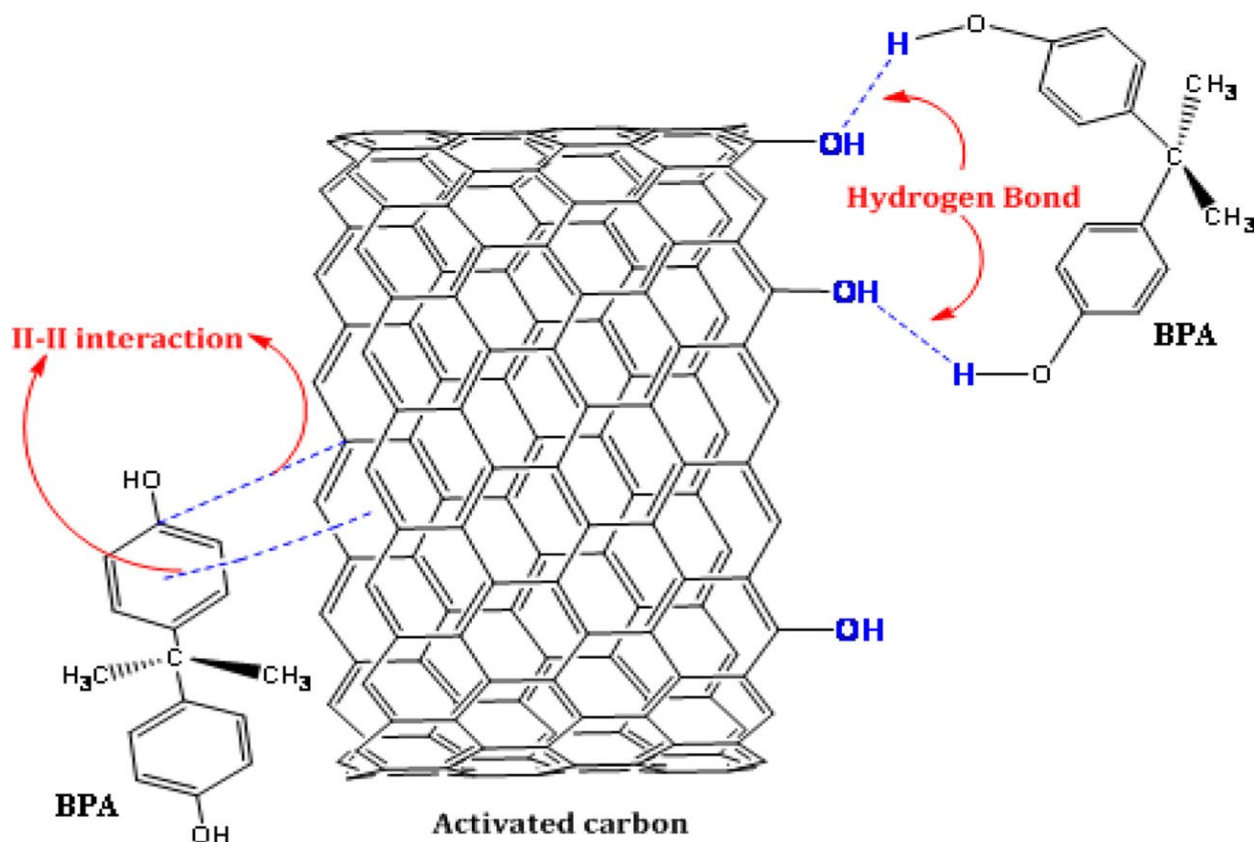


Figure 4: Schematic representation of the π - π interaction and hydrogen bonding between BPA and AC-HP

The presence of several functional groups, especially oxygenated ones, on the hydro-char was also reported, which results in higher adsorption capacity of contaminants [87]. Furthermore, bio-waste from the agricultural sector has shown to be a good source for AC production because these materials typically have a large surface area, high micro-porosity and selectivity. Thus, biomass is useful in the removal of pollutants from wastewater effluent [88]. Biomaterials are a more attractive resource to reduce big issues because they can provide a solution for the petroleum resources reduction, the landfill space shortage, and concerns over emissions caused by synthetic material usage [89]. They are typically made from forestry feed stocks and renewable agricultural sources including and natural plant fibers, wood, and agricultural waste. There is a need for developing activated carbon adsorbents from inexpensive and efficient alternative precursors [90,91].

Waste woodchips are one of the alternative options due to their continuous availability, renewability, and low cost. In this research, waste woodchips have been used to prepare activated carbons. Activated carbons (ACs) can be prepared by chemical and physical activation [92]. Chemical activation is completed in a single step by combining the carbonization and activation process, which showed better development of a porous structure. It is also accomplished at lower temperatures than the physical activation process. However, the disadvantages of the chemical activation process are the corrosiveness of the process and the addition of a washing stage [93]. Whereas, physical activation is performed in two steps: (1) carbonization of the precursor material, and (2) gasification of the char in steam or carbon dioxide environment [92]. In addition, chemical activation was prioritized in this work because of the energy-saving advantages. Activating agent concentration is one of the important parameters for chemical activation and has been studied in literature at around 35–80% [94,95,96,97].

One of the purposes of this study was to reduce the cost of the AC preparation by reducing the activating agent concentration. Phosphoric acid (H_3PO_4) was used as the chemical activating agent. H_3PO_4 is commonly used in literature due to its easy recovery by water washing. It also functions as a dehydrating agent and inhibits the formation of tar [98]. Carbonization temperature is another significant factor in AC production since the carbonization step creates porosity in the char [94].

Therefore, carbonization temperature should be sufficient to volatilize non-carbon substances to obtain desired properties for activated carbon [96].

Wood consists of three main compounds: hemicellulose, cellulose, and lignin, which have been reported to decompose at 160 – 900°C, 230 – 400°C, and 180 – 380°C, respectively [94]. In many studies, [94, 96, 99] carbonization temperatures were chosen based on these assumptions which might not be accurate for this study since each and every type of wood has a different percentage of hemicellulose, cellulose, and lignin. Defining carbonization temperatures would also help to lower the cost. The adsorption capacity of an AC generally relies on the amount of carbon pores [100].

AC is preferable for gas purification and removal of organic pollutants from water because of their porous structure [101]. Choosing the appropriate activated carbon pore size is also an important factor since pore size has a significant contribution to adsorption. For example, adsorbate gas molecules with diameters larger than 2nm were demonstrated to be adsorbed efficiently in mesopores (2–50 nm) but not in micropores (<2 nm) [102]. Although it is desirable for ACs to be highly mesoporous for some important applications, such as energy conversion, waste water treatment, storage materials, and biomedical engineering material applications, mesoporous activated carbons have been reported less in the literature because of their costly and complex manufacturing process [102].

Studies of microporous activated carbons from natural fibers have been widely reported in literature. Phan et al. reported studies on microporous AC fiber adsorbents derived from natural fibers (jute, coconut) for water treatment applications [103]. The authors observed high specific surface area (1500 m²/g) leading to high adsorption capacity attributed to chemical activation by phosphoric acid [99]. On the other hand, lignocellulosic materials are also great alternatives for mesoporous ACs production. The study showed that mesoporous AC can be obtained from coconut shells and palm seeds by chemical and physical activation methods, and have higher adsorption capacities compared to microporous AC for larger adsorbates, such as phenol [95]. Wang et al. studied mesoporous AC derived from bamboo chips for CO₂ adsorption [104]. Even though there are some natural fiber-derived AC studies in the literature, comparison of groups based on their origin has not been done. In this work, bast and leaf-derived AC characteristics

were evaluated. Natural fibers are considered to be “green” alternative sources to prepare low-cost, high quality mesoporous ACs. The purposes of this study are to produce and characterize (bast and leaf fibers) mesoporous activated carbon adsorbents from natural fibers including hemp, sisal, and flax by cost-effective methods. Impregnating the natural fibers with a low concentration of activating agent was one of the methods to reduce the cost. Carbonization temperature for each material can be determined by thermal analysis method. Physical adsorption characteristics, chemical compositions, surface morphology as well as the main functional groups were obtained and compared for bast fiber and leaf fiber derived ACs [105]. In other words, the chemical activation involves addition the activating reagent to the biochar. Low concentration of activating agent is one of the methods to reduce the cost. In this study, phosphoric acid (H_3PO_4) is selected to activate the biochar instead NaOH because the AC-HP showed a higher specific surface area ($1372 \text{ m}^2/\text{g}$) compared to AC-Na ($798 \text{ m}^2/\text{g}$) [106]. Followed by washing to neutralize the pH of AC formed. These processes generate porosities in the adsorbents with large micro pore volume and narrower size distribution.

2.6. Electrocoagulation

The electrocoagulation-electroflotation (ECF) technique is an electrical method used to treat mirage contaminants in an aqueous solution by applying an electrical field instead of adding coagulants. Accordingly, this method considers very economical techniques because it uses ions instead of chemical coagulants; in addition, it is simple equipment, rapid sedimentation process, easy automation, low amount of sludge produced.

The principle of this method is described by electrochemical reactions whose cell may help to produce ions that are able to electrically settle contaminants in the wastewater. More precisely, electrocoagulation process can help to produce coagulants via at the anode by the dissolution of metallic ions while the hydrogen gas is released at the cathode as shown in equations 1 and 2 [107]:

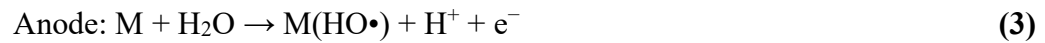


Iron and aluminum are the most common materials used for sacrificial electrodes of electrocoagulation, while iron plates have been well documented [108]. Sometimes carbon electrodes are very effective for organic pollutants. Nevertheless, a number of factors affect the electrocoagulation process, for example, contamination type and its concentration, pH, current density, floc stability [109]. However, this method has also some disadvantages. For example, dissolved electrodes as well as control of conductivity might contribute to high maintenance costs. Therefore, it possible to combine it with other methods to increase the system cost- effectiveness. In this study, electro-adsorptive system for removal of pharmaceutical products from an aqueous solution has been established to increase the cost- effectiveness.

➤ **Electro-oxidation**

Electro-oxidation can happen in one of the following options: 1. Directly, by hydroxyl radicals (HO•) produced on anode's surface (the oxidation of water molecules produces to the formation of physisorbed hydroxyl radical (M (•OH)) as shown in the equation 3; 2. Indirectly, by oxidant formation at the electrode chlorine or hydrogen peroxide/ ozone [110].

Indirect oxidation happens when e.g., active chloride ions, may be hydroxyl free radicals, also produced at an anode, and destroy pollutants. Precisely, the oxidation of pollutants in this process happens at the electrode surface or directly by the electron transfer to the anode as shown in the equation 3 [112].



2.7. Sorption kinetics

Sorption is a complex process, where adsorption is understood as “chemical adhering on the surface” and absorption as a “chemical penetrating the surface”, or a combination of both. On another hand, it can be described as a surface process through which solutes (ions, molecules and compounds) are accumulated at the interface between solid phases and liquid. In this process, dissolved solutes from water/wastewater are attracted through chemical and physical interactions and then bonded to the surface of the various media constituents (adsorptive materials). Chemical chemisorption or adsorption refers to a high affinity, specific adsorption owing to chemical bonding forces. Whereas, physical sorption refers to the interaction between contaminants and media surfaces due to electrostatic attraction because of the charge deficiencies of the media constituents. However, it is not always easy to distinguish between these interaction-mechanisms while studying contaminant sorption within the media. Different mechanisms are responsible for the interaction between contaminants and media surfaces, For example, 1. Ionic forces (appearing between charged media constituents and polar molecules); 2. Hydrogen bonding (dominating the bonding type between media organic matter and media particles); 3. Van der Waals forces (common bonding mechanism for non-polar molecules); 4. Strong chemical bonding (resultant from the valence forces between ions which penetrate the coordination shell of the structural atoms and structural cations through oxygen and hydroxide groups) [111,112,113].

2.8. EDC Adsorption

The fate of estrogens once bound to solids is an important consideration in terms of potential exposure to organisms, transportation, and degradation [114,115,116,117,118,119,120,121,122]. Since estrogens are hydrophobic organic compounds of low volatility, it is likely that sorption is a significant factor in reducing aqueous phase concentrations [47]. Inorganic and water-soluble materials remain in the water layer and more organic molecules stays in an organic layer. In a typical example, the product with a fairly large organic molecule, is not very soluble in water. Whereas, if the product has a lower molecular weight or “small” molecule, it might be at least partially water-soluble. Therefore, it might not completely “move” into the organic layer, but partially dissolve in the aqueous layer. A quantitative measure of how an organic compound distributes between aqueous and organic phases is called the distribution or partition coefficient (K), or ratio of the solubility of solute dissolved in the organic layer to the solubility of material dissolved in the aqueous layer as shown in the equation 4 [47].

$$K = \frac{\text{solubility in organic layer (g/100 mL)}}{\text{solubility in water (g/100 mL)}} \quad (4)$$

The constant K (independent of the actual amounts of the two solvents mixed) is essentially the ratio of the concentrations of the solute in the two different solvents once the system reaches equilibrium. At equilibrium, the molecules naturally distribute themselves in the solvent where they are more soluble. Since the distribution coefficient is a ratio, unless K is very large, not all of a solute resides in the organic layer in a single extraction. Usually two, three, or four extractions of the aqueous layer with an organic solvent are carried out in sequence in order to remove as much of the desired product from the aqueous layer as possible. For example, estrogens in saline waters, e.g. estuarine or marine environment, were shown to exhibit greater removal from the aqueous phase than in freshwaters. It is likely that increased removal of estrogens is due to

aggregation and flocculation in the higher ionic strength medium, resulting in high rates of settling [128, 118]. The octanol-water (K_{ow}) and organic carbon (K_{oc}) partition coefficients are frequently used indicators of the tendency of compounds to partition to organic matter. The greater these coefficient values are for a given compound, the greater its tendency to partition to organic matter, e.g. organic carbon rich matrices [114, 116, 118,123,124].

Understanding the partitioning of natural and synthetic steroidal estrogens between liquid and solid phases is critical for the prediction of their fates in environmental systems. The distribution and partitioning of estrogenic steroids in the environment are determined by their physicochemical properties and site-specific environmental conditions. Moreover, sorption depends on the structure and position of functional groups of the sorbate, sorbent binding site availability, competition for binding sites, the chemical characteristics of the sorbate, mineralogical composition, mineral particle size and surface area, organic matter content, cation exchange capacity, microbial activity of the sorbent, salinity of the aqueous phase, infiltration velocity, particle transport, residence time, and ground-water hydraulics [118, 128, 125, 126, 127]. Several different mechanisms, which are suspected to be responsible for estrogens sorption include surface adsorption to mineral constituents, sorption to organic matter, ion exchange, complex formation with H-bonding and metal ions. However, sorption to organic matter has been frequently reported being the most important, indicating hydrophobic partitioning as the dominant sorption mechanism [118,128,129,130]. The extent of adsorption is influenced by the availability of adsorption sites, which is highly dependent on porosity or the surface area of the adsorbent. Since a single site is unable to accommodate two or more different adsorbates, the adsorption process is essentially competitive. Furthermore, different adsorption sites possess different adsorption energies and affinity because the surfaces of most adsorptive media are heterogeneous. This heterogeneity is principally responsible for the nonlinearity of adsorption isotherms [111,112,113]. Other work has shown that a microscopic surface roughness could affect the sorption of small N_2 molecules. “Sorption on the interlayer surface of bentonite exhibits diffusion-controlled behavior” [131].

2.9. Influence pH change on EDCs sorption behavior

Chemical reactions in the aqueous solution are affected by its acidity or alkalinity. The impact of pH on the aggregation of polymer-coated nanoscale zero valent iron (nZVI) and its deposition on clay and sand (kaolinite) surfaces was investigated [132]. The study showed that at pH lower than pH of the isoelectric point (pH_{iep}) of nZVI, the conformation change of the adsorbed polyanion layer may lead to an aggregation because of the underlying particle surface becomes positively charged [128]. Due to the charge, associated electrostatics repulsion, and a low pK_a for an adsorbed weak polyanion which shows more sensitivity to pH than a strong polyanion [133]. This shows a competition for vacant adsorbent site between metal ions and the H⁺ ion as shown in Fig.5 [128]. A conceptual model of physicochemical processes showing aggregation and deposition of surface modified nZVI in heterogeneous porous media (clay, metal oxides, and sand) was defined.

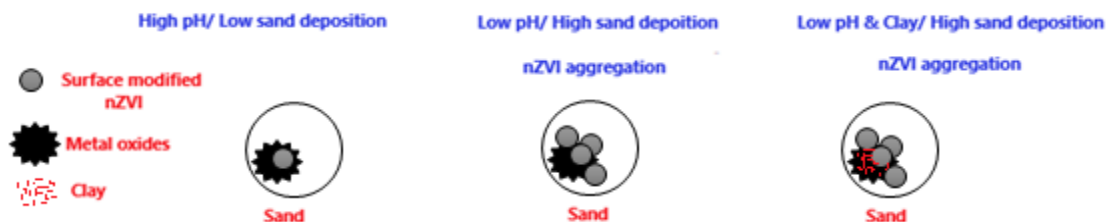


Figure 5: Conceptual model of physicochemical processes showing aggregation and deposition of surface modified nZVI in heterogeneous porous media

These conclusions are consistent with the results obtained by Boudrahem et al. [134,135]. They studied adsorption of lead using tree leaves of pH to achieve an optimal value 5.8. Above pH 6, the adsorption capacity remained constant and uptake of metal ions was observed, which could be attributed to the precipitation and metal hydrolysis at higher pH [134]. The flat basal surface of mineral soils carries a permanent negative charge due to isomorphous substitutions in the crystal lattice of clay minerals. However, due to imperfections and distortions of the clay minerals, their

edge surfaces are characterized by the resultant variable charges [136,137]. At these edges, the broken bonds generate the amphoteric Al-OH and Si-OH surface function groups. The arising charge on these surface hydroxyls results from protonation and deprotonation processes depending on the pH of the solution. If S represents a single site for surface protonation [138,139], at a pH below the point of zero charge for a specific mineral, the edge is rich with S-OH²⁺ relative to S-O⁻, resulting in a net positive charge. Other studies showed the pH effect on the organic materials. Some hydrophobic EDCs are less soluble in saline environments than in pure water, but this does not seem to have been tested. There mentions of effect of pH on the solubility of estradiol but none for the other solutes. Salting out, or decreased solubility in the presence of electrolytes, is a characteristic of a wide range of sparingly soluble organic compounds [140,141,142]. It is believed the sorption mechanism of EE2 onto clay minerals is probably governed by a combination of hydrogen bonding with uncharged mineral surfaces and hydrophobic interaction with siloxane surface, attributed to nonspecific, short-range van der Waals interactions [145].

Another study observed no correlation between sorption of the natural estrogen (E2) to absorbent and ambient pH, while it was indicated that van der Waals forces were principally responsible for the sorption process [143]. It was concluded that sorption of E2 to clay minerals (absorbent) involved weak hydrophobic interaction with the siloxane face of the minerals. An alternative argument is proposed in this study while studying the sorption of the natural estrogen, 17 β -estradiol [125]. They hypothesized the association between sorption rates and cation exchange capacity (CEC). This hypothesis, however, is rather unlikely. 17- β -estradiol possesses a phenolic group with a pKa of 10.6 that would dissociate under very basic conditions, forming an organic anion. Thus, developing a positively charged molecule that is essential for cation exchange is certainly inconceivable. Several authors proposed hydrophobic interactions to be the dominant mechanism of non-polar organic compounds binding to solid phases [144, 118, 129, 142, 143,145]. Accordingly, non-polar EE2, which also has a phenolic group within its structural arrangement, analogous to natural E2, is never suitable for cation exchange. Furthermore, since EE2 ionization only occurs at high pH, consequently, ion exchange is entirely disregarded as a potential sorption mechanism applicable to this current investigation [1]. Finally, by changing the pH of the aqueous phase, the distribution coefficient is drastically changed, thus pulling molecules into either an organic layer or aqueous layer. For example, phenols, amines, carboxylic acids can be separated

from neutral components. However, all other common functional groups are not affected by changes in aqueous pH and so they would always distribute between layers the same way because their distribution coefficient is unaffected by pH (could be one of these groups shown in the section 2.12.3).

2.10. Temperature effect on adsorption

The temperature effect on adsorption was investigated. It was mostly observed that adsorption was an endothermic process due to the rising of temperature with the increase of adsorption capacity [146,147,148]. For example, the uptake of Pb^{2+} is an endothermic process because of the rapid diffusion of metal ions through the solution at high temperature, and due to decrease in the solution viscosity [147, 148]. However, another publications, the adsorption of metallic ions was observed to be decreased when the temperature increased, resulting in an exothermic reaction [146,147, 149]. The activation energy is also taken into consideration when the effect of temperature is studied, and it also depends on the initial concentration of adsorption (metal ions). A higher activation value is reported at low initial metal ions concentration [147].

2.11. Conclusion

It becomes an urgent need to develop a better adsorbent that can achieve a high adsorption rate. In other words, achieving high partitioning rate of synthetic steroidal estrogenic compounds (17 α -ethynylestradiol) from the aqueous solution requires a high-performance adsorbent, perhaps with modification of functional groups on the adsorbents surface. On the other hand, such new adsorbent might increase the treatment costs. Therefore, this work proposes to minimize cost by using waste material to produce new adsorbents. The assessment of a new adsorbent efficiency should be evaluated in various environmental conditions (e.g. pH).

2.12. Waste materials

In previous sections, a wide spread knowledge of EDCS impact on environmental and public health, physicochemical properties, removal technologies, was spread. However, a sustainable and cost-effective system to restrain their negative impacts is still under search.

In this part of study, a broad investigation was made on waste-materials to find new adsorptive materials. Specifically, forestry waste-wood and fishery residues could be a good choice to increase cost-effectiveness due to their huge availability in Canada.

2.12.1. First source of new adsorptive materials (wood)

Wood is a fibrous and porous structural tissue found in the roots and stems of trees could be source of a new adsorption material. Two diverse types of wood are proposed to use in this study: 1. Coniferous (small and needle leaves) is generally called softwood (e.g. pine trees); 2. Non-coniferous or deciduous (broad leaves) is generally called hardwood or deciduous wood (e.g. mesquite, oak trees).

2.12.1.1. Key words of wood

In this part, some keywords are presented to provide a general view of wood.

Wood: it is a polymeric material with low molecular weight organic compounds. These are the most important characteristics which form wood, so it is most likely influencing wood effectiveness when using wood in the applications, such as EDC removal.

Bark: it is the outer layer for the tree body and consists of two layers: a thin inner phloem of living cells, and a dead outer phloem of dry corky material. Its primary functions are nutrient conduction and protection. The appearance and thickness of bark vary substantially relying on age and the species of the tree.

Sapwood: its functions are the mechanical transport of sap and food storage. The radial thickness of sapwood is commonly between 35 to 50 mm but may be 75 to 150 mm for some species.

Heartwood: it is composed of an inner core of wood cells that have varied both physically and chemically, from the cells of the outer sapwood as a result of deposits of various materials.

The cambium: it is a continuous ring of reproductive tissue located between the sapwood and the inner layer of bark.

Hardwoods: this term does not refer to the actual hardness of the wood. It is used as a general botanical group of trees, which possess broad leaves compared to softwoods or the conifers.

Softwoods: this term does not refer to the actual hardness of the wood. It is used for defining a general botanical group of trees, which in most cases, possess scale like or needlelike leaves (the conifers).

Early wood: it is mechanically weaker than late wood "older wood" and usually less dense because it is formed in the early part of the growing season "portion of the annual growth ring".

Latewood: it is mechanically stronger than early wood and usually denser than early wood because it is formed after early part has ceased in the growing season "portion of the annual growth ring".

Annual growth ring: additional layer of wood which may be growing on a tree in a single growing season. In the temperate zone, for many species (e. g., pines and oaks), the annual growth rings are easily distinguished because of differences in the cell's formation in the early and late parts of the season, whereas, in some temperate zones, many tropical species (e.g., sweet gum and black gum), the annual growth rings are not readily recognized.

Diffuse-porous wood: it is shown in hardwoods in which the pores are uniformly distributed and sized throughout each annual ring or in other words, it can be defined as a decrease in size gradually and slightly toward the outer border of the ring.

Ring-porous woods: they are hardwoods in which the pores are somewhat large at the beginning of each annual ring and then tend to decrease in size more or less suddenly toward the outer portion of the ring. Furthermore, the mechanism can generate a distinct inner zone of pores in the early wood and an outer zone with smaller pores in the latewood.









Anisotropic: showing different properties along different axes, such as fibrous materials.

Orthotropic (growing vertically): possessing unique and independent properties in three mutually orthogonal (perpendicular) planes of symmetry; three special cases of anisotropy.

2.12.1.2. Wood sources and types

Forestry is a major industry in Canada, contributing billion to the economy, where leading provinces are Quebec, British Columbia and Ontario. The most popular types of Canadian wood (including trees' location) and characteristics are presented in Table 4 [150,151].

Table 4: Wood types with their characteristics

Species Included in Combination	Characteristics	Species Combination Abbreviation/ Ranges
Douglas Fir (hardwood) Western Larch (the hardest softwoods)	Reddish brown to yellow, high degree of hardness, and good resistance to decay	Douglas Fir-Larch(D. Fir-L or DF-L) 
Pacific Coast Hemlock (softwood) Amabilis Fir (softwood)	Yellow brown to white, works easily, takes paint well, holds nails well, and good gluing characteristics	Hem-Fir (Hem-Fir or H-F) 
White Spruce, Engleman Spruce, Red Spruce, Black Spruce, Jack Pine and Lodgepole Pine, Balsam Fir, Alpine, and Fir (softwood and hardwood)	White to pale yellow, works easily, takes paint well, holds nail well, and good gluing characteristics	Spruce-Pine-Fir (S-P-F) 
Western Red Cedar (softwood)	Reddish brown heartwood, light sapwood, exceptional resistance to decay, moderate strength, high in appearance qualities, works easily, takes fine finishes, and lowest shrinkage	Northern Species (North) 
Red Pine (softwood)	Works easily	Northern Species 
Ponderosa Pine (softwood)	Takes finishes well, holds nails well, holds screws well, and seasons with little checking or cupping	Northern Species 
Western White Pine and Eastern White Pine (softwood)	Creamy white to light straw brown heartwood, almost white sapwood, works easily, finishes well, doesn't tend to split or splinter, holds nails well, low shrinkage, and takes stain, paints & varnishes well	Northern Species 
Trembling Aspen, Large tooth Aspen, and Balsam Poplar (softwood and hardwood)	Works easily, finishes well, and holds nails well	Northern Species 

2.12.1.3. Woodchip

Wood comminution is performed using specific machinery able to cut the biomass into small parts or chips, generating simultaneously waste chips and sawdust. The woodchip can be at different mesh size as shown in Table 5 [152]. Over 100 types of wood chips are commercially available. The most common types of wood chips include alder wood chips, apple wood chips, cherry wood chips, grape wood chips, hickory wood chips, maple wood chips, mesquite wood chips, mulberry wood chips, oak wood chips, peach wood chips, persimmon wood chips, pear wood chips, pecan wood chips, plum wood chips, walnut wood chips, and Douglas Fir. In this study, the comparison between two types of wood chips was established including: 1. Hardwood chips which are mixture from maple, oak, birch; 2. Softwood chips which are mixture from pine and spruce, pine, fir.

Table 5: Diverse types of wood chips

Particle size ≤ 4mm	Particle size ≤ 3mm	Particle size ≤ 2mm	Particle size ≤ 1mm	Particle size ≤ 0mm
4.75 x 3.35	3.35 x 1.70	2.36 x 1.40	1.70 x 0.85	0.85 x 0.300
4.75 x 2.36	3.35 x 1.40	2.36 x 1.18	1.70 x 0.60	0.60 x 0.250
4.75 x 2.00	3.35 x 1.18	2.00 x 1.00	1.70 x 0.425	0.60 x 0.212
-	-	-	1.40 x 0.60	0.300 x 0.150
-	-	-	1.00 x 0.50	0.300 x 0.075
-	-	-	1.00 x 0.425	0.250 x 0.075

Woodchips are the most common types of biomass because it offers benefits in terms of increased load density and homogeneity size [153,154]. Woodchips are the major form in which wood biomass is traded due to its high load density and uniform size [155]. Woodchips can be obtained

by comminuting wood harvested immediately in forests [156] or in short-rotation coppice [157]. Basic investigations about wood chip material properties were conducted in the past [158,159,160,161,162,163]. Many investigations have been done on wood chips, focusing on different areas of application, such as bridging behavior, rotary kilns or fixed-beds [164, 165,166]. Woodchips are most commonly used in some applications because of their availability at low costs, high C/N ratio (1-part carbon to 1-part nitrogen), and good hydraulic permeability and long persistence as a carbon source [167,168]. Furthermore, woodchip denitrifying bioreactors have a high longevity “life expectancy” (5–15 years) and require minimum maintenance given that wood is degraded more slowly under anoxic compared to aerobic conditions [167,168]. The most common application of solid organic carbon sources (generally, woodchips) is the treatment of nitrate (NO_3) in agricultural tile drainage, although their use has much wider potential (wash water [169], wastewater [170], aquacultural effluents [171,172]) [173]. Several studies have examined the potential of wood-based products to treat several types of wastewaters [174,175,176,177,178,179,180]. However, humic substances are important groups of the organic precursors to form disinfection byproducts (DBPs) in drinking water disinfection treatments [181,182, 183, 184, 185]. The organic matter released from woodchips may be highly reactive with chlorine forming haloacetic acids (HAAs), trihalomethanes (THMs), and total organic halogen (TOX) [185,186,187,188,189].

To resume, a decrease in pH is commonly considered to be a result of the release of dissolved organic substances, deduce from a concurrent reduction in pH and high release of dissolved organics typically noticed in the initial period after woodchip bioreactor start-up [168,190, 191]. Moreover, the observations seem to contradict expectations that heterotrophic denitrification is the primary process which takes place in the reactors as this process releases hydroxyl ions (OH^-) which raise pH along the woodchip beds, as also confirmed in a single study [192, 193].

Overall, Figure 6 shows reuse of woodchips in various environmental applications. Synthesis of ACs from biomass starts with pre-treatment of the sample. This process includes crushing, drying (at $\sim 100^\circ\text{C}$), followed by sieving to obtain small particles within a specific size range. The second step is AC production. This step is done through carbonization of biomass in a dry inert atmosphere ($300\text{-}500^\circ\text{C}$) that facilitates elimination of volatile matters and tars, while leading to formation of

biochar [189]. Other study shows a procedure for activated carbon production using the hemp stem. The hemp stem was carbonized at 500°C in dry inert atmosphere (N₂ environment) for 1h. The carbonized material was then ground and mixed with the activating chemical (KOH solution), then, the carbonized material was dried and activated at 800°C (N₂ environment). The use of other activating reagents like ZnCl₂ has been also reported, as it reacts with the char and governs the pore distribution during the heat treatment [194].

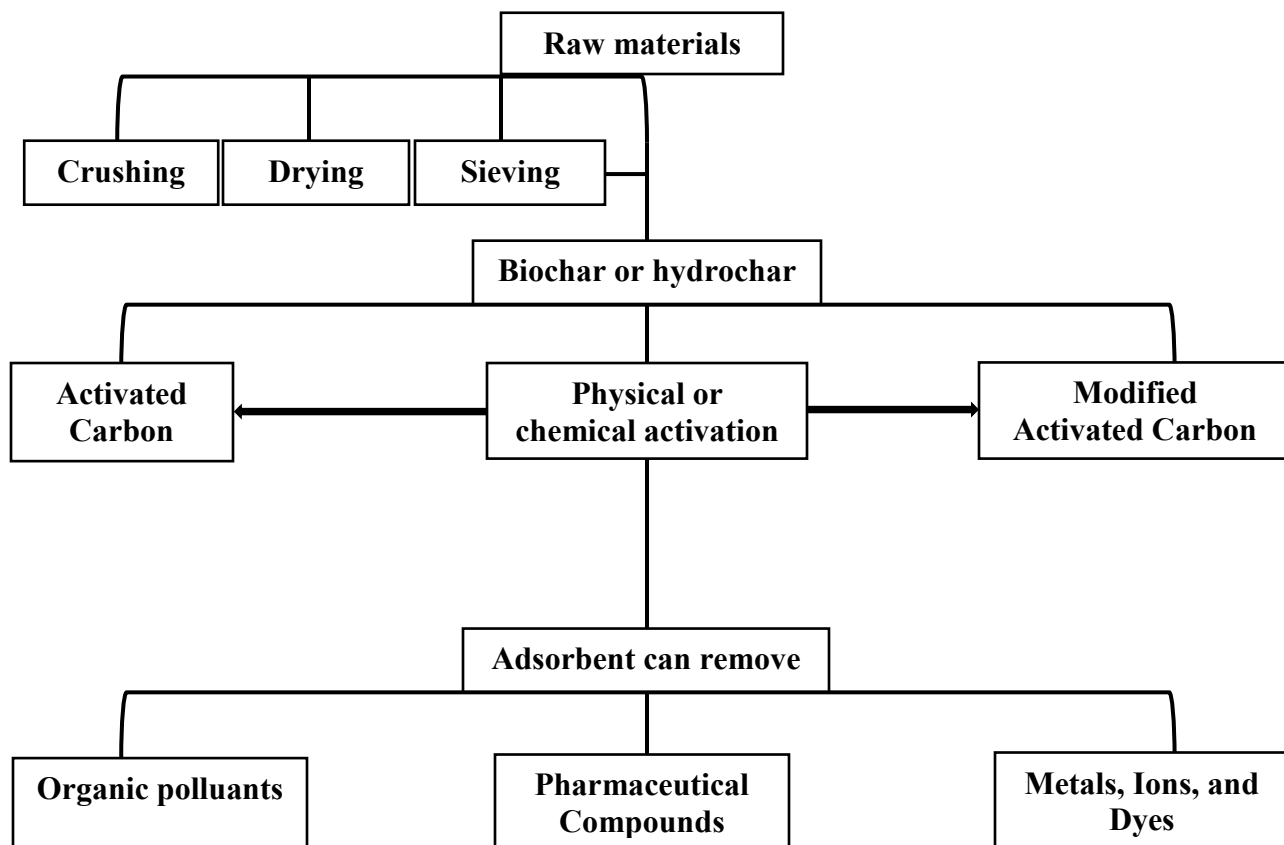


Figure 6: Synthesis routes of ACs

2.12.1.4. Wood structure

Wood is an extremely versatile material with a large range of mechanical and physical properties. In general, wood as shown in Fig. 7, consists of three main parts are bark, wood, and cambium [195]. The primary functions of wood are storage, nutrient conduction and support (done by the inner sections of trunk).

Wood comprises both fibrous structural and porous tissues found in the stem roots. The primary structural building block of wood is the fiber cell or tracheid. Cells vary from 870 to 4000 microns long and from 16 to 42 microns in diameter. In addition, a cubic centimeter of wood may contain more than 1.5 million wood cells. These can form a stronger structure when they are put together. Each single wood cell is multilayered, so it is more structurally advanced, as shown in Fig. 8. Each individual cell contains four distinct cell wall layers (Primary, S1, S2, and S3). Each layer is made from a combination of three chemical polymers: cellulose, hemicellulose, and lignin.

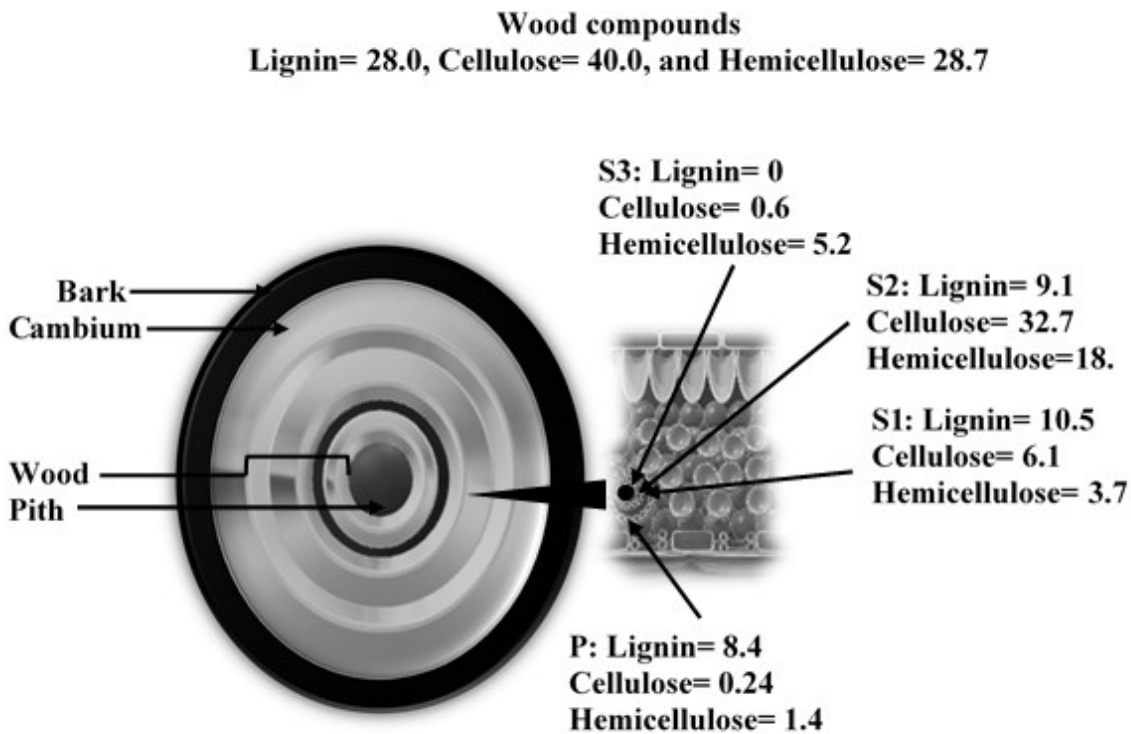


Figure 7: Percentages of cell wall layers, (P), S1, S2, and S3 in scotch pine

The chemical composition of wood varies from species to species, but is approximately 1% nitrogen, 6% hydrogen, 42% oxygen, 50% carbon, whereas 1% other elements (mainly manganese, iron, magnesium, sodium, calcium, and potassium) by weight [196]. Wood also contains phosphorus, silicon, sulfur, chlorine, and other elements in small quantities. Wood is a complex polymeric material consisting of mainly lignin, cellulose, and hemicelluloses, as shown in Fig.8 with a minor proportion of extractives [197,198]. Extractives in the wood means low molecular weight organic compounds.

Lignin represents 23% in deciduous trees vs 27% in coniferous wood. Lignin confers the hydrophobic properties reflecting the fact that it is based on aromatic rings [199]. Cellulose percentage between 41–43%, is a crystalline polymer derived from glucose [200]. Hemicellulose represents 20%– 35% of wood structural polymers and is the most unstable and hydrophilic polymer of wood [197,201].

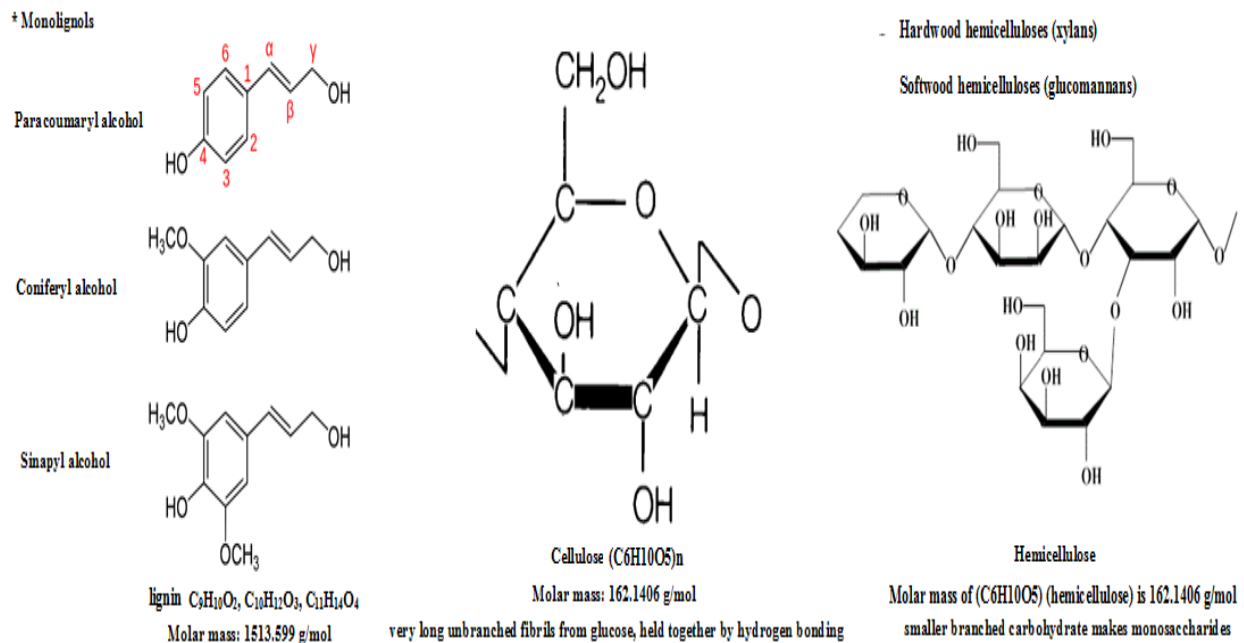


Figure 8: Molecular motif of lignin, cellulose, and hemicellulose

In chemical terms, there is a difference between softwood and hardwood that is reflected in the composition of the constituent lignin. Softwood lignin is mainly derived from coniferyl alcohol. Hardwood lignin is primarily derived from coniferyl alcohol and sinapyl alcohol [202]. Hydroxyl groups in hemicellulose can readily form hydrogen bonds with water. This can lead to a high rate of water uptake and then to increase the thickness or "swelling" in wood. Thus, using wood particles with a less hydrophilic property can improve the dimensional stability of wood. However, a major drawback of thermal treatment is wood strength is reduced [197,203]. In addition, hydrothermal treatment (described as heating wood under wet conditions) is one of the most effective methods to improve the dimensional stability of wood. In many processes, the water-soluble extractives and hemicellulose are removed from wood [197,204]. No chemicals other than hot water were used in the process and thus hydrothermal treatment has been considered as an environmentally friendly technology [205]. After the extraction of hemicellulose, surfaces of the wood are covered with lignin components, which are less hydrophilic [206]. Reducing the hygroscopic sites of wood can be made by the removal of hemicelluloses leading to decreasing amounts of hydroxyl groups, thus, enhancement in the dimensional stability of wood is achieved. In the literature, the effect of chip size on the extraction of hemicelluloses in wood was investigated [205]. They reported that total extraction yield, as well as the yields of hemicelluloses and monosaccharides, increased clearly with decreasing particle size.

2.12.1.5. Wood properties

The physical to mechanical properties of wood are shown in this part.

➤ Physical properties

Physical properties are the quantitative characteristics of wood and its behavior responding to external impacts other than applied forces.

These properties could be chemical, decay resistance, directional properties, dimensional stability, density, moisture content, thermal and pyrolytic (fire) properties, or electrical properties.

In this section, the focus would be on the related properties.

1) Directional properties

Wood is an anisotropic and orthotropic material due to a tree's increase in diameter and due to the orientation of the wood fibers as it grows. Thus, properties vary along three mutually perpendicular axes: radial, longitudinal, and tangential. The radial axis is normal to the growth rings and perpendicular to the grain direction. The longitudinal axis is parallel to the grain (fiber) direction, and the tangential axis is perpendicular to the fiber (grain) direction and tangent to the growth rings [197].

2) Moisture content

The general definition of the moisture content of wood is defined as the weight of water in given wood over dry weight. The moisture content (MC) is written as follows in Equation 5 [195]:

$$MC = \frac{\text{moist weight} - \text{dry weight}}{\text{dry weight}} \times 100\% \quad (5)$$

In living trees, moisture content relies on the type of wood; thus, it may range from approximately 25% to more than 250%. In other words, it is equal to 2.5 times the weight of the dry wood material [195]. In addition, for the most species, the moisture content of heartwood is less than that of sapwood. Furthermore, the water in the wood can be in the cell wall (bound water) or in the cell cavity (free water). If the water exits as bound water, it means it is bonded (hydrogen bonds or via secondary) within the wood cell walls. Whereas, if the water exists as free water, it is simply present in the cell cavities. The separation rate of the free water in drying wood occurs at a faster rate than a bound water because of the accessibility and the absence of secondary bonding. The moisture content at which the cell walls are still saturated but virtually no water exists in the cell cavities is called the fiber saturation point, which usually varies between 21 and 28% [195]. Many factors can control the moisture content in the wood, such as temperature, humidity conditions, but the equilibrium state can be reached when there is neither a gain nor lose moisture.

3) Thermal expansion

Wood contracts when cooled and expands when heated. Thermal expansion of dry wood is positive in all directions. When moist wood is heated, it tends to expand because of normal thermal expansion and shrink because of moisture loss from increased temperature. Unless the initial moisture content of the wood is very low (3 to 4%), the net dimensional change on heating is negative. Wood with intermediate moisture contents of approximately 8 to 20% expands when first heated, and then gradually shrinks to a volume smaller than the initial volume as moisture is lost in the heated condition.

➤ Mechanical properties

The mechanical properties are the characteristics of a material in response to externally applied forces. In addition, many factors can affect the properties of wood, such as anatomical factors (creep, slope of grain, etc.) and environmental (moisture content, temperature, and decay and insect damage).

2.12.2. Second source of new adsorptive materials (chitin)

Chitin, a natural material, is the second most abundant biopolymer on earth. Every year, 6 million to 8 million tons of waste crab, shrimp and lobster shells are produced globally [207]. Chitin ($C_8H_{13}O_5N)_n$ a long-chain polymer of *N*-acetylglucosamine, is a derivative of glucose. This biopolymer is synthesized by an enormous number of living organisms.

2.12.2.1. Chitin

Chitin has more applications while transformed to chitosan. Chitin shells of shrimp and other crustaceans can be transformed to chitosan by treating with an alkaline substance, like sodium hydroxide. Chitosan is an all-natural fiber that comes from the ocean. Chitosan is a linear polysaccharide composed of randomly distributed β -(1 \rightarrow 4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit) as shown in Fig.9. It is made by treating the chitin shells of shrimp and other crustaceans with an alkaline substance, like sodium hydroxide. Thermal degradation of the chitosan structure was assessed using the thermogravimetric method (TGA). This is involving two or even three degradation stages of a complex reaction (the evaporation of the residual water present in the polymer sample and the polymer decomposition). Chitosan has three types of reactive functional groups, an amino/acetamido group as well as both primary and secondary hydroxyl groups at the C-2, C-3 and C-6 positions, respectively. The amino contents are the main factors contributing to differences in their structures and physicochemical properties, and its distribution is random, which makes it easy to generate intra- and inter-molecular hydrogen bonds [207]. Chitosan can be used in hydrology as a part of a filtration process [208]. Chitosan causes the fine sediment particles to bind together and is subsequently removed with the sediment during sand filtration. It also removes heavy minerals, dyes, and oils from the water [208]. As an additive in water filtration, chitosan combined with sand filtration removes up to 99% of turbidity [209]. Chitosan is among the biological adsorbents used for heavy metals removal without negative environmental impacts [208]. In summarization, Chitin or chitosan can be defined as:

1. An all-natural fibre that comes from the carapace of oceanic organisms.

2. A natural product derived from chitin, a polysaccharide, also known as, a deep-sea squid extract, and it is similar to that of cellulose in plant fiber.
3. Specification: Chitosan powder 90% D.A.C. (bulk density is 0.3 g/cm³).
4. Features:
 - Biocompatible
 - Biodegradable
 - Non-toxic
 - Abundant and non-costly
 - Wasted material from renewable resource
5. Limitations:
 - Sensitive to pH and temperature

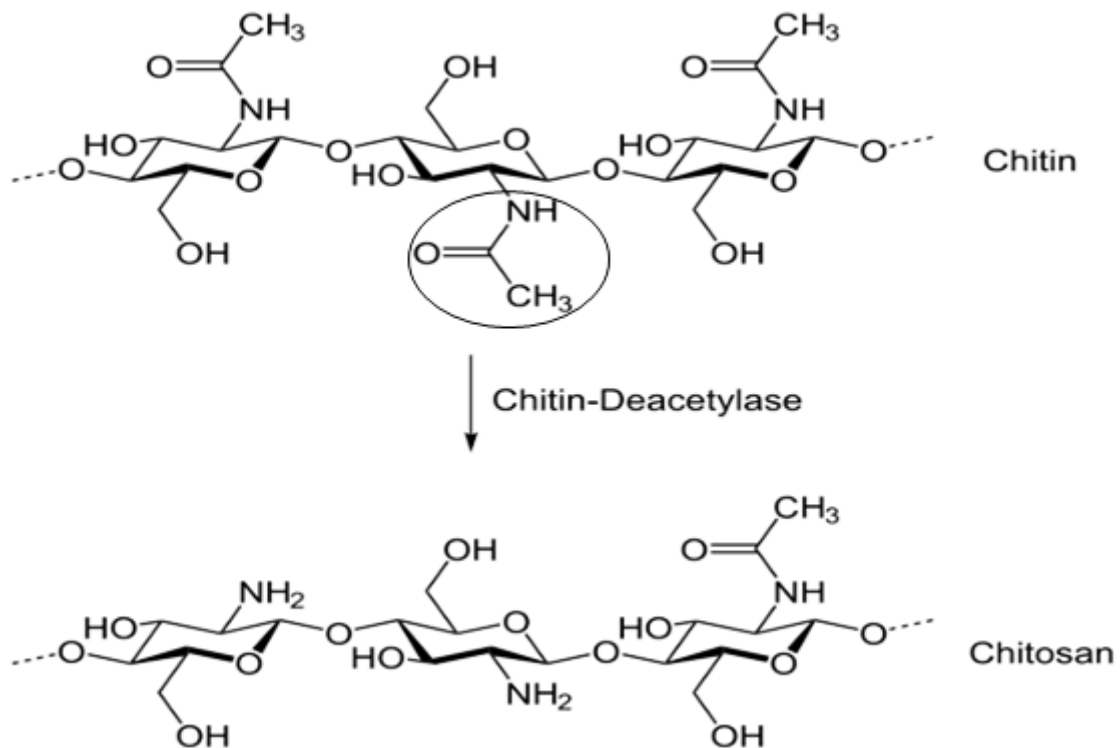


Figure 9: Chitosan production by partial deacetylation of chitin

- **Acetylation**

Acetylation describes a reaction that introduces an acetyl functional group into a chemical compound. The acetyl group contains a methyl group single-bonded to a carbonyl. The carbonyl center of an acyl radical has one non-bonded electron which forms a chemical bond to the remainder *R* of the molecule [210].

- **Deacetylation**

Deacetylation is the removal of an acetyl group. Acetylation refers to the process of introducing an acetyl group (resulting in an acetoxy group) into a compound, namely the substitution of an acetyl group for an active hydrogen atom. A reaction involving the replacement of the hydrogen atom of a hydroxyl group with an acetyl group (CH₃CO) yields a specific ester, the acetate. Acetic anhydride is commonly used as an acetylating agent reacting with free hydroxyl groups [211].

2.13. Summary of this research work

To summarize this research work, the problem formulation and proposed solution are shown in this part.

Both domestic and industrial wastewaters contain micro-pollutants, such as EDCs which are not entirely removed by conventional wastewater treatment plant (WWTP) processes; therefore, they are continually discharged into the aquatic environment. Thus, technologies that are more sophisticated are required. Up to date, commercial ACs used in wastewater treatment are produced from coconut shells, coals, bones and lignite showed a good removal capacity to some types of micro-pollutants. However, they are not used at a large scale; there is still a need for developing an adsorption system from inexpensive and efficient alternative precursors. Subsequently, sources of new materials, are recommended for EE2 removal in this research, are from wood and chitin.

2.13.1. Research novelty

Novelty was established based on a research objective. It was found adsorptive ability of combination of various systems, HIT1-S2T2, chitin, ENAM, CACA, and electric field, was excellent for EDC removal from an aqueous solution.

In this study, the efficiency or capacity of an established novel system was evaluated practically (establishing electro-adsorptive system using a commercial adsorbent) and theoretically (compared with an adsorptive phenomena within other works).

2.13.2. Hypothesis

Based on a literature review, the hypothesis can be shaped as follows:

1. *Synthetic steroidal estrogen (17 α -ethynylestradiol) is a good representative of pharmaceutical products and its removal from aqueous solution is possible.*

This compound does not undergo the biodegradation process, and it is always present in WWTP effluents. Since effluents are discharged to water resources (rivers, lakes), pharmaceutical compounds might be present in water uptake facilities. Thus, removal of such compounds by building a new operation unit dedicated to removal of EDCs is an important improvement of wastewater and water treatment facilities.

2. *Adsorption could be a good option to efficiently remove EE2 from the aqueous solution.*

The target pharmaceutical compound (EE2) has a high k_{ow} value showing the possibility of its high partitioning to a solid surface.

3. *Wood chip is a promising material for producing of a new adsorbent, e.g. activated carbon.*

In this study, adsorbent made from the waste wood chip (adsorbent made from the New Material seems to be an excellent choice to make an effective adsorbent for EE2 removal from the aqueous solution. However, no comparative study has been conducted with respect to effectiveness of soft wood versus hardwood when applied for EE2 removal from aqueous solution.

4. *Activated carbon modified with chitosan might improve the removal of EE2.*

Combining chitosan (or even chitin) with other materials has been shown already for excellent removal of turbidity and metals. Thus, ENAM (enhanced new adsorption material) might be more effective than individual formulated adsorbent.

5. *Combining the adsorption with electrokinetic system might enhance the EE2 removal capacity.*

Electrokinetics applied to colloidal solutions initiated the electro-coagulation process, formation of flocs which can settle leading to separate of liquid and solid phases. In this study, EE2 adsorbed to the formulated adsorbents.

2.13.3. The research aims

The aim of this research is to gain a greater insight into the distribution and behavior of EDCs within an adsorptive system in order to completely remove EE2 from an aqueous solution to a satisfaction level of 99%. Furthermore, a sustainable approach with respect to material, energy, cost suppose to be considered during the development of a new removal system.

In general, EDCs, present in sewage, do not undergo treatment in wastewater treatment plants (WWTP). Therefore, estrone (E1), 17- β -estradiol (E2), and estriol (E3) and other hormones as well as steroids can be found in WWTP effluents. 17 α -ethynylestradiol is a widely used pharmaceutical industry as a major ingredient of hormone replacement therapy and oral contraceptive formulations [212]. Since 17 α -ethynylestradiol (EE2) is a very potent steroid compounds as shown by vivo and in vitro studies (section 1.4. problem formulation), it was selected as a target steroidal estrogenic compound representing pharmaceutical products (EDCs) as shown in Fig. 10.

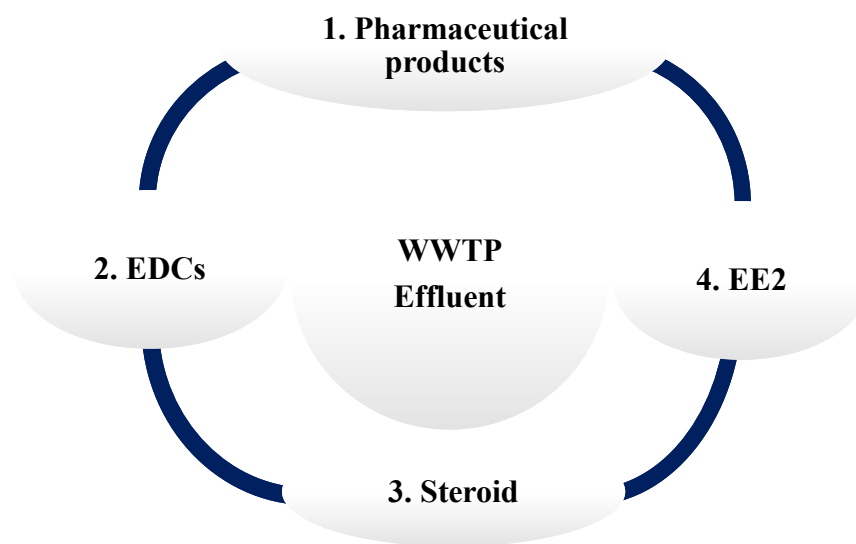


Figure 10: Pharmaceutical products representative (EE2)

The environmental source of EE2 is its leaching from sludge, biosolids, and recycled water used in agriculture. The hydrophobic estrogen is intended to easily interact with dissolved organics integrated within biosolids. This interaction facilitates its partitioning into aqueous phase. Thus, the application of such material with the chemistry of their complex matrix is anticipated to greatly affect the affinity and mobility of EE2 in the environment.

EE2 is a hydrophobic compound possessing low aqueous solubility and relatively high K_{ow} . Based on its physicochemical properties (Table 1) the synthetic steroid hormone is hypothesized to be principally related to the solid phase. Thus, adsorption phenomena can be proposed to remove EE2 from aqueous solution.

Chapter 3: Methodology

3.1. Methodological approach

To study the adsorption of EE2, activated carbon formulations based on waste wood chips were prepared. The surface properties of the resulting adsorbents were investigated to analyze their interaction with EE2. Eight types of adsorbents with modifications were prepared and tested for the EE2 removal from aqueous solutions. The pyrolysis method was used for production of adsorbent media. Based on the adsorption capacity of the formulated adsorbents, the maximum achievable partitioning of EDCs from the aqueous solutions was determined. In addition, studying a correlation between the initial characteristics of formulated adsorbents with the maximum achievable partitioning of EDCs represented another important objective, due to potential significant variation of the wood composition (hemicellulose, cellulose, and lignin). Under the same pyrolysis conditions, the degradation percentage of these constituents in waste wood chips may not be the same; this may lead to a change in the adsorption behavior of EE2 and the removal capacity of wood-derived adsorbents.

Equally important, non-polar 17 α -ethynylestradiol is expected to primarily interact with the adsorbent via hydrophobic attraction, hydrogen bonding, or by ion exchange. The surface compound degradation plays an important role in the adsorption process (capacity and behavior). Since the surfaces of the adsorbent are electrically charged, they are directly influenced by the chemistry (especially pH) of the pore fluid. At low pH, there is an excess of hydrogen ions in the pore fluid, which are adsorbed onto the adsorbent surfaces yielding a net positive charge. Conversely, in alkaline condition, the increasing concentration of hydroxyl ions in the pore fluid induces the formulated adsorbent particles to release their protons increasing the negative charge on their surfaces. As such, EE2 interaction with these surfaces is expected to be affected by changes in the resulting charges, as a function of aqueous pH. The affinity of EE2 partitioning and hence its mobility may be significantly controlled by such changes. Moreover, the availability of oxygen molecules within the adsorbent media may have an influence on the mobility of EE2. It is hypothesized that the hydrophobic, non-polar, synthetic steroidal estrogenic hormone (EE2) is primarily connected to the solid phase once it is released into the environment.

The range of its interaction with different formulated adsorbents is expected to vary as these media possess different functional groups, structures, and surface properties. Furthermore, the degree of interaction of this compound with individual formulated adsorbent is considered to be influenced by the electrical charges on their surfaces. Most of these charges are pH-dependent. The formulated adsorbents are typically negatively charged at high pH. This negative charge is reduced as pH values are decreased until there is no more charge on the surface (zero charge) at the pH of the isoelectric point. When the pH decreases below this point, the surface becomes positively charged. Consequently, it is hypothesized that an extent of EE2 adsorption, and hence, its mobility in the subsurface is directly affected by changes in pH. Therefore, sorption experiments were designed to simulate environmental conditions in isolated systems to demonstrate the surface charge influence on the behavior and distribution of the synthetic estrogen.

The electro-adsorptive system was also used to investigate absorption phenomena at a larger extent such as electro-oxidation, electro-coagulation, settling, flocculation, floating, and electrode reactions.

EE2 once adsorbed on an adequate adsorptive system is expected to be removed from the aqueous solution. However, adsorptive materials might also form stable suspensions, which should be demulsified. The application of electrokinetics induces demulsification, electrocoagulation of materials and settling or up-floating thereby leading to an advanced removal of particles. Application of DC electrical fields changes the properties of the diffused double layers and facilitates coagulation of dispersed particles. This can generate O_2 and Cl_2 at the anode (due to oxidation) and hydrogen at the cathode due to reducing conditions (see equations in the section 2.6). Simple materials used for electrodes can be used as sustainable means. Hence, investigations of adequate electrokinetics cell configurations can be further looked into. Moreover, voltage limitations should be posed to design the system within sustainable principles.

To achieve the research objectives, an adequate methodological approach was adopted. It comprised of six phases as shown in Fig. 11. Phase 1 involved surveying manufacturing procedures, which can satisfy adsorptive properties of waste materials. Phase 2 enabled upgrading of the adsorptive system to achieve the maximum removal capacity. Phase 3 comprised of experimental studies on optimal conditions for the EE2 removal using developed adsorbents. Phase 4 was dedicated to the development of a removal technology (electro-adsorptive system) to achieve

maximum extraction of EE2 and all remaining particles from aqueous solutions. Phase 5 compared the formulated adsorbent with a commercial adsorbent using the developed Electro-Adsorptive System. Phase 6 involved generating software codes that can help to decrease manufacturing steps and the raw material delivery cost.

➤ **Materials and chemicals**

Materials and chemicals were provided from many places due to their manufacturing and storage sensitivity.

- 1) The first source of adsorptive materials (wood) was provided by Mirabûches, a wood and sawmill company located in Mirabel, Quebec.
- 2) The second material (chitin) was purchased from Sigma-Aldrich, Canada.
- 3) Chemicals (HCl, NaOH, H₃PO₄, and methanol SEQ-4L) were purchased from Fisher Scientific, Canada.
- 4) Desiccator plate 230MM and tubes conic 50ML W/RACK 500/CS were also procured from Fisher Scientific, Canada.

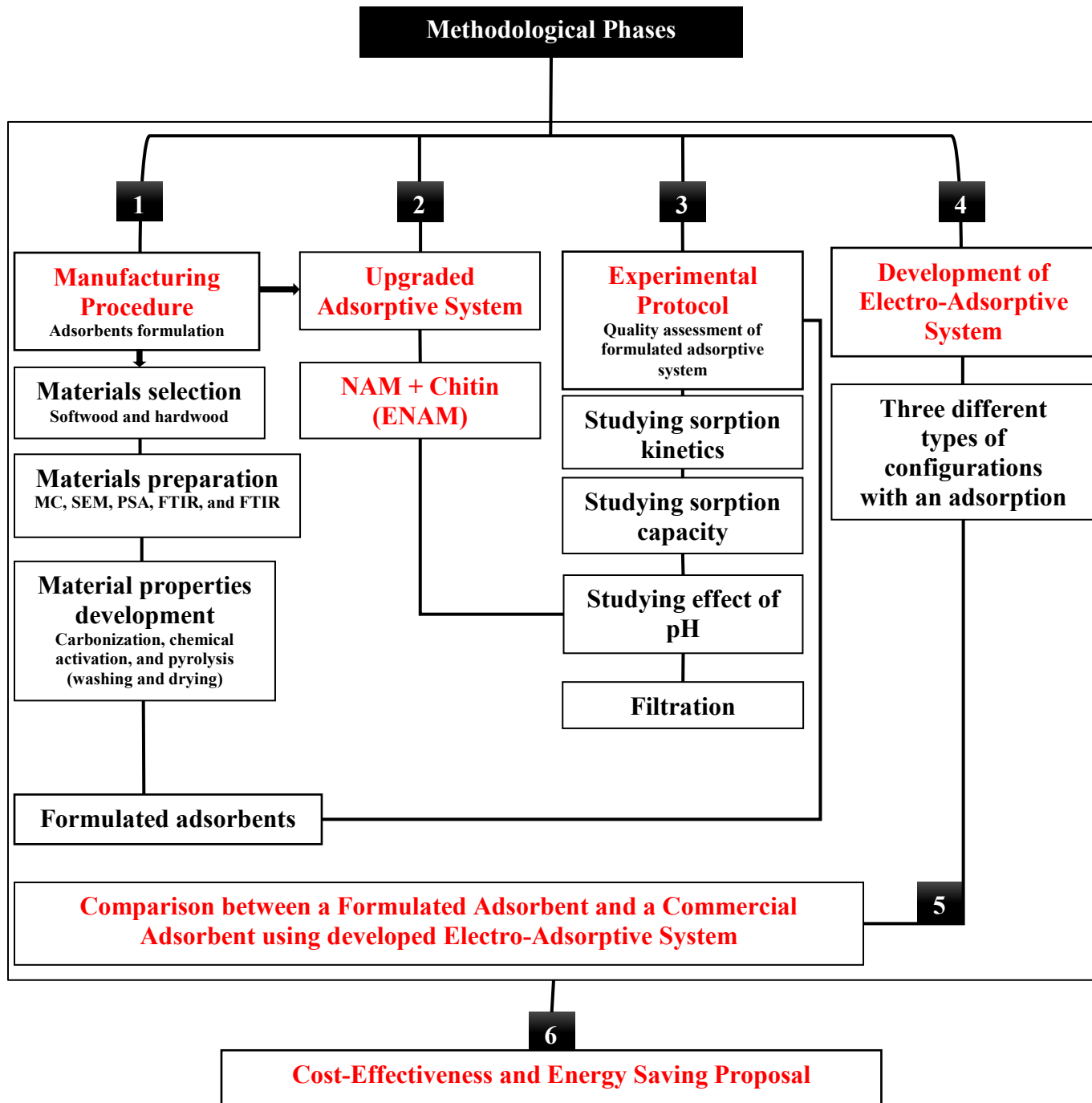


Figure 11: Methodological phases

3.1.1. Phase 1: Preparation procedures - Adsorbents formulation

This section includes procedures for formulating adsorbents from the first adsorptive material (wood) and includes description on an enhancement process using the second source of adsorptive materials (chitin) (Fig. 12 and Table 6).

Table 6: Abbreviations of formulated adsorbents

Material	Definition
Wood	First source of new adsorptive materials from waste
Chitin	Second source of new adsorptive materials from waste
NAM	The best formulated adsorbent among eight adsorbents (New adsorptive materials)
ENAM	Enhanced best formulated adsorbent (Enhanced New Adsorptive Material)
CACA	Commercial activated carbon adsorbent
S1T1	Formulated adsorbent from softwood, particle size $\leq 1\text{mm}$, and at 600°C
S1T2	Formulated adsorbent from softwood, particle size $\leq 1\text{mm}$, and at 800°C
S2T1	Formulated adsorbent from softwood, particle size $\leq 2\text{mm}$, and at 600°C
S2T2	Formulated adsorbent from softwood, particle size $\leq 2\text{mm}$, and at 800°C
H1T1	Formulated adsorbent from hardwood, particle size $\leq 1\text{mm}$, and at 600°C
H1T2	Formulated adsorbent from hardwood, particle size $\leq 1\text{mm}$, and at 800°C
H2T1	Formulated adsorbent from hardwood, particle size $\leq 2\text{mm}$, and at 600°C

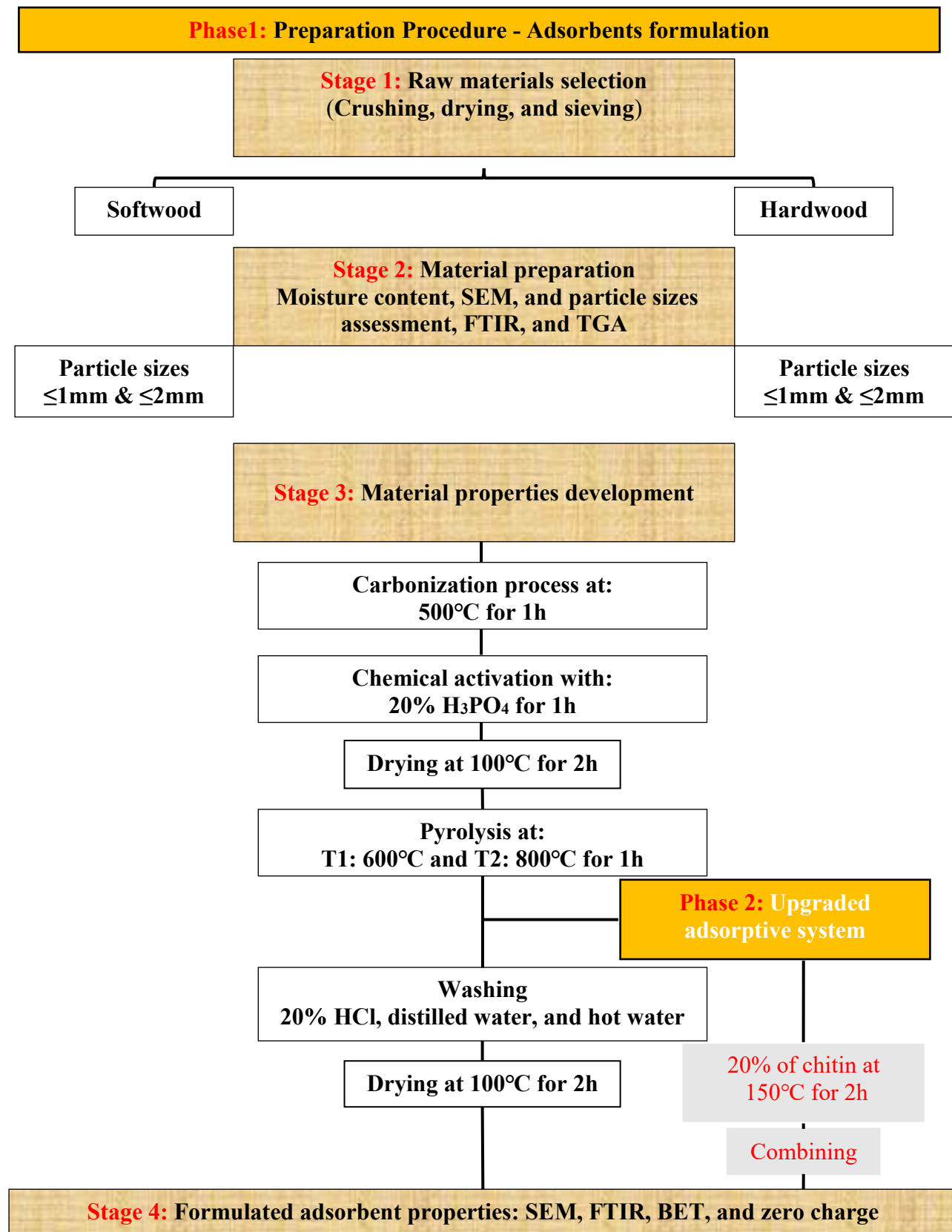


Figure 12: Preparation of adsorbents

In the first phase, which included four stages, the materials were processed and conditioned (based on the generated method, Fig. 12) to be effective adsorbents of EE2. The method developed from a previous approach (REF) seemed to be effective because it could already help to produce an activated carbon (AC) or an activated charcoal. A study confirms that AC is effective in removal process for many pollutants from aqueous solutions, including personal care products (PPCPs), pharmaceuticals, dyes, organic pollutants, and heavy metals [189]. Therefore, AC is a preferential material to be used to generate a high surface area with low-volume pores for favorable chemical reactions and adsorption. In this study, two different types of wood were used to formulate the adsorbents: 1) Coniferous wood also referred to as softwood; and 2) Non-coniferous wood, generally termed as hardwood or deciduous wood.

3.1.1.1. Stage 1: Raw materials selection

Coniferous and non-coniferous wood wastes were used to prepare the adsorbent formulation. They were provided by Mirabûches located in Mirabel, QC, Canada. The samples had the following characteristics:

The coniferous (softwood) chips contained 50% pine tree and 50% fir tree. They were obtained mainly from pine and spruce trees (Sapin et épinette) from the boreal forests located in Northern Quebec (e.g. Abitibi-Témiscamingue, QC).

The non-coniferous (hardwood) chips contained 60% maple tree, 30% oak tree, and 10% birch tree. The company Mirabûches received their hardwood supplies mainly from maple trees grown in the Beauce region located in Southern Quebec.

3.1.1.2. Stage 2: Material property assessment

A good adsorptive material should have a high surface area, a number of available adsorptive sites and adequate functional groups for efficient adsorption. Several analyses were conducted to characterize the primary ingredients used for adsorptive material production and eventually assessed for EE2 removal. Such preparation included moisture content, SEM investigation of adsorptive surface, particle size analysis, Fourier Transform Infra-Red (FTIR) analyses of functional groups and thermal gravimetric analysis (TGA). These analyses enabled screening the different raw samples in view of preparing the adsorbent media with optimal properties.

3.1.1.2.1. Moisture content

Moisture content analysis of the raw softwood and hardwood was done using a gravity convection drying oven (Quincy Lab 20GC, 1.27 Cu. Ft., 115V 750W). The samples heated at 120°C for 2h. They were weighed before and after drying. The moisture by weight lost was calculated and expressed as percentage (%).

3.1.1.2.2. Morphology analysis - Scanning Electron Microscopy images

Scanning electron-microscopy (SEM) was used to assess the topography, morphology, surface texture and porosity of the raw materials and resulting adsorbents. This was carried out using the Hitachi, S-3400N-Variable Pressure Scanning Electron Microscope.

3.1.1.2.3. Particle size analysis

To evaluate the correlation between representative surfaces of the adsorptive materials and the maximum achievable partitioning of EE2 from the aqueous solution, two sizes of the first source (wood) used to prepare the adsorptive material were investigated. Analysis of particle size distribution was carried out using a set of sieves namely 2.38, 2.36, 2, 1.18, 1mm, and pan (or by sieve number 4, 6, 8, 10, 16, and 18, respectively). The sieves were placed on an electric shaker

(Humboldt MFG. co., Testing equipment/ Laboratory apparatus made in USA/ Norridge, IL60656 USA). The shaker was turned on for 15min for each batch of raw material and samples were collected from a pan. Analysis of particle size distribution of the second source of new adsorptive materials (chitin) was performed using a Laser Scattering Particle Size Distribution Analyzer (LA-950 type HORIBA), under the following conditions: Transmittance (R): 97.4%, Transmittance (B): 98.3%, Circulation Speed: 6, Agitation Speed: 4, Ultra Sonic: OFF, Form of Distribution: Manual, Distribution Base: Area, Material: STD, Source: Horiba, Sample Number: 1, Test or Assay. Number: 1, Refractive Index (R): Antonio Mina test [Quartz (1.440 - 0.100i), water (1.333)], and Refractive Index (B): Antonio Mina test [Quartz (1.440 - 0.100i), water (1.333)].

3.1.1.2.4. Functional groups analysis - Fourier Transform Infrared Spectrometry

The functional groups located on the surface of the raw materials and resulting adsorbent media were analyzed using Fourier Transform Infrared Spectrometry (FTIR) (NICOLET 6700 FTIR Spectrometer) with a resolution of 1cm^{-1} .

3.1.1.2.5. Thermal behavior and a mass loss - Thermal Gravimetric Analysis (TGA)

Assessment of material's thermal behavior is crucial for designing an adequate production of adsorptive material through heat treatment (e.g. pyrolysis). The prediction of thermal behavior and mass loss of different types of wood during a heat treatment process were carried out by thermal gravimetric analysis (TGA). This test can show how much mass is required to perform a task. Wood consists of three main compounds namely hemicellulose, cellulose, and lignin. The behavior and characteristics of these constituents are not stable under a heat treatment. Some published temperature ranges in the literature review resulting in wood decomposition are: 160–900°C, 230–400°C, and 180–380°C. However, it appears that some information is lacking regarding these tests or temperature ranges with respect to type of wood, particle size of wood, as well as gas type and flowrate. Hence, it is recommended to conduct TGA tests in view of improving accuracy. Softwood and hardwood involving all particle size groups were thermally predicted using TGA under controlled environment of “N₂” to identify the temperature inducing wood decomposition.

In the current study, a small amount of raw materials (woodchips) was placed centrally in a small pan. The system was purged with N₂ gas at a flowrate of 100ml/min for 1h and a heating rate of 10°C/min. The continuous weight loss and temperature were recorded and analyzed.

3.1.1.3. Stage 3: Material property development

The properties of the new adsorptive material were developed by applying heat and chemicals to the raw woodchips. The application of various conditions can help to understand the phenomena underlying the production of efficient adsorbents. In this study, based on TGA analyses, two pyrolysis temperatures, 600°C and 800°C, were applied to the softwood and hardwood samples comprising of two different chip sizes. Eight new materials were produced and used for determining any correlation between the manufacturing conditions (applied to produce a new adsorbent) and the maximum achievable partitioning of EE2 from the aqueous solution.

Characterization of developed adsorptive materials was done in NanoQAM at UQAM and Concordia University. Both carbonization and pyrolysis were carried out using High-Temperature Tube Furnace (HTF) (Equipment Model: MTI Corporation, OTF-1200X-III). The OTF-1200X-III high temperature tube furnace uses SiC rods as heating elements. The maximum temperature inside the furnace could reach 1200°C under different flowing gases (N₂, mixture Ar/H₂, O₂, etc...). The furnace temperature profile can use 3 distinct gradients that can be set up by 51 segments and run automatically using the 708P type advanced temperature controller. This furnace is mainly used for material research to develop various new materials. In the current study, softwood and hardwood were treated individually under the same conditions in two separated steps: 1. Carbonization; 2. Pyrolysis. Afterward, the treated samples were sent back to Concordia University for activation and drying by oven.

In the carbonization step, the wood was placed centrally in the furnace and the system was purged with nitrogen (N₂) gas at a flowrate of 100 ml/ min for 1h at a pre-determined carbonization temperature by TGA (500°C), a heating rate of 10°C/min. The collected samples from the carbonization step were activated using phosphoric acid (H₃PO₄). The precursors were impregnated with H₃PO₄ (20ml V%: 80ml V% of DI water) for 1h at room temperature. The ratio of new material by weight (g) to the activating agent solution by volume (mL) was fixed at 1:10 throughout the experiment. The samples were then placed in the oven for 2h at temperature 100°C. In the pyrolysis step, the dried samples obtained from the previous step, were placed centrally in the High-Temperature Tube Furnace (HTF) (Equipment Model: MTI Corporation, OTF-1200X-III). The system was purged with nitrogen (N₂) gas at a flowrate of 100 ml/ min for 1h at a

temperature of 600°C for the first run and 800°C for the second run. The heating rate was adjusted to 10°C/ min.

The resulting samples from this step were repeatedly washed with hydrochloric acid (20ml V% HCl: 80ml V% DI water) to neutralize the pH, as well as with hot water, and Milli-Q water. Finally, the washed samples were dried at 100°C for 2h.

3.1.1.4. Stage 4: Analysis of adsorbent properties

The properties of the formulated adsorbents were analyzed by FTIR and SEM as described in Chap. 3.1.1.3. Furthermore, surface area of the new adsorbent was measured using the Brunauer Emmett Teller (BET) method. The surface charge depends on the pH of the environment; hence, the neutrality of surface charge was found by measuring the zero charge.

3.1.1.4.1. Zero charge measurements

The zero charge (pH_{zc}) was determined by the following procedure [217]. A series of 20 mL of 0.1 mol L⁻¹ NaCl solutions was prepared in glass bottles. The initial pH of the NaCl solutions was adjusted by using 0.1 mol/ L of HCl or NaOH to 2, 7, and 12. Then 0.01g of formulated adsorbent was added to each glass bottle and sealed. The bottles were allowed to equilibrate at the room temperature for 2 days. The final pH was measured and plotted against ΔpH.

3.1.1.4.2. Surface area - Brunauer Emmett Teller (BET)

To measure the surface area of formulated adsorbent particles, surface properties analysis was carried out using the Instruments-Quantachrome Autosorb Automated Gas Sorption System.

3.1.2. Phase 2: Preparation procedures - Upgraded adsorptive system

Enhanced adsorptive system (ENAM) was designed by combining the best individual formulated adsorbent with chitin. Chitin, a primary component of sea organism carapaces, is a main waste from the fishery industry. In this study, chitin was used as a second source of new adsorptive materials and was purchased from Sigma-Aldrich, Oakville, ON L6H 6J8. Chitin and its derivatives (chitosan) are the second most available biopolymers after cellulose in Canada. Chitin or chitosan were used as an additive to the formulated adsorbents to enhance their performance for the EE2 removal from aqueous solutions (Fig. 12, Phase 2).

The main objective of adding these enhancers was to achieve a higher adsorption capacity of EE2 from the aqueous solutions. It was hypothesized that the mixing of chitin with NAM would increase the number of available functional groups, such as carbonyls, hydroxyls and carboxyl within the system (ENAM). Thus, a high removal rate in a short time and at less costs would be achieved. Hence, the partitioning process using ENAM would be economical, faster, and more efficient compared to other types of adsorbents. In addition, this would represent a sustainable solution to EE2 removal.

The upgraded adsorptive system was generated by combining 80% of the best formulated adsorbent (NAM) with 20% of chitin at room temperature. Then upgraded adsorptive system was exposed to 150°C for 2h, then, the collected samples were repeatedly washed with hydrochloric acid (20ml V% HCl: 80ml V% DI water) to neutralize the pH of material, then with hot water, and Milli-Q water. In the last step, the washed samples were dried at 100°C for 2h.

➤ **Material preparation**

The properties of the second source of new adsorptive materials (chitin) were analyzed using SEM, FTIR, and TGA. In addition, particle size assessment was carried out using a Laser Scattering Particle Size Distribution Analyzer- LA-950 (Horiba).

➤ **Analysis of adsorbent properties**

The properties of formulated adsorbents were demonstrated using SEM, FITR, BET, and zero charge measurements.

➤ **Analysis of upgraded adsorptive system properties**

The analysis of upgraded adsorptive system properties was assumed to involve the combined properties of NAM and chitin and were determined using the analytical methods already described above.

3.1.3. Phase 3: Experimental protocol - Quality assessment

The experimental protocol provided in this section was adopted to evaluate the performance of formulated adsorbents under different conditions (Fig. 13). The protocol design focused on simulating all major conditions controlling EE2 absorption to biosolids. Firstly, the sorption kinetics were determined for the partitioning of EE2 into individual formulated adsorbent. Secondly, the sorption capacity of the formulated adsorbents on the extent partitioning of EE2, and sorption isotherms were investigated. Thirdly, the effect of pH on the partitioning behavior of EE2 into individual formulated adsorbent and upgraded adsorptive system was studied.

All samples and measurements were done in triplicate. Statistical analyses were performed for these measurements to find respective mean values, standard deviations, and experimental errors.

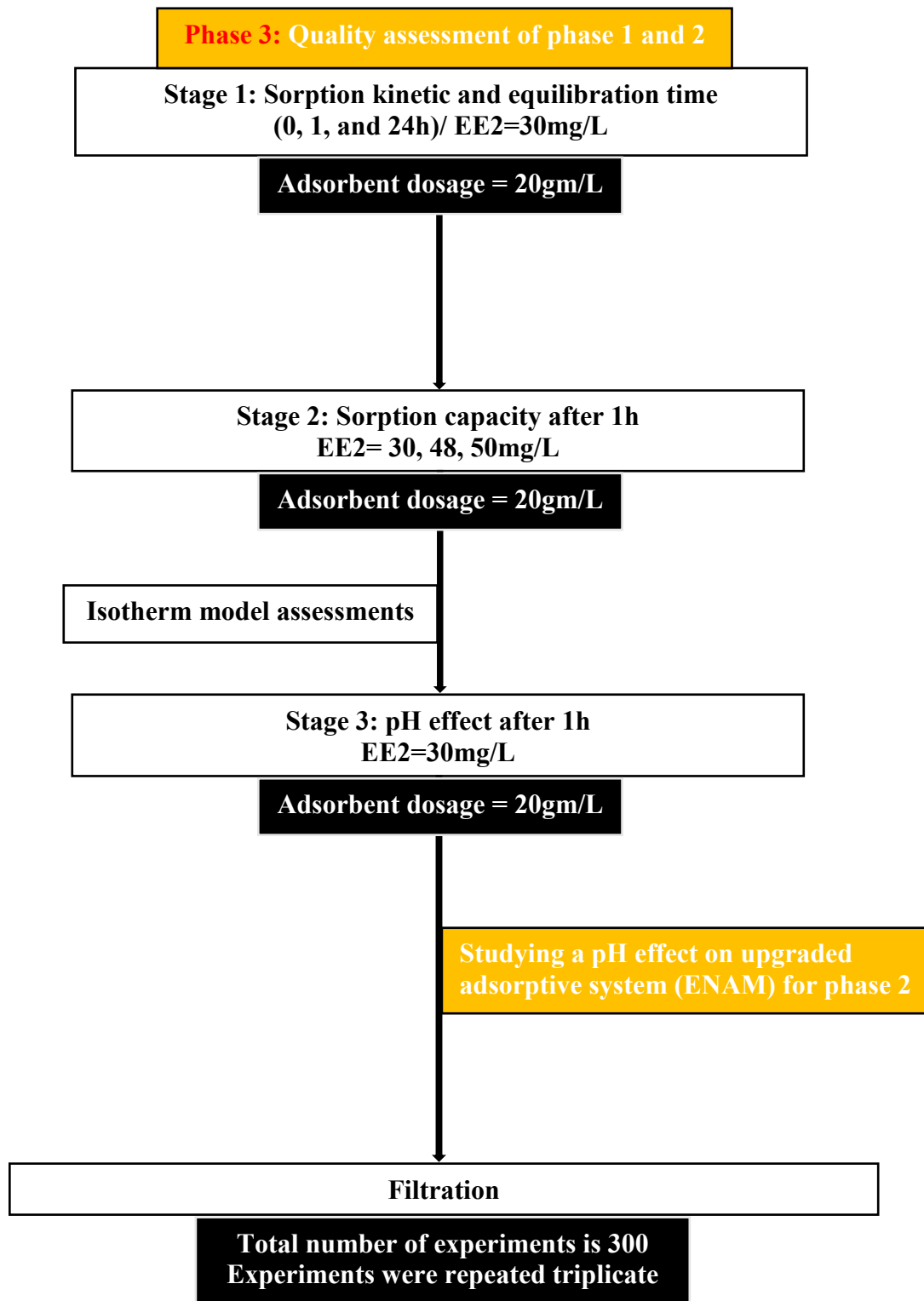


Figure 13: Scheme of experimental protocol- Quality assessment of formulated adsorptive systems

3.1.3.1. Stage 1: Sorption kinetics and equilibration time

Kinetic studies or kinetics of sorption from a solution onto an adsorbent describe the interactions between the adsorbent and adsorbate. The mass balance was evaluated by measuring the EE2 equilibrium concentration in the aqueous phase assuming the remaining EE2 concentration to be associated with the formulated adsorbents using Equations 6 and 7 [215].

$$q_e = \frac{C_0 - C_e V}{M} \quad (6)$$

$$\text{Efficiency} = \frac{C_0 - C}{C_0} \times 100 \quad (7)$$

Where C_e and C_0 are the equilibrium and initial concentrations of EE2 (mg/L), q_e is the equilibrium EE2 concentration on the adsorbent (mg/g), V is the volume of EE2 solution (L), M is the mass of adsorbent (g).

➤ Objective

Kinetics of EE2 sorption to the different optimized wood chips were studied. This enabled a better understanding of the rates and extent of mechanisms responsible for sorption of the estrogenic hormone to each individual formulated adsorbent. Furthermore, the results of this set of experiments allowed the determination of the relationship between the type of waste woodchip and the maximum achievable partitioning of EE2. Based on the results, the evaluation of the correlation between represented surface area of the adsorptive materials and the maximum achievable partitioning of EE2 was also possible. The expected results from this proposed set of experiments helped to assess the time required for the equilibration of each studied system, and enabled determining the time required to design the remaining batch-experiments throughout the rest of this research.

➤ Procedure

A batch-equilibration method was used to measure the sorption of 17 α -ethynylestradiol by the formulated adsorbents from aqueous solutions. In this experiment, two different adsorbents made from softwood and hardwood respectively, were added individually to 50mL centrifuge tube. The solid adsorbent samples were weighed (20g/L) individually, and added to each tube. Milli-Q water was added to each tube in a volume of 10mL. All tubes were spiked with the hormone solution to yield a final concentration of 30mg/L. An adsorbent weight (g) to solution volume (mL) ratio of 1:10 was used throughout the experiment. The tubes were capped and mixed using a mechanical end-over-end shaker (10 rpm) at a controlled temperature of 30°C. Kinetic experiments were conducted by measuring EE2 concentration periodically for 24 hours starting immediately after the addition of the hormone. At each sampling time, a sample tube for each adsorbent type, was used for analysis. The tubes containing the samples were centrifuged, and the respective supernatants were collected for extraction and analysis. Samples were collected at 0, 1, 24h time interval. All measurements were done in triplicates. The experiment also included analysis of EE2 in the solution without the addition of any adsorbent as control.

3.1.3.2. Stage 2: Sorption capacity

In order to assess the maximum amount of EE2 that the formulated adsorbent can contain, the changes induced on the adsorbent surface in presence of different EE2 concentrations was investigated under constant environmental conditions.

➤ Objective

The experiments were designed to assess the adsorbent's sorption capacities by varying the initial hormone concentration (30, 48, and 50 mg/L) under constant conditions of time, temperature and pH. The main objective of this test (result) was to gain insight on the maximum concentrations to be applicable for the remaining experimental stages. The resulting data was evaluated using sorption isotherms using Eqs.11, 12, and 13 to find the model that best describes the findings.

➤ Procedure

Batch-equilibrium tests were performed for all formulated adsorbents by individually weighing 1g in 50 mL centrifuge tubes, followed by addition of 10mL Milli-Q water to each tube. Afterward, the hormone solution at the appropriate dilution, was added to produce the desired final concentration in each tube. The concentrations used in this test were as follows: 30, 48, and 50mg/L (equivalent to: 30×10^7 , 4.8×10^7 , and 50×10^7 ng/g of adsorbent). Lower concentrations might be tested in the future to practically simulate environmental levels of EE2. The test tubes were capped and mixed on an end-over-end shaker at a pre-set temperature of 30°C, for 1-2 hour, to enable enough sorption (>90%) to take place. At the end of the experiment, the tubes were centrifuged, and the supernatant was collected, extracted and the concentration of EE2 determined. All experiments were run in triplicate.

3.1.3.3. Stage 3: pH effect

This step was conducted to investigate the partitioning of EE2 to the formulated adsorbents under different pH.

➤ Objectives

This step was necessary to evaluate the effect on the adsorbent chip's surface charges as a result of changes incurred in the adsorbent-suspension pH over the range between acidic and alkaline conditions with respect to the partitioning of the synthetic estrogen. The results of these experiments were expected to improve the understanding of rates and extent of mechanisms responsible for sorption of the estrogenic hormone to the formulated adsorbent material.

➤ Procedure

Batch-equilibration tests were performed as described in the section. They enabled assessment of the effect of variation of suspension pH on the partitioning of EE2 between the aqueous and solid phases. Adsorbents were weighed (20g/Lg) individually in 50mL centrifuge tubes, and 10mL of Milli-Q water was added to each tube. The suspension pH was adjusted by adding sodium hydroxide (NaOH) or acetic acid (AcOH), and the suspension was pre-equilibrated for 1h. After equilibrium, the diluted hormone solution was added to yield a final concentration of 30mg/L (equivalent to 30×10^7 ng/g of adsorbent). The tubes were capped and mixed on an end-over-end shaker at a controlled temperature 30°C for 1-2 h. At the end of the test, the tubes were centrifuged, and the supernatant was collected, extracted and analyzed for EE2. All tests were run in triplicates, and samples were analyzed under the same conditions. For each sample, sorption of EE2 was studied under three suspension pH values, carefully selected to reflect the effect of variation of aqueous chemistry and adsorbent-surface charges on the rate and extent of sorption of the organic estrogen, EE2, to different types of adsorbents. For each type, three pH values were selected to represent neutral (~7), acidic (~2), and basic (~10) conditions, respectively.

➤ **Studying pH effect on the upgraded adsorptive system**

The effect of pH on the upgraded adsorptive system was studied under similar conditions that were used in previous section (3.1.3.3. Stage 3: pH effect).

Batch-equilibration experiments were carried out for all types of ENAM in Milli-Q water. Solid samples were weighed (20g/L) individually in pre-weighed centrifuge tubes (50mL) followed by the addition of 10 mL of water to each tube. The pH of the suspension was adjusted to the required value by the addition of sodium hydroxide (NaOH) or acetic acid (AcOH), and the suspension was pre-equilibrated for 1h. After equilibration, the diluted hormone solution was added to yield a final concentration of 30mg/L (equivalent to 30×10^7 ng/g of adsorbent) in each tube. The tubes were capped and mixed on an end-over-end shaker under the same condition (controlled temperature, 30°C, for 1-2 hour). At the end of the test, the tubes were centrifuged, and the supernatant were collected, extracted, filtered, and analyzed for the EE2 concentration. In addition, batch-equilibration experiments were executed on a commercial adsorbent in Mill-Q water to find any difference between the formulated adsorptive system and the commercial adsorbent.

➤ **Additional preparations and calculations for phase 3.**

This section includes additional preparations and calculations that were done during the assessment phase.

➤ **Stock solution preparation**

Stock solutions of EE2 were prepared in methanol using Eq. 8 and were kept refrigerated (-16°C) when not in use.

$$(\text{Concentration solute (w/v\%)}) = \frac{\text{mass of solute (g)}}{\text{volume of solution (ml)}} \times 100 \quad (8)$$

Dilutions and added volumes using deionized water were carefully selected to mimic environmental concentrations while ensuring the aqueous concentrations' range above the detection limit and minimizing the volume fraction of methanol in experiments to avoid its interference with the partitioning processes during chromatographic analysis. To dilute a stock solution of known concentration, the following equation was used (Equation 9):

$$\text{Concentration}_{(start)} \times \text{Volume}_{(start)} = \text{Concentration}_{(final)} \times \text{Volume}_{(final)} \quad (9)$$

After preparation of stock solutions and their respective dilutions, the samples were scanned using UV-VIS to measure the final concentration of EE2 in the aqueous solutions and methanol as shown in A1-2 to A1-6. Furthermore, a group of standard solutions was prepared for UV-VIS measurements as shown in A1-7 as well as a calibration curve as shown in A1-8.

➤ Analytical techniques

Some recent studies have focused their research on designing analytical procedures for the analysis and detection of steroid hormones in various environmental ecosystems [121]. Given the low concentrations (sub- $\mu\text{g/L}$ to low- $\mu\text{g/L}$) to be detected, the analytical step had to be as selective and sensitive as possible. This step is critical to prevent the loss of target analytes. Unfortunately, a unique methodology has not been defined for such practices. In this section, an analytical procedure that may help to achieve max extraction and detection efficiency of 17α -ethynylestradiol (the synthetic estrogenic compound) from an aqueous phase was developed. In addition, internal standards (IS) with similar physicochemical properties to the analyte provide multiple advantages in liquid such as: improvement in the intra-injection reproducibility, reduction of the analysis run time, impact reduction of matrix and ionization effects.

➤ **Required chemicals and solutions for an extraction**

This includes the chemicals and solutions used for the extraction. The purity of these chemicals and solutions was high (99.98 %) to avoid potential damage and contamination to HPLC equipment. Following is a list of the chemicals and solutions used for this work:

1. HPLC-grade water; 2. Acetonitrile; 3. Methanol; 4. Dichloromethane (DCM); 5. The internal standard: 17 α -Ethinylestradiol-2, 4, 16, 16-d4 (D4).

The internal standard was prepared in methanol and kept under fridge conditions (-16°C) when not in use.

➤ **Extraction procedure**

All experimental sample tubes were centrifuged at 2700 rpm for 35 minute. The supernatant (10mL) was then collected and subjected to solvent extraction (liquid-liquid extraction).

1. Before commencing the extraction procedure, the internal standard was added at a concentration comparable to the EE2 concentration in collected supernatants.
2. About 2mL of DCM was added three times to the supernatants under these conditions with 60 seconds shaking at each extraction.
3. The aliquot of the organic layer was collected in the vessel and then dried using a vacuum rotary dryer.
4. The vessel was triple washed with trace volumes (0.0001L) of DCM.
5. The collected aliquots were transferred to HPLC macro vials.

➤ **Analysis procedure**

For HPLC, the vials were dried under a stream of nitrogen gas (350 mL/min at 250°C), and the residues were re-suspended in 40µL solvent mixture of 40% acetonitrile and analyzed. The specifications of the used HPLC system were Hewlett Packard, Series 1100, equipped with a reverse-phase column (Luna C8 (2), 3micron, 50x1mm) from Phenomenex, Torrance, CA.

1. The mobile phase used was water and acetonitrile at volume ratio of (50:50), 2mM NH₄OAC (ammonium acetate) pH 7.4 (adjusted with NH₄OH), delivered at a constant flow rate of 1.5 mL/min. The injection volume of the standards and samples was 40 µL and the total run time for then HPLC analysis was around 30 minutes.
2. The wash between injected samples was done periodically as follows: around 50 min with 98% acetonitrile, 2mM NH₄OAC, and then with the same time with 50% acetonitrile, 2mM NH₄OAC.

➤ **Filtration**

Suspended particle removal was carried out manually. A syringe with pore size equal to 0.44µm was used, followed by another syringe bearing pore size equal to 0.22µm to ensure that all suspended particles of adsorbent were removed. The smaller pore size was very useful to reach a maximum removal capacity. However, since there was still the presence of residual of suspended particles of adsorbents, electrical techniques were applied to enhance the water quality. There are many factors that can reduce the efficiency of the system and include: corrosion, scaling, fouling, and microbiological activity. Thus, the proposed combination system may help to minimize these effects by providing extra heat to clean the surfaces.

➤ **Assessment approach**

The adsorption data was fitted to the Langmuir and Freundlich isotherms, and pseudo first and second order models for the kinetic study. These linear models were generated using Equation 10 and involved the correlation between two variables. This correlation can have a value of:

1. (1) is a perfect positive correlation (correlation is positive when the values increase together).
2. (-1) is a perfect negative correlation (correlation is negative when one value decreases as the other increases).
3. (0) is no correlation (the values are not linked at all).

The two sets of data "x" and "y" (in this study x is time and y is the amount of EE2 adsorbed).

Step 1: Find the mean of x, and the mean of y

Step 2: Subtract the mean of x from every x value (call them "a"), the same for y (call them "b")

Step 3: Calculate: ab, a² and b² for every value

Step 4: Sum up ab, sum up a² and sum up b²

Step 5: Divide the sum of ab by the square root of [(sum of a²) × (sum of b²)]

$$r_{xy} = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2 \sum_{i=1}^n (y_i - \bar{y})^2}} \quad (10)$$

Where: Σ is sigma, the symbol for "sum up"; $(x_i - \bar{x})$: Each x-value minus the mean of x (called "a" above); and $(y_i - \bar{y})$: Each y-value minus the mean of y (called "b" above).

➤ **The equilibrium of adsorption**

The equilibrium of adsorption is usually evaluated by Freundlich and Langmuir isotherm models.

✓ *The Freundlich isotherm model is an empirical equation, which in its linear form is expressed as in Equation 11:*

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (11)$$

✓ *The Langmuir isotherm model is expressed as in Equation 12 and 13:*

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{q_0 b C_e} \quad (12)$$

$$R_L = \frac{1}{1 + b C_0} \quad (13)$$

Where q_e (mg/g) is the amount of solute adsorbed at equilibrium and C_e (mg/L) is the equilibrium concentration of solute in the solution.

q_0 (mg/g) is denoted as the maximum adsorption capacity (10.12), b (L/mg) is the binding energy constant (0.033 L/mg), and C_0 is the initial concentration of the solute.

R_L is the dimensionless separation factor (0.92). The R_L value indicates the adsorption situation to be irreversible: $R_L = 0$, favorable: $0 < R_L < 1$, linear: $R_L = 1$ and unfavorable: $R_L > 1$.

$k_f \text{ mg/g (mg/L)}^{-1/n}$ is the measure of adsorption capacity (0.346mg/g) and the Freundlich intensity parameter $1/n$ indicates the intensity of adsorptive interactions (1.043).

If $1/n > 1$, it indicates cooperative adsorption and if $1/n < 1$, it shows a normal adsorption. However, if $1/n = 1$, the partitioning between the two phases are not concentration dependent.

3.1.4. Phase 4: Development of electro adsorptive system

Electrokinetic processes including electrocoagulation were combined with the adsorptive system to create an electro-adsorptive system. Coagulation is the one of the most important physicochemical techniques used in water treatment. In this section, electrocoagulation was applied using a DC electric field to: i) Generate electrical charges for ion releases from electrodes, ii) Decrease diffuse double layer of colloids, iii) Create flocs (organic and inorganic) in solution, iv) Increase the density of flocs, v) Promote separation of phases, vi) Change morphology of flocs leading to settling and/or floatation.

Before the electrical system was turned, all measurements were done such as water resistance and conductivity, which were equal to 3.067 k Ω - cm and 280.7 μ S/cm, respectively. The feasibility of the process was tested by using 10g/L of chitin. The main purpose of the anode material change was to determine the best electrical system, which may help in electrocoagulation and removal of EE2.

In this study, the electrokinetic (EK) cell consisted of electrodes (anode and cathode) carefully placed in a polyethylene container with dimension 4 X 6 X 6 cm equal to 144 cm³. These electrodes were connected to a DC power supply by thin cables (DC Power Supply, 30V, 5A variable regulated adjustable linear DC lab test Kit 110V with US power cord).

The dimensions of the electrodes were as follows: The iron cathode had a width = 5cm and height = 7.5cm; and the anodes consisted of iron, aluminum, and carbon had a width = 5, 5.4, and 5 cm respectively, and height = 7.5, 7.6, and 5 cm, respectively. The supplied voltage gradient to the system was adjusted to 1V/cm, 2V/cm, 3V/cm, 4V/cm, and 6V/cm. (Fig. 14). The electro-adsorptive system was optimized based on the electrode type, the distance between electrodes, and voltage gradient. As a result, it was found that iron-iron (at 1V/cm) provided the best configuration compared to others. Therefore, iron, an easily available material, was used as electrodes in the tests with variable voltage of 5V, 10V, 15V, 20V, and 30V, keeping the distance between electrodes constant.

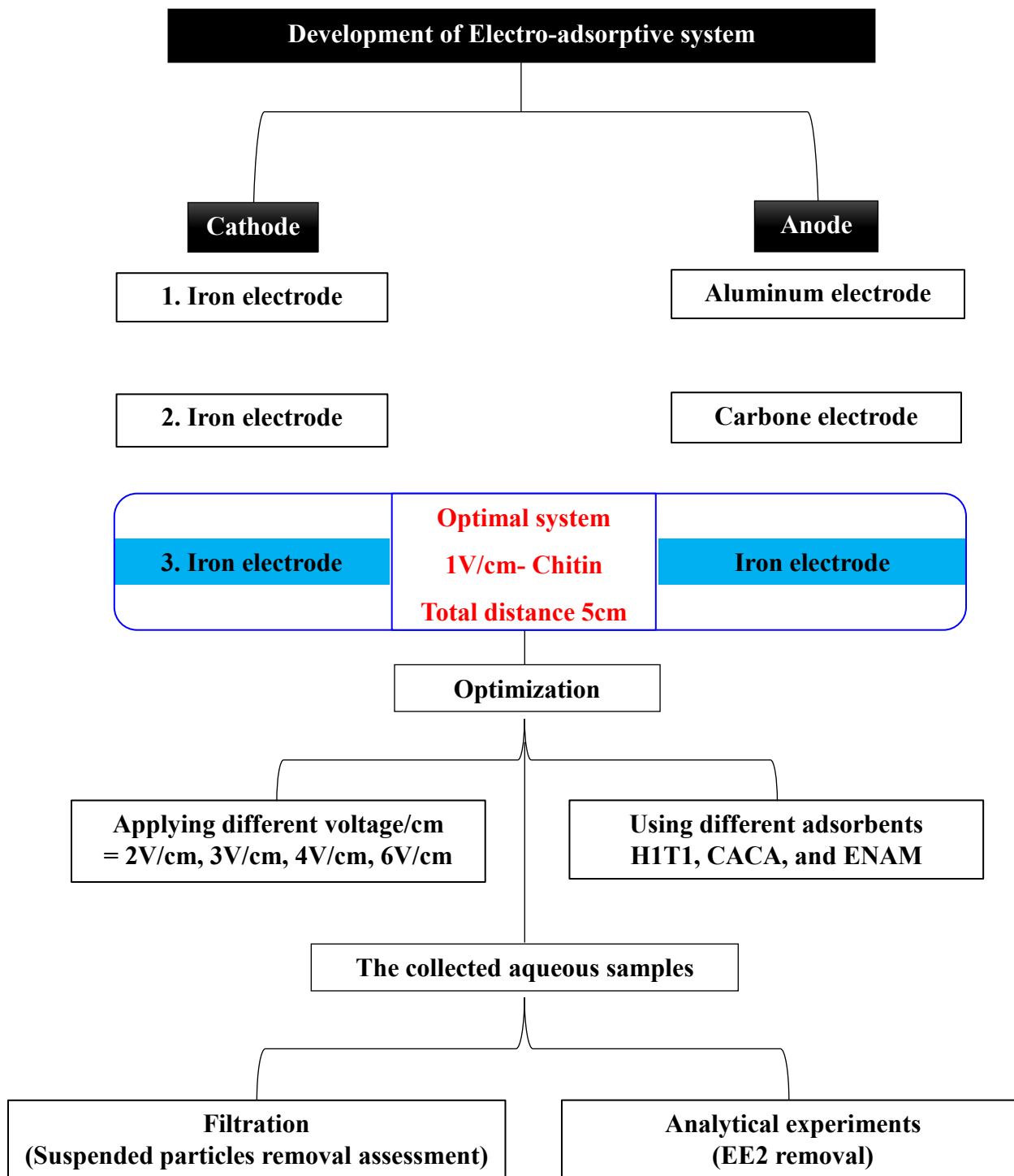
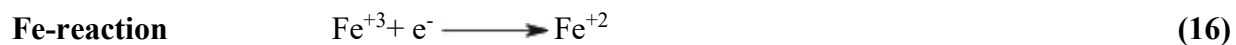
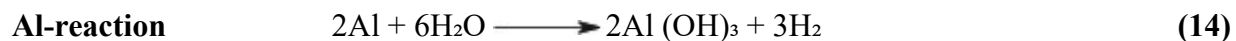


Figure 14: Scheme of developed electro-adsorptive system

Since the treated solution contained organic and inorganic components with unknown properties various electrical field strengths were tested. Three different types of materials were used for the anode, while iron was used for the cathode. Ion production under these configurations are described as follows in Equations 14, 15, and 16:



3.1.5. Phase 5: Electro adsorptive system - Comparison

In order to better assess the performance of the developed electro-adsorptive system, a comparison was established between the developed electro-adsorptive system and a commercial system under similar operational conditions.

3.1.6. Phase 6: Cost effectiveness increase and energy saving

Statistically, studying small population of a big application requires a small amount of materials with a high cost. Accordingly, two optimization models were generated to increase cost-effectiveness of this work: 1. Materials distribution optimization model; 2. Energy saving optimization model. Furthermore, results showed other approaches to increase cost effectiveness and to save energy of entire research work (production of a new material).

▣ Materials distribution optimization model - Cost effectiveness of delivered materials

In this technology, materials can be provided from different companies. Furthermore, the produced materials have to be delivered to customers in different locations (WWTPs and water treatment faculties). The minimizing distance for delivering the product, by salesman seemed possible using MILP model (Table 7). It was simulated by an annealing (Appendix 2).

The model objective was minimizing the sum of the distances moved in a total of M moves (Equation 17). It was assumed that the first location was the first and last location to be visited (the Equations 18 to 26).

Table 7: Mixed integer linear programming-MILP

Indexes and Data	
N	Number of locations where are indexed as $i=1, 2, \dots, N$
j	Index for sequence of visitation of the locations $j=1, 2, \dots, (N+1)$
m	Index of move $m=1, 2, \dots, =N$
$D_{i,i'}$	Distance between locations i and i'
Φ	Large positive number
Decision Variables	
$y_{i,j}$	A binary variable equal to 1 if locations i is the j^{th} location to be visited, 0 otherwise
s_m	A continuous variable which equal to the distance travelled in the m^{th} move

Eq. (17) is the objective function used to minimize the sum of the distances moved.

Eq. (18) is the location #1.

Eq. (19) states that location #1 cannot be $2^{nd}, 3^{rd}, \dots, N^{th}$ location to be visited.

Eq. (20) states any other location cannot be neither the first nor the last location to be visited. The first location was visited twice, at the beginning and at the end of the trip.

Eq. (21) states that other locations can be visited only once.

Eq. (22) states that in one stop only one location can be visited.

Eq. (23 & 24) set the distance travelled s_j equal to $D_{i,i'}$, if location i and location i' are the j^{th} and $(j+1)^{th}$ locations to be visited, respectively.

Eq. (25 & 26) are the integrality (binary) and non-negativity constraints.

Objective function (Minimization):

$$Z = \sum_{m=1}^m S_m \quad (17)$$

Subject to:

$$y_{1,1} = 1; y_{N+1} = 1 \quad (18)$$

$$y_{1,j} = 0; \forall j \in \{2, 3, \dots, N\} \quad (19)$$

$$y_{i,1} = 0; y_{i,N+1} = 0; \forall i \in \{2, 3, \dots, N\} \quad (20)$$

$$\sum_{j=2}^N y_{i,j} = 1; \forall i \in \{2, 3, \dots, N\} \quad (21)$$

$$\sum_{j=2}^N y_{i,j} = 1; \forall i \in \{2, 3, \dots, N\} \quad (22)$$

$$S_j \geq D_{i,i'} + \Phi(y_{i,j} + y_{i',j+1}) - 2\Phi; i \neq i' \ \& \ \forall j \in \{1, 2, \dots, N\} \quad (23)$$

$$S_j \leq D_{i,i'} - \Phi(y_{i,j} + y_{i',j+1}) + 2\Phi; i \neq i' \ \& \ \forall j \in \{1, 2, \dots, N\} \quad (24)$$

$$y_{i,j} \text{ is binary for all } i \text{ and } j \quad (25)$$

$$S_m \geq 0 \quad (26)$$

➤ **Energy saving optimization model**

It was assumed to complete a given collection of tasks on a single process that can accommodate to one job at a time X . Otherwise, the separable programming model will require if the process time is not the same in all tasks. The separable programming model is a nonlinear programming problem used to select n decision variables x_1, x_2, \dots, x_n from a given feasible region made by optimizing (minimize or maximize) a given objective function $f(x_1, x_2, \dots, x_n)$ as shown in Equation 27 of the decision variables as shown in Equation 28.

Minimize

$$f(x) = \sum_{j=1}^n f_j(x_j) = f_1(x_1) + \dots + f_n(x_n) \quad (27)$$

Subject to:

$$\sum_{j=1}^n a_{i,j}(x_j) \leq b_i, \quad i = 1 \dots, m \quad (28)$$

$$0 \leq x_j, j=1, \dots, n$$

Note: For linearization, Approximating Separable Programs as MILP has to be used to form a piecewise linear approximation.

Chapter 4: Results

4.1. Introduction

In this chapter, the qualitative and quantitative results from the design and testing of the adsorptive system for EE2 removal from the aqueous solutions are presented. A holistic approach was adopted by presenting the expected as well as the actual results to better frame and study the objectives set.

4.2. Expected results

The following results were expected from this work as a response to the research objectives.

1. Removal of EE2 by 95% from aqueous solutions through the development of a new adsorptive material. However, this value might be decreased or increased depending on the existing environmental conditions, e.g. properties of WWTP effluents.
2. Removal of EE2 by 99% or more from aqueous solutions due to the presence of a higher number of active sites (e.g. carbonyl, hydroxyl and carboxyl groups) on the new material's surface created by chitin. However, any reduction in this value (99% removal capacity) might be attributed to the sensitivity of chitin to pH and temperature.

4.3. Results from phase 1: Preparation procedures - Adsorbents formulation

This section includes actual results obtained from phase 1 of this study.

4.3.1. Stage 1: Raw material selection

Raw softwood and hardwood were found to have different surface properties. Developing these new materials under similar conditions demonstrated a good knowledge about the properties and behaviours of the adsorbents, considering both preparation conditions and application of generated products in environmental engineering.

4.3.2. Stage 2: Results of material property assessment

This section includes the results from the following analysis: 1. Moisture content; 2. Morphology (scanning electron-microscopy images); 3. Particle size analysis; 4. Organic functional groups analysis - Fourier Transform Infrared spectrometry; 5. Thermal behavior and a mass loss-Thermal Gravimetric Analysis.

4.3.2.1. Moisture content

The moisture content for each type of wood chips namely softwood and hardwood, was determined using a drying method in the oven at 100°C for 2h. The results showed in Fig. 15 indicate that softwood contains a higher moisture content which is equal to 1.8g out of the total wood weight of 5g (36.34% of the dry wood material) compared to the hardwood which contains a moisture content equal to 0.3g out of the total wood weight of 5g (6.2% of the dry wood material). These moisture contents (36.3% for softwood and 6.3% hardwood) are in agreement with previous studies. According to published data, the moisture content in living trees depends on the type of wood and can range from 25% to 250% of the dry wood material, and the moisture content of heartwood is less than that of sapwood. In both cases, the moisture content is attributed to the accumulation of water in the cell cavity (free water) or could be attributed to bound water to the

cell wall (bound water). In the present study, the wood was dried and stored for a long time; however, the moisture content still shows similar values to mention in scientific literature. It can safely be affirmed that the moisture content in softwood is due to the bound water (bound water to cell wall).

The bound water is part of the wood structure which is slightly affected by transformation from a living to the dry state. However, 6.3% of the moisture content could be attributed to the water adsorption from the environment (free water) which has an obvious effect on the wood water composition. The percentage of free water in the wood can vary depending on the surface area of the wood, number of pores and their size, humidity, and as well as on the wood type.

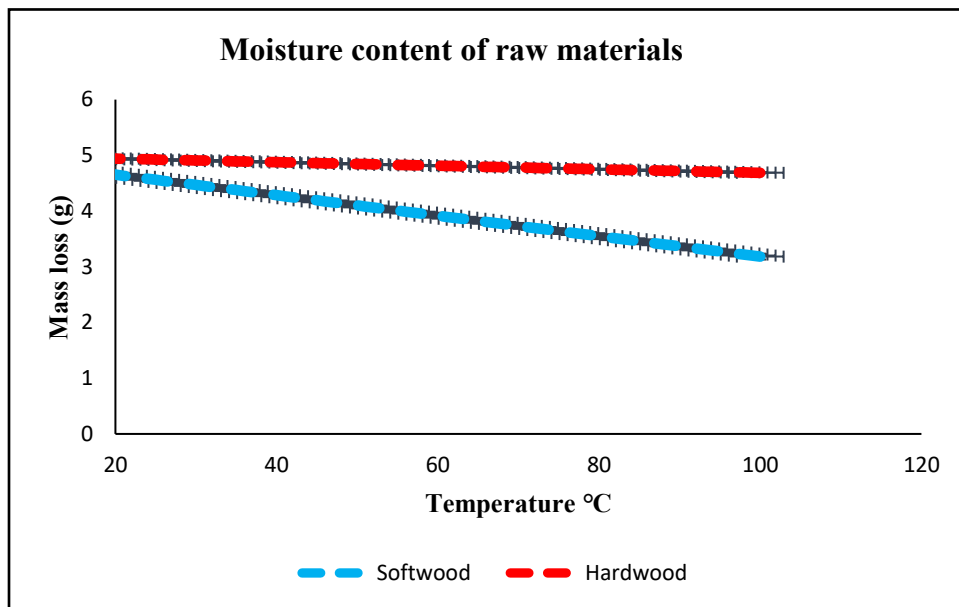


Figure 15: Moisture content of raw materials (softwood and hardwood)

4.3.2.2. Morphology analysis - Scanning Electron Microscopy images

Scanning electron-microscopy (SEM) was applied to study both the softwood and hardwood in view of assessing topography, morphology, surface texture and porosity of these materials. The SEM images showed that the raw softwood with particle size $\leq 1\text{mm}$ had pores along structure. On the contrary, the raw hardwood with particle size $\leq 1\text{mm}$ displayed accumulation of wood particles with no visible pores (Fig.16). The SEM images with respect to morphology are strongly consistent with the final results obtained for EE2 removal; adsorbents with large pores had lower number of active sites on the surface and displayed a lower removal capacity.

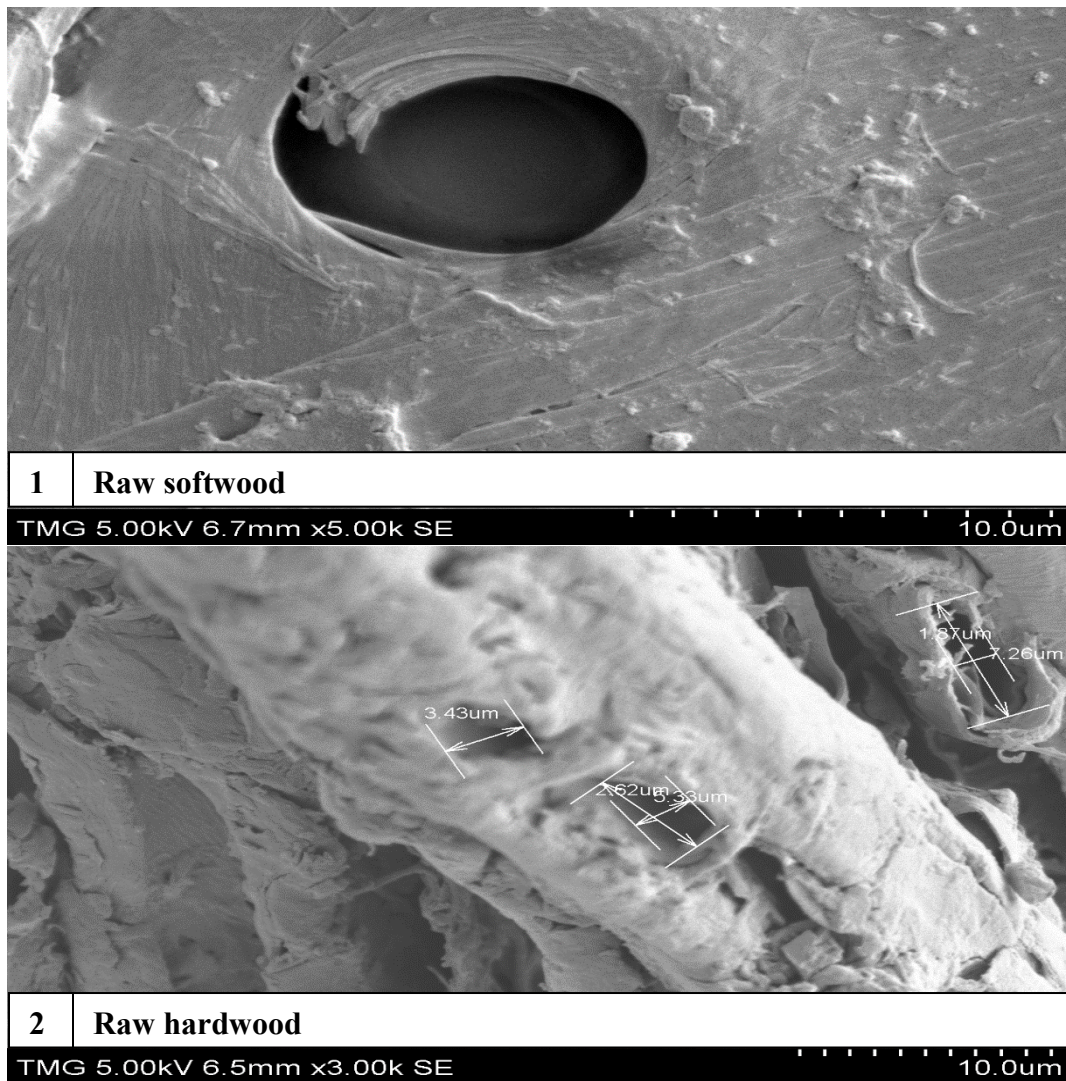


Figure 16: Raw material morphology difference (softwood and hardwood)

4.3.2.3. Particle size analysis

Particle size distribution of raw wood was assessed using the sieve method. The collected samples from the sieves were classified based on particle size in five groups for each type of wood as shown in Figure 17:

1. The first group comprised of particle size $\leq 2.38\text{mm}$ (bag 1 and 2 with softwood and bag 11 and 12 with hardwood).
2. The second group included particle size $\leq 2.36\text{mm}$ (bag 3A and 7B).
3. The third group involved particle size $\leq 2\text{mm}$ (bag 4A and 8B).
4. The fourth group comprised of particle size $\leq 1.18\text{mm}$ (bag 5A and 9B).
5. The fifth group covered particle size $\leq 1\text{mm}$ (bag 6A and 10B).



Figure 17: Particle size assessment of raw materials (softwood and hardwood)

Statistical analyses were performed for collected samples to find out suitable particle size for this work (Figs. 18 and 19). It was found the materials with particle size $\leq 1\text{mm}$ represented the best choice for the adsorbent design due to their higher surface area. However, particle size $< 2\text{mm}$ was also tested to assess differences between properties. It should be noted that more input energy was required to shred the materials to lower size.

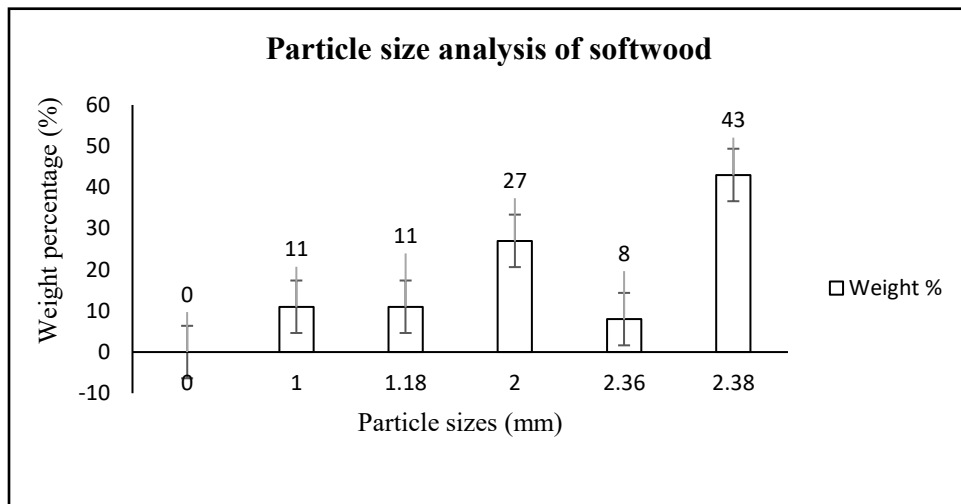


Figure 18: Particle size analysis of softwood

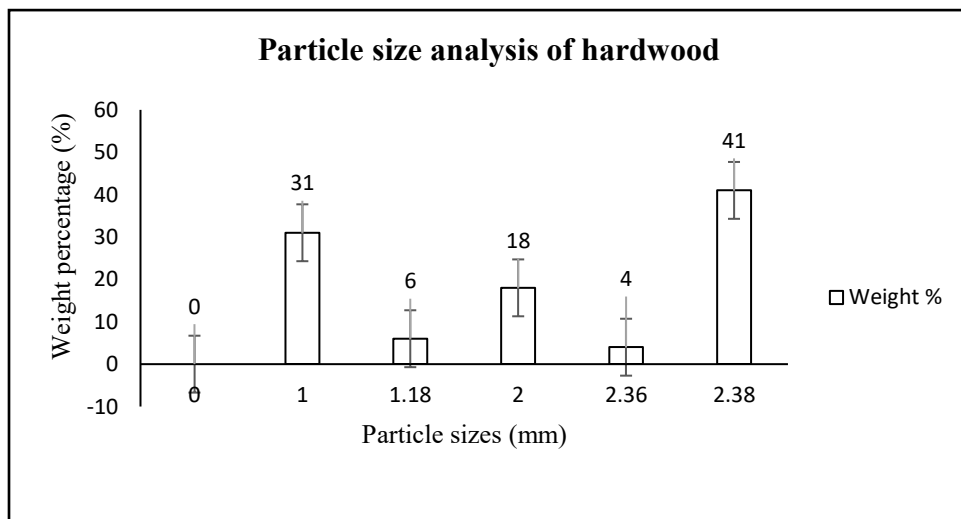


Figure 19: Particle size analysis of hardwood

4.3.2.4. Functional groups analysis - Fourier Transform Infrared Spectrometry

The organic functional groups present on the surface of the raw materials were analyzed using Fourier Transform Infrared Spectrometry (FTIR) with a resolution of 1cm^{-1} .

Results from FTIR analyses were used to define carbon-related functional groups present on the surface of the raw wood. Thus, 50mg of each raw material (softwood and hardwood with particle size $\leq 1\text{mm}$ and $\leq 2\text{mm}$) were individually dispersed in a KBR pellet and subjected to FTIR spectral analysis in the range of 450 to 4000 cm^{-1} . The observed transmission bands for the raw materials as well as their corresponding assignments are shown in Table 8.

It was found that hardwood had higher intensity of C-H & C-O deformation vibration (due to the presence of lignin) at 1032 than softwood. In addition, at 1370 for C-H in plane bending (cellulose and hemicellulose), at 1422 for H-C-H & O-C-H in plane bending (cellulose), at 1454 for H-C-H & O-C-H in plane bending (cellulose), at 1504 for $\text{C}\equiv\text{C}$ aromatic stretching (lignin), at 1593 for $\text{C}\equiv\text{C}$ alkene stretching, at 1732 for $\text{C}=\text{O}$ stretching vibrations (cellulose), and at 2892 for C-H stretching vibration of methyl and methylene groups (cellulose).

The organic functional groups observed from the FTIR spectra, demonstrated differences between the two types of wood through band intensities (Fig. 20). It was found that particle size was strongly consistent with the final results of EE2 removal; higher particle size ($\leq 2\text{mm}$) had lower number of organic functional groups available.

Table 8: Band assignment of organic functional groups

Band assignment of Raw materials and formulated adsorbents				Functional groups
Wave number cm ⁻¹	Wave number cm ⁻¹	Wave number cm ⁻¹	Wave number cm ⁻¹	
3334.78	3336.08	3347.76	3332.41	O-H Stretching Vibration of alcohol (Lignin)
2921.95	2919.93	2890.51	2892.46	C-H Stretching vibration of methyl and methylene groups-(Cellulose)
1728.34	1728.40	1732.78	1732.14	C=O stretching vibrations (Cellulose)
1640.00	1639.92	1593.65	1593.36	C=C alkene stretching
1509.52	1509.68	1504.85	1505.82	C=C aromatic stretching (Lignin)
1454.61	1453.36	1454.98	1455.82	H-C-H & O-C-H In plane bending (Cellulose)
1424.10	1424.50	1422.10	1422.03	H-C-H & O-C-H In plane bending (Cellulose)
1370.39	1370.76	1370.05	1370.15	C-H in plane bending (cellulose and hemi cellulose)
1263.82	1262.97	1235.49	1235.75	G-Ring stretching vibration (Lignin)
1158.11	1159.07	1157.29	1156.03	S-Ring stretching vibration (Lignin)
1104.11	1104.15	-	-	Aromatic C-H in plane deformation- S-Ring (Lignin)
1053.66	1053.91	-	-	C-C, C-OH, C-H ring and side group vibrations
1030.77	1030.75	1032.54	1031.30	C-H & C-O deformation vibration (Lignin)
-	-	897.43	897.81	C=C stretching vibration (Cellulose)
652.94	664.57	-	-	G-Ring stretching vibration (Lignin)

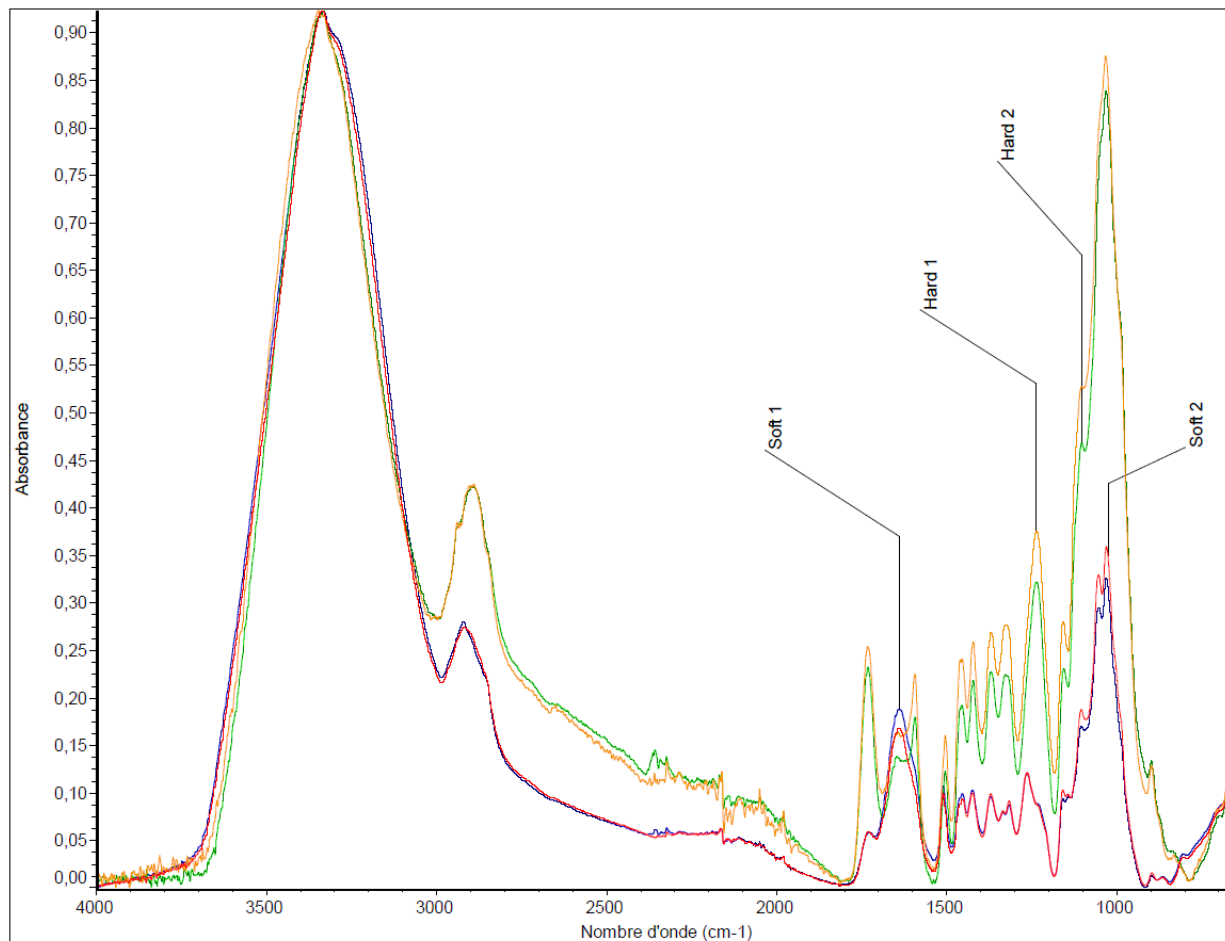


Figure 20: Intensity of organic functional groups on the surface of softwood with particle sizes $\leq 1\text{mm}$ and $\leq 2\text{mm}$ and hardwood with particle sizes $\leq 1\text{mm}$ and $\leq 2\text{mm}$

4.3.2.5. Thermal behavior and mass loss - Thermal Gravimetric Analysis (TGA)

Thermal Gravimetric Analysis (TGA) can show how a material thermally behaves under a range of temperatures. The TG curves, shown in Fig. 21 show the thermal behavior and mass loss of a diverse type of wood with different particle sizes in the temperature range of 29-1000°C. The relative mass loss (TGA) and their first derivative (DTG) curves are presented for both raw wood materials. The difference in percentage of water desorption observed by an endothermic mass loss for both softwood and hardwood (Table 9) can be attributed to the difference in the initial moisture content and particle size. The lower particle size ($\leq 1\text{mm}$) showed the lowest water desorption percentage equal to 1.7% and 0.2% for softwood and hardwood, respectively. In contrast, the higher particle size ($\leq 2\text{mm}$) showed a higher water desorption percentage equal to 4.2% and 3.5%, respectively, for softwood and hardwood. This could be due to the larger particle size of the wood ($\leq 2\text{mm}$) bearing large cavities capable of accommodating higher amounts of adsorbed water from environment, and the capacity to preserve it as a free water in addition to the cell wall bound-water.

The second phase of mass loss observed on the TG curve above 100°C can be associated to the decomposition of organic substances and as well as the desorption of the remaining water at temperatures 175°C and 250°C (Fig. 21). Beyond the desorption of the remaining water, thermal degradation of the main components of the wood occurred beyond the desorption of the remaining water [218, 219]. The hemicellulose fraction was found to degrade at 250°C-350°C for the softwood with particle size $\leq 1\text{mm}$ while the hemicellulose fraction was degraded at 200°C-350°C for the softwood with particle size $\leq 2\text{mm}$ and as well for the hardwood with particle size $\leq 1\text{mm}$ and $\leq 2\text{mm}$. This was followed by the degradation of cellulose at a temperature of 350°C to 410. Above 410°C, lignin started to degrade. The difference between the ranges of degradation temperature for the hemicellulose (250°C to 350°C and 200°C to 350°C) could be attributed to the higher surface area of the wood which can enhance exposure to high temperature.

These observations were supported by the TGA results which showed higher degradation of hemicellulose in softwood (particle size $\leq 1\text{mm}$) in the temperature range of 250°C-350°C compared to the degradation of hemicellulose in hardwood (particle size $\leq 1\text{mm}$) in the range of 250°C-350°C. These observations could be explained by the steam generated and water within the inner body of softwood. Accordingly, the higher moisture content in the softwood compared to the hardwood for both particle sizes showed partial disappearance of the hemicellulose degradation

phases (Fig 21). Thus, the higher moisture content affected mass losses; it showed lower mass losses of 78.2 wt. %, 80.1 wt. % for softwood with particle size $\leq 1\text{mm}$ and $\leq 2\text{mm}$, respectively, compared to mass losses equal to 82.4 wt. % and 82.1 wt. % in hardwood with particle size $\leq 1\text{mm}$ and $\leq 2\text{mm}$, respectively. It seems that the higher ratio of hemicellulose in the softwood, which is the most unstable compound in the wood, may help to protect the most stable compounds (cellulose and lignin) from degradation and loss. This shielding phenomenon helped to reduce mass loss from the softwood. With regard to cellulose and lignin, the obvious effect of moisture content was shown on their degradation. Lignin can be hydrolyzed by cleavage of the ether bonds, which are catalyzed by $[\text{H}^+]$, and $[\text{OH}^-]$ or water molecules [220].

For all TGA tests, there were corresponding increases in wood mass (Table 9). Softwood with particle size $\leq 1\text{mm}$ and $\leq 2\text{mm}$ showed 62.5 wt.% and 54.2 wt.% increase, respectively. However, hardwood with particle size $\leq 1\text{mm}$ and $\leq 2\text{mm}$ showed 47.3 wt.%, 48.7 wt.% increase, respectively. These increases in mass could be attributed to a change in the chemical composition of the wood. The results showed a carbon monoxide content of $\sim 80\text{-}370\text{ g/kg}$ wood and $\sim 14\text{-}25\text{ g/kg}$ wood of methane. This increase in mass can be due to the release these compounds (CO and CH_4) from the surface of the wood during the process (Fig. 21) between 200 to 400°C . Based on the TGA results (Fig. 21 and Tables 9), it was found that hardwood with particle size $\leq 1\text{mm}$ can produce better adsorbent due to its lowest thermal degradation of lignin (32.3%).

Table 9: Mass loss of different types of wood with different particle sizes

Time (min)	T (°C)	Compound degradation	Softwood		Hardwood	
			Particle size		Particle size	
			≤ 1mm	≤ 2mm	≤ 1mm	≤ 2mm
Mass loss %						
4.0	30.2	Water desorption				
8.8	100		1.7	4.2	0.2	3.55
8.8	100	Decomposition of organic substances				
23.8	250		1.71	0.5	0.5	0.39
23.8	250	Thermal degradation of hemicellulose				
33.7	350		31.3	29.2	25.5	20.19
33.7	350	Thermal degradation of cellulose				
39.7	410		61.7	61.6	71.1	71.24
39.7	410	Thermal degradation of lignin				
96.9	983.4		44.4	38.7	32.3	35.5
Total mass loss			140.7	134.3	129.7	130.9
Actual mass loss			78.2	80.1	82.4	82.1
Total deposition of CO and CH ₄			62.5	54.2	47.3	48.7

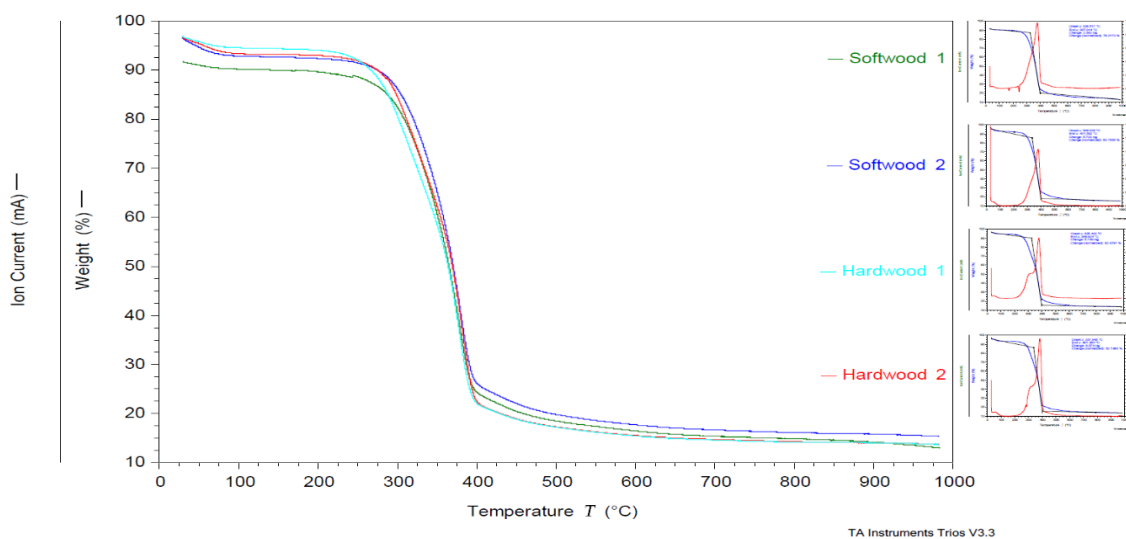


Figure 21: TGA trace of raw materials with particle sizes $\leq 1\text{mm}$ & $\leq 2\text{mm}$

4.3.3. Stage 3: Material property assessment

The properties of the new adsorptive material were assessed by applying various chemical and heat conditions to the wood chips in view of understanding the phenomena underlying the production of good adsorbents for removing the targeted compound from aqueous solutions. Based on the TGA analyses, two pyrolysis temperatures 600°C and 800°C were applied to the softwood and hardwood samples comprising of two different chip sizes. Thus, eight new materials were formulated and used to assess possible correlations between the preparation conditions (applied to produce new adsorbents) and the maximum achievable partitioning of the target compound (EE2) from the aqueous solutions.

4.3.4. Stage 4: Analysis of adsorbent properties

The properties of the eight new adsorbents were analyzed using FTIR, SEM, and BET under a series of pH conditions. Then a comparison was drawn based on the identified properties of parent raw materials.

➤ Zero charge measurements

The zero charge (pH_{zc}) values for the new adsorptive materials generated from softwood or hardwood are shown in Figs. 22 and 23.

The results of pH_{zc} measurements showed non-similar surface charges for the eight formulated adsorbents. This difference in surface charges was attributed to the different thermal degradation extent of the wood components as shown in Tables 9. Below pH_{zc}, the surface charge was found to be positive, but above pH_{zc}, the surface charge was negative.

Based on an extensive literature review regarding the characteristics of the targeted compound (EE2), it was found that the positive surface charge of formulated adsorbent could enhance the EE2 removal from aqueous solutions. At pH between 2 to 9, EE2 mostly exists in a non-dissociated form because the pK_a value of EE2 is 10.7. The most efficient EE2 removal is, therefore, expected when pH of the aqueous phase is higher than pH_{zc}. To support this argument, the surface organic functional groups was analyzed.

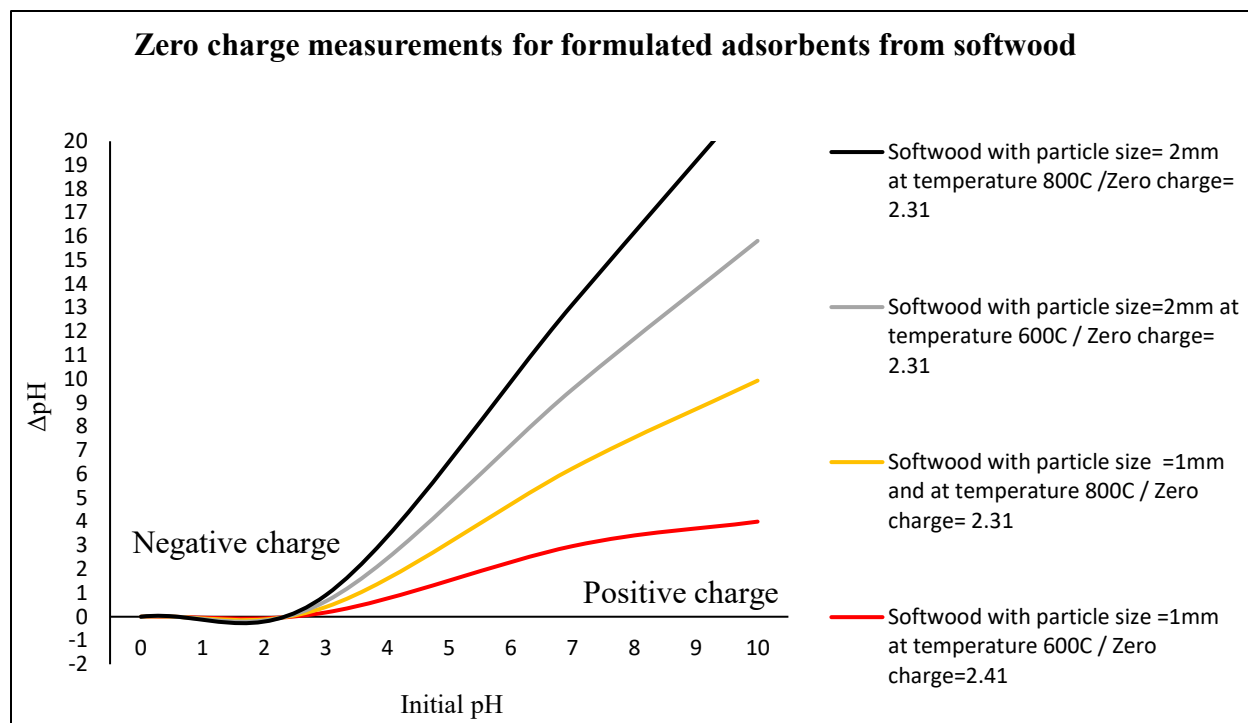


Figure 22: Zero charge measurements for formulated adsorbents from softwood

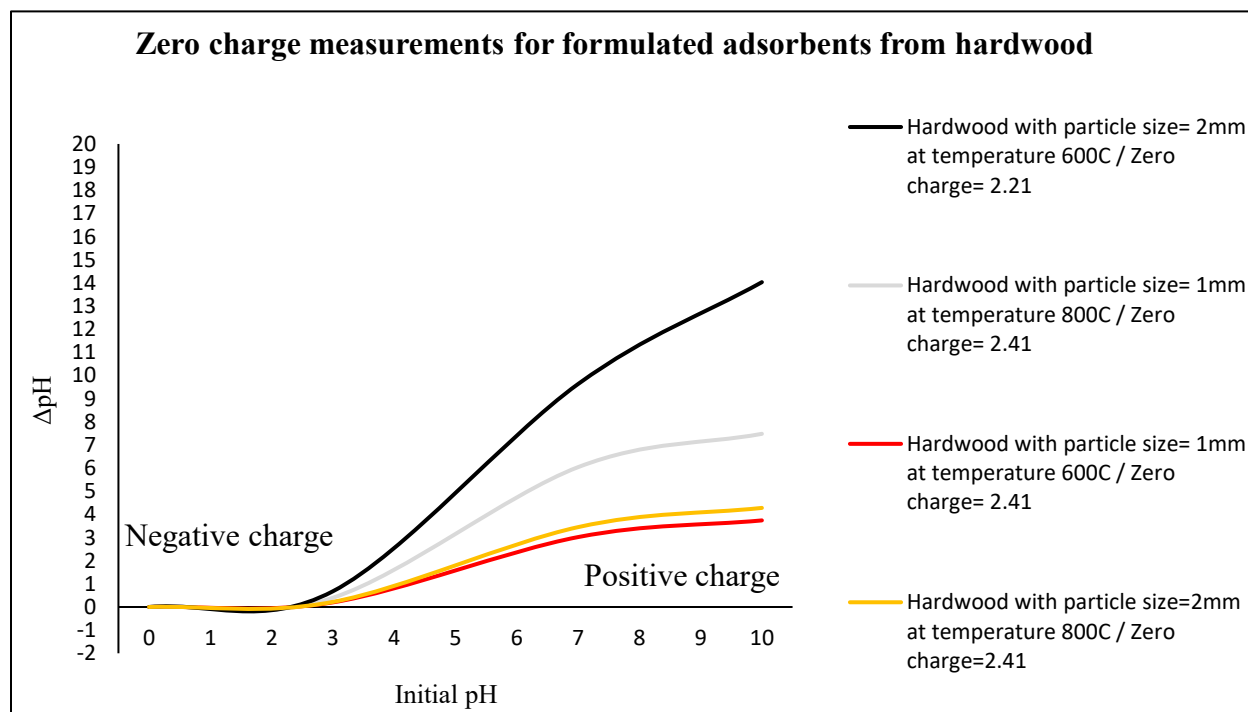


Figure 23: Zero charge measurements for formulated adsorbent from hardwood

➤ **Functional groups analysis - Fourier Transform Infrared Spectrometry**

To analyze the organic functional groups, of the raw materials and the generated adsorbent Fourier Transform Infrared Spectrometry (FTIR) with a resolution of 1 cm^{-1} was used (Fig.24). FTIR analysis allowed investigating potential changes to the wood surface using thermal and chemical treatments as shown in A1-9 to A1-20.

FTIR was applied to the raw materials (softwood and hardwood) and formulated adsorbents at 600°C with particle size $\leq 1\text{mm}$ (Fig.24). About 50mg of each material was individually dispersed in a KBR pellet and subjected to FTIR spectral analysis in the range of 450 to 4000 cm^{-1} .

The results are shown in Fig. 24 and Figs. A1-9 to A1-20, where wave numbers were assigned in accordance with previous studies [221, 222]. It was found that cellulose, lignin and hemicelluloses were present in all samples. Specifically, the bands at $3334, 78\text{cm}^{-1}$ were assigned to O-H alcohol. However, the O-H stretching vibration also occurred in the same region. G-ring (Guaicyl) and S-ring (Syriny) indicated that the samples were as a hardwood in nature. The bands observed around $1263, 1158, 1104, 11053, \text{ and } 1030\text{ cm}^{-1}$ were typical of lignin.

Equally important, it was found that the applied pyrolysis temperature of 600°C helped to establish additional chemical bands on the surface of the hardwood due to a low thermal degradation of lignin as shown at $2500\text{-}2000\text{ cm}^{-1}$ for C-OH groups. Vice versa, it caused a disappearance of the chemical bands of lignin, specifically, between $2500\text{-}2000\text{ cm}^{-1}$. These results together with the findings of the pHzc measurements oriented our focus on adsorbents generated from hardwood because their results were strongly consistent with the final results of EE2 removal. Thus, a large density of functional groups would exhibit a higher EE2 removal from aqueous solutions. Further investigations were carried out by SEM analysis.

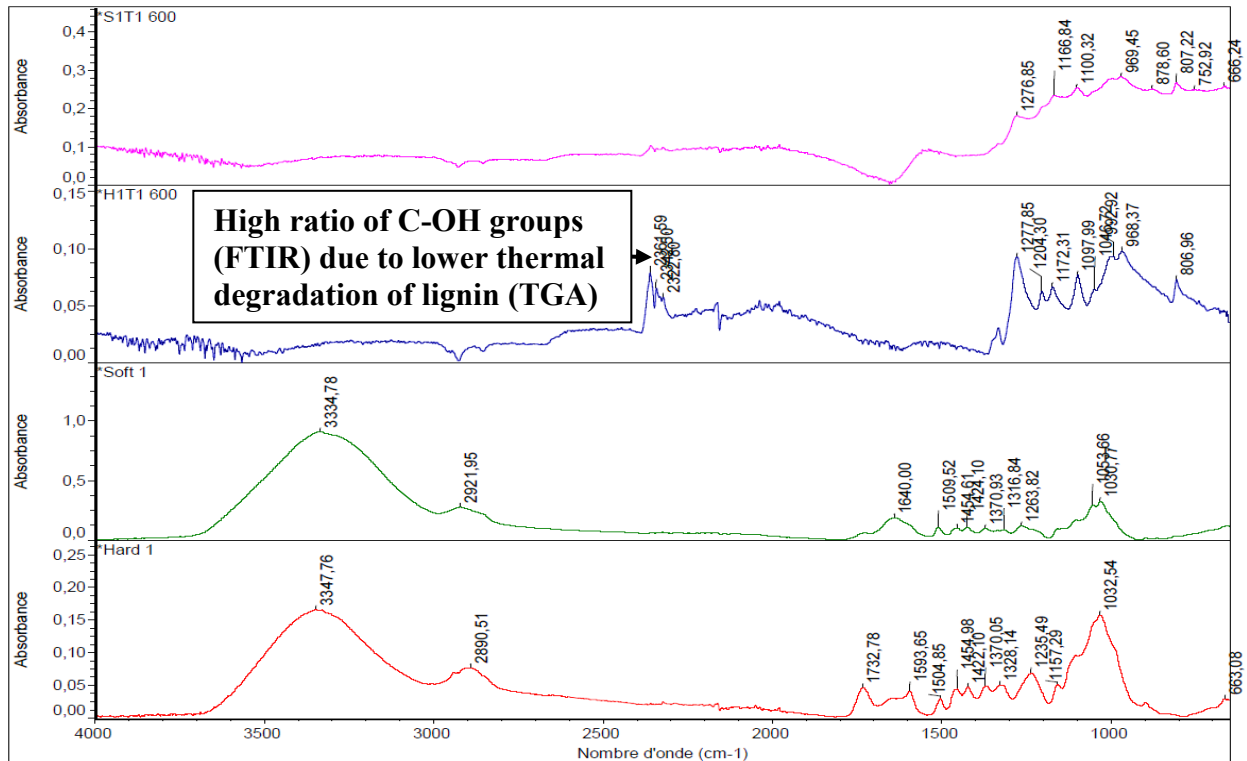


Figure 24: FTIR analysis of raw materials and formulated adsorbents (softwood and hardwood) with particle size $\leq 1\text{mm}$ and $\leq 2\text{mm}$

➤ **Morphology analysis - Scanning Electron - Microscopy images**

SEM images of two types of formulated adsorbents under similar conditions (pyrolysis and particle sizes) were employed to assess differences in topography, morphology, surface texture and porosity after pyrolysis and chemical activation processes. SEM images (Fig. 25) were captured for the formulated adsorbents from: 1. S1T1 before use for EE2 removal; 2. H1T1 before use for EE2 removal; 3. H1T1 after use for EE2 removal. The adsorbent made from softwood with particle size $\leq 1\text{mm}$ had pores along structure (Fig. 25-1). Conversely, the adsorbent made from hardwood with particle size $\leq 1\text{mm}$ showed accumulation of wood particles with no visible pores (Fig. 25-2). The SEM images with respect to morphology are strongly consistent with the final results of EE2 removal, thus, an adsorbent with smaller pores, has higher porosity and number of active surface sites (Fig. 25-3).

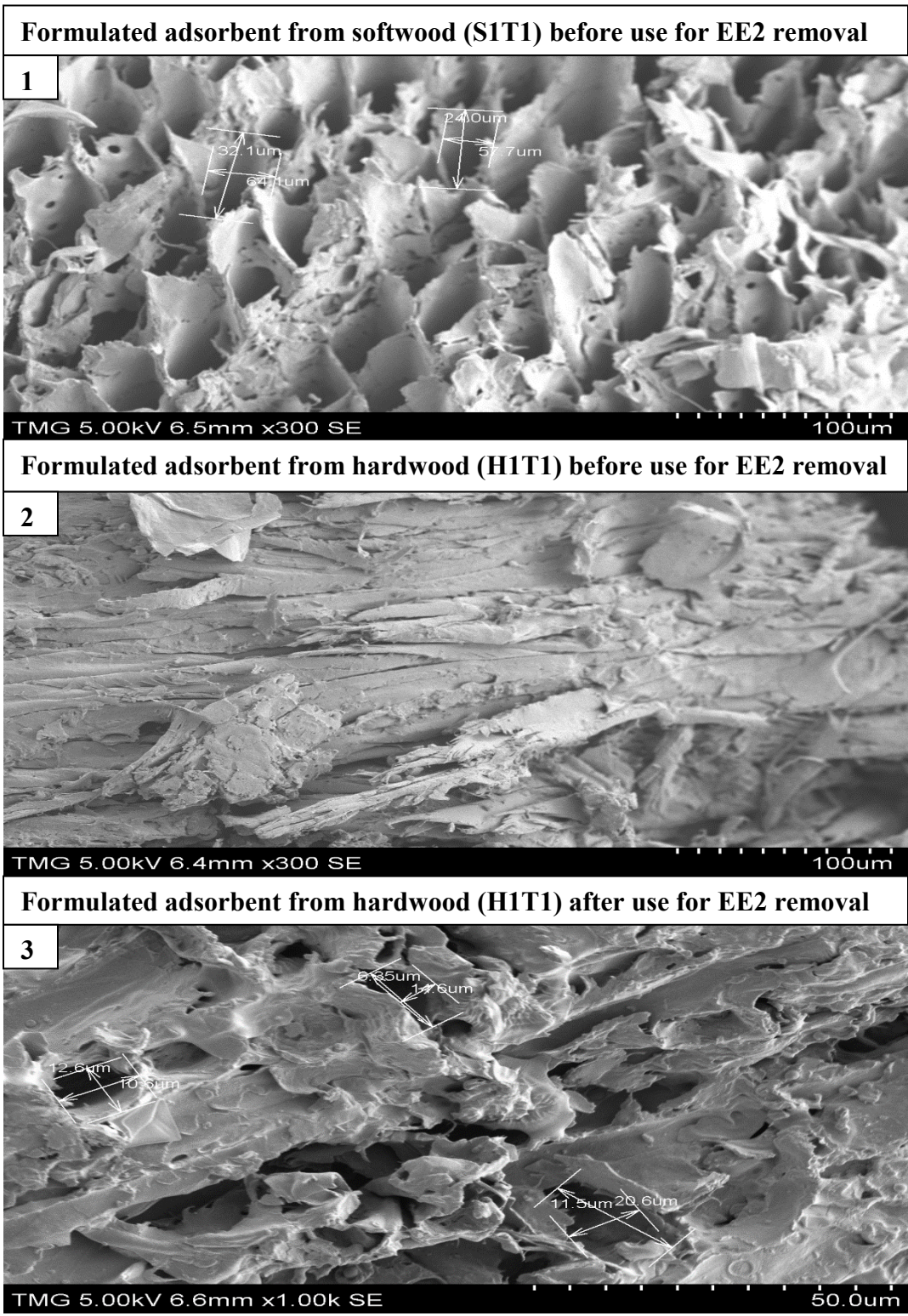


Figure 25: SEM images for formulated adsorbents from: 1. S1T1; 2. H1T1

The SEM images in Fig. 25-3 are for adsorbents after centrifugation at 2700 rpm for 30 minutes; the supernatants were collected from the mechanical shaking of 30mg/L EE2 concentration in an aqueous solution. The SEM images display the morphology of the adsorbent (NAM) used for EE2 removal from the aqueous solution. Shiny spots shown on the adsorbent surface represent EE2 accumulation. The analysis, showed 82% efficiency in the EE2 removal, and this may be due to the presence of a high number of active sites on the adsorbent with small pores. To verify porosity effect, surface area measurements were made.

➤ **Surface area - Brunauer Emmett Teller (BET)**

The results from the BETs test are shown in Table 10. The NAM was found to exhibit a large surface area (5.81m²/g), which is strongly consistent with SEM results and deemed to be advantageous for its application in removing EE2 from aqueous solutions.

Table 10: Surface area of the best formulated adsorbent (NAM)

Types of adsorbent	Sample weight (g)	X sect. area Å²/mol.	Analysis gas	Time (h)	Area (m²/g)
NAM	1.3422	16.2	Nitrogen	3	5.81

Further to the quality assessment of the formulated adsorptive system (phase 3) testing EE2 portioning under different pH, the best obtained results showed 82% of EE2 removal as expected. Henceforth, the development of a new adsorptive system by modifying the functional groups became the objective to enhance the EE2 removal. For this reason, chitin was used to upgrade the formulated adsorptive system.

4.4. Results from phase 2: Preparation procedures - Upgraded adsorptive system

Upgraded adsorptive system (ENAM) was generated by combining the best individual formulated adsorbent (NAM) with chitin. Chitin is the second source of the waste material used to enhance the best formulated adsorbent from the first source of the waste material (wood). The results of the manufacturing procedure were divided into two stages to fully demonstrate the contribution of chitin: 1. Material preparation; 2. Adsorbent properties.

4.4.1. Stage 1: Material preparation

This section includes the results from particle size assessment, thermal behavior and mass loss-thermal gravimetric analysis.

➤ Particle size assessment

Particle size assessment of chitin was done using a Laser Scattering Particle Size Distribution Analyzer- LA-950 (Horiba). The results are shown in Fig. 26.

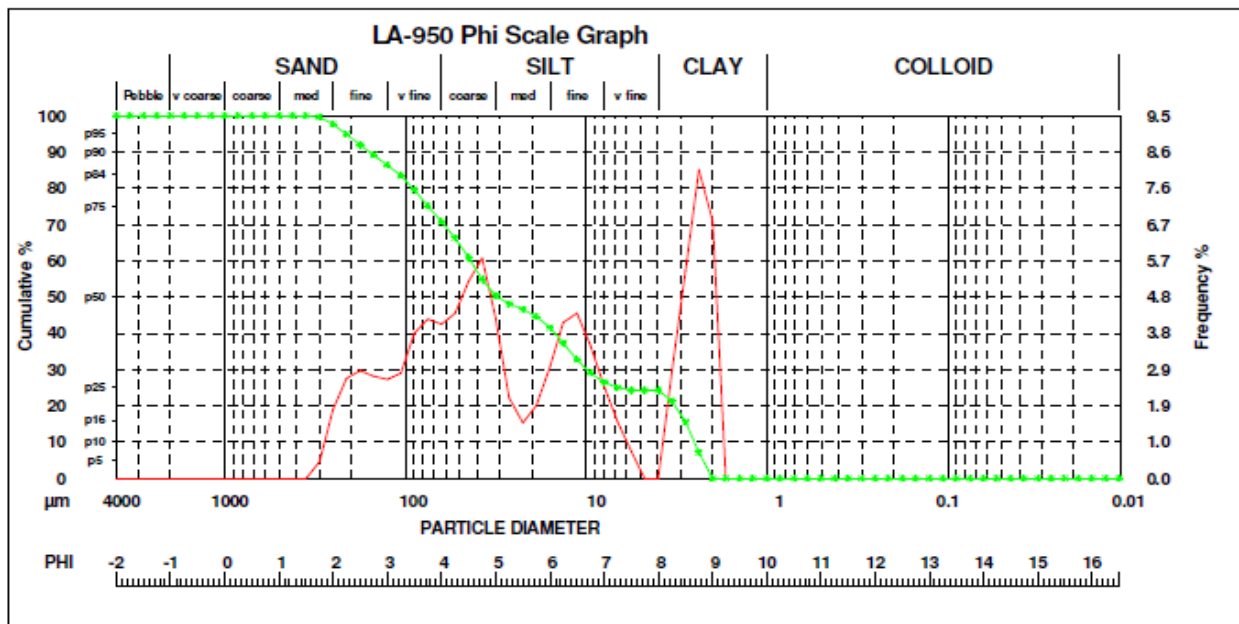


Figure 26: Particle size assessment of chitin

Fig. 26 showed that chitin has Mean Size= 54.21790(μm), Variance= 4440.6(μm^2), Std. Dev.= 66.6375(μm), and Mode Size= 2.4260(μm), Span= OFF, Geo. Mean Size= 22.1474(μm), Geo. Variance= 2.6678(μm^2), Skewness= 1.7329, Kurtosis= 5.5142, and Diameter on Cumulative %= (1) 5.000 (%)- 2.2244 (μm) and (9) 90.00 (%)- 157.0602 (μm). This information helped to generate information regarding the surface area of chitin, considering that small particle size has a higher surface area.

➤ **Thermal behavior and a mass loss - Thermal Gravimetric Analysis**

Thermal Gravimetric Analysis (TGA) can show how a material thermally behaves under a range of temperatures (30-1000°C) (Fig. 27). The mass loss of the chitin varied between water desorption and compounds degradation. For example, in the temperature range of 100°C-250°C, the chitin lost was 0.21% of its weight as indicated in the decomposition in the band O-H and N-H. This was the lowest loss in mass observed as shown in shown in the Table 11.

Table 11: Mass loss of chitin shown by TGA

T (min)	T (°C)	Compound degradation	Mass loss% of chitin
4	30.2	Water desorption	0.5
8.9	100		
8.9	100.1	Decomposition of O–H and N–H	0.21
23.870	250		
23.879	250.1	Thermal degradation of amide I	39
37.80	390		
37.81	390.1	Thermal degradation of amide II	72
43.78	450.		
43.79	450.1	Thermal degradation of C-O-C in the glucose ring	36
96.98	982.9		
Total mass loss			82.5

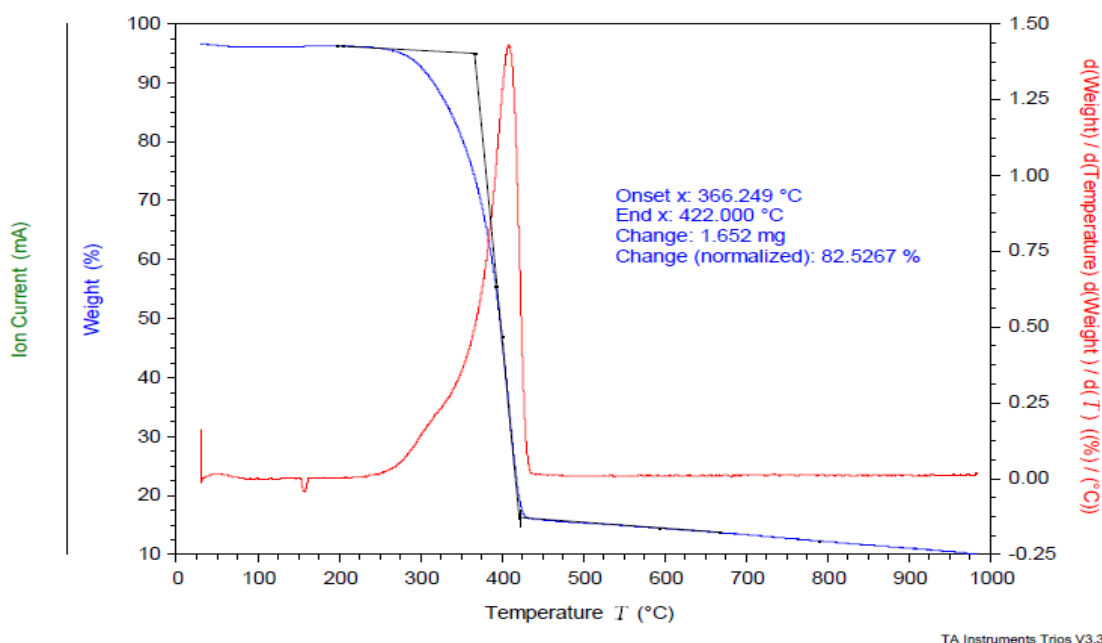


Figure 27: TGA trace of chitin

4.4.2. Stage 2: Adsorbent properties

This section includes the results from zero charge measurements, organic functional groups analyzed by Fourier Transform Infrared Spectrometry, morphology analysed by Scanning Electron-Microscopy images, and surface area of adsorptive material measured by Brunauer Emmett Teller method.

➤ Zero charge measurements

Adsorption property, such as zero charge (pH_z) for chitin was analyzed under six pH conditions (2-12), where the aqueous solution's pH was adjusted with HCl and NaOH. Statistical analyses were performed for these measurements to find a zero charge of the adsorbent (Fig. 28).

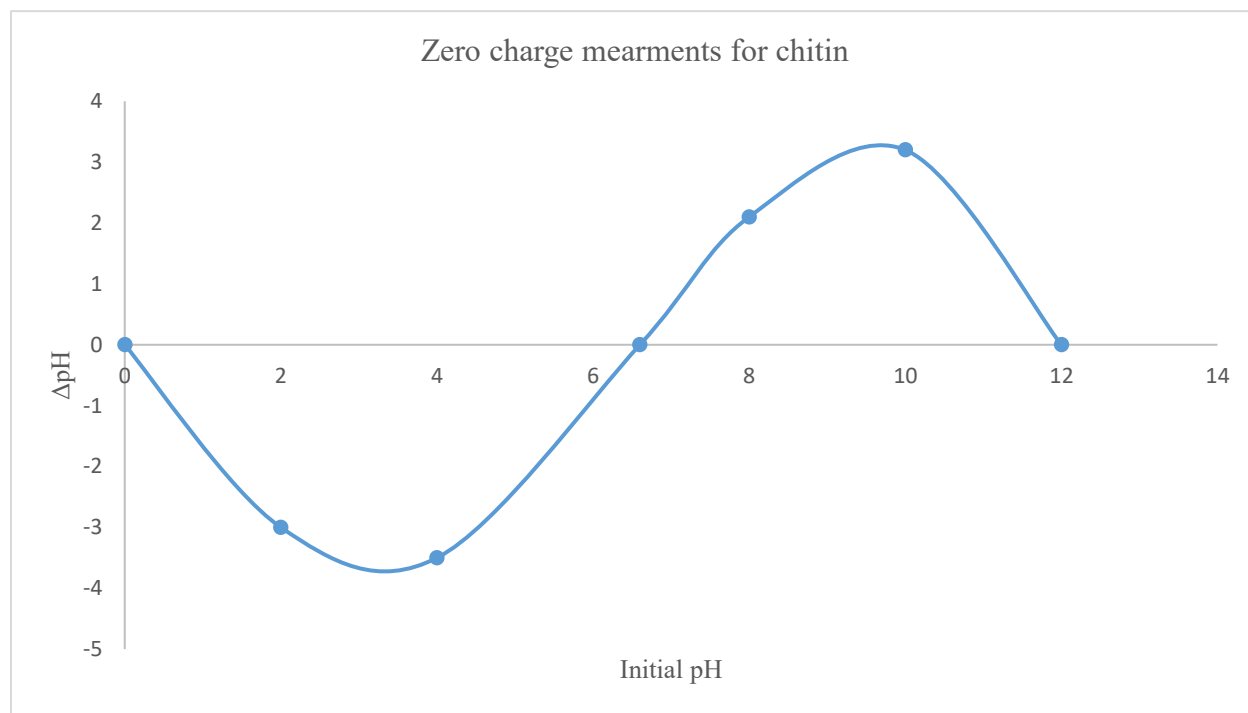


Figure 28: Zero charge measurements for chitin

Fig. 28 shows that the zero charge of the adsorbent was around 6.6. Below pHzc (6.6), the surface charge was positive and above pHzc (6.6), the surface was more negative.

The findings of this study, which are in agreement with previously published data, confirmed that the positive charge of the formulated adsorbent enhanced the EE2 removal from the aqueous solutions. To emphasize, at pH from 2 to 9, EE2 is mostly in a non-dissociated form because the pKa value of EE2 is 10.7. The best removal capacity of EE2 can be achieved when the pH of the aqueous phase is higher than pHzc. To support these findings, a functional group analysis was conducted.

➤ **Functional groups analysis - Fourier Transform Infrared Spectrometry**

The results of FTIR on chitin samples are shown in Fig. 29. The main bands in their spectra are shown in Table 12. The band of amide II had a higher intensity than the band of amide I that proposes an efficient deacetylation (Fig. 29). The increase in the intensity of amide II band indicates to NH₂ formation groups [223].

Amide bond is often referred to as a peptide bond and consists of two amino acids linked together by an amide bond. Amide I and amide II bands were the two major bands of the chitin infrared spectrum. The amide I band (between 1600 and 1700 cm⁻¹) is mainly associated with the C=O stretching vibration with a high percentage and represented the most intense absorption band. It is primarily governed by the stretching vibrations of the C=O and C-N groups.

Amide II results from the N-H bending vibration with medium percentage and from the C-N stretching vibration with a low percentage. It is more complex than amide I. Amide II is mainly derived from in-plane N-H bending. The rest of the potential energy arises from the C-N and the C-C stretching vibrations.

Because both the C=O and the N—H bonds are connected through hydrogen bonding, the locations of both the Amide I and Amide II bands are sensitive to the secondary structure content of chitin. Therefore, these bands are considered very important in chitin beside O—H and N—H stretching vibration of alcohol, -H the asymmetric and symmetric stretching vibrations of -CH groups

because they rendered the chitin a good adsorbent compared to wood. Thus, synthetic adsorbent made from wood can be impregnated with chitin to increase the adsorption capacity.

Table 12: FTIR band assignment of chitin

Wave number cm^{-1}	Band assignment
3000-3500	O—H and N—H Stretching vibration of alcohol
2876.54	-H the asymmetric and symmetric stretching vibrations of -CH groups
1652.12 and 1620.30	amide I (Intensive double absorption bands)
1552.80	amide II (isolated band)
1112.86-1427.95	the special β (1-4) glycosidic bond in the polysaccharide unit
688.67-1066.44	the stretching of C-O-C in the glucose ring

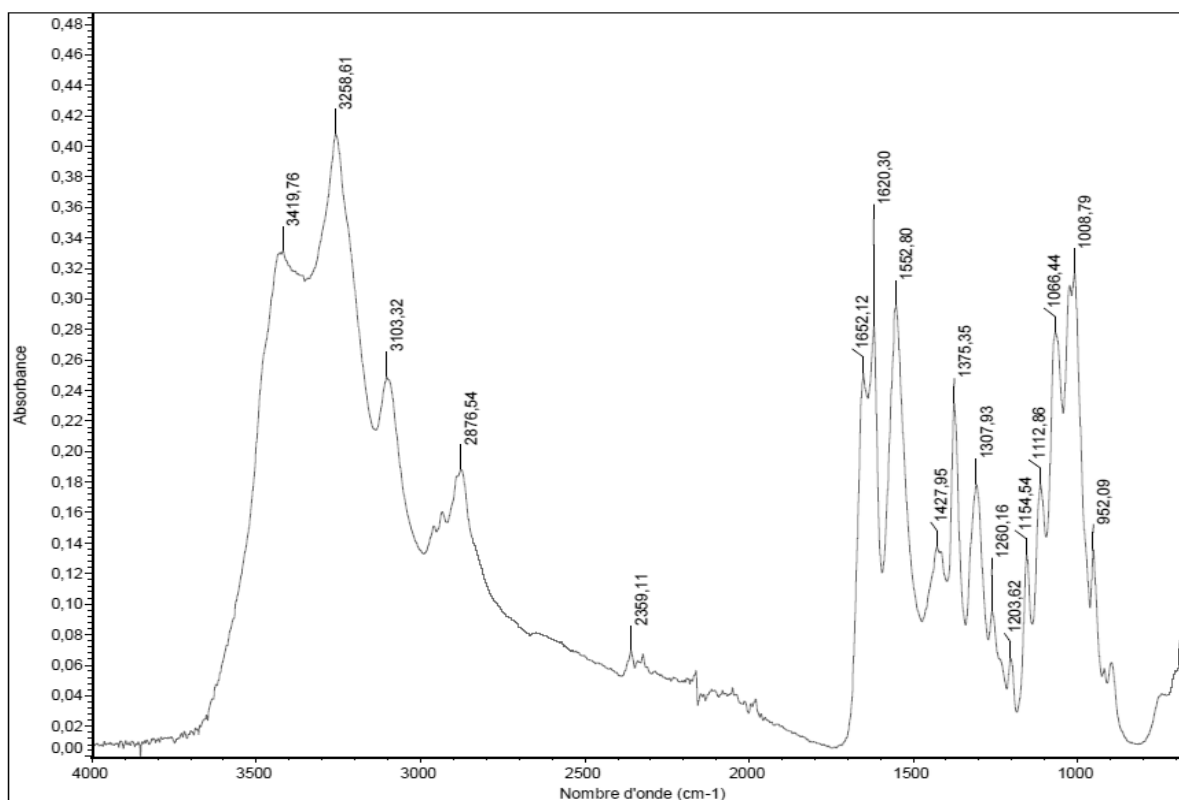


Figure 29: FTIR spectra of chitin

➤ **Morphology analysis - Scanning Electron-Microscopy images**

Raw chitin seems to be a material with non-significant pores (Fig. 30). However, small-sized particles enabled generating a matrix with a high surface area. The SEM images with respect to porosity and surface area are strongly consistent with the final results of EE2 removal.

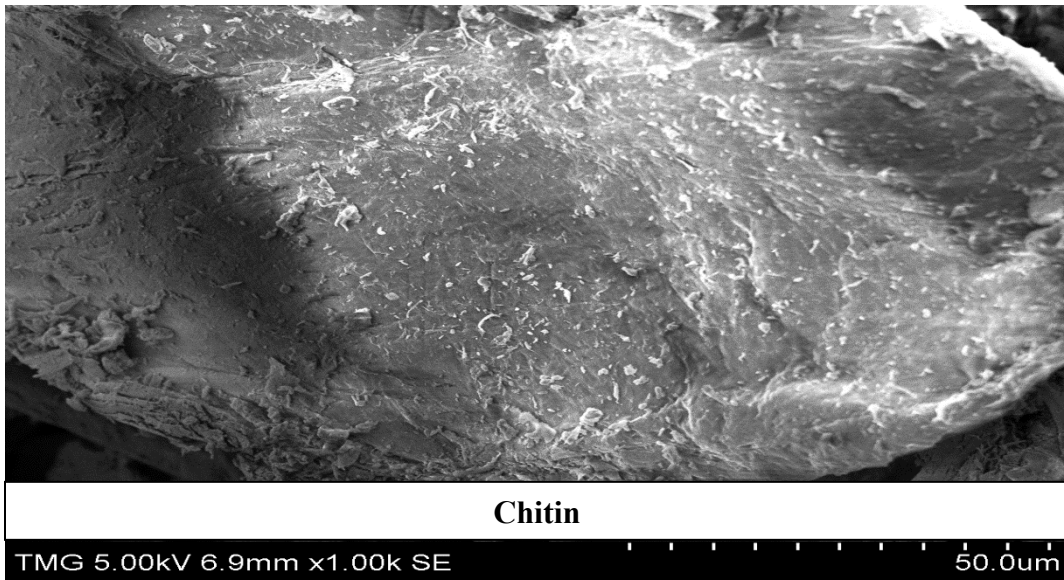


Figure 30: SEM image of chitin before use for EE2 removal

➤ **Surface area of adsorptive material - Brunauer Emmett Teller (BET)**

The results of the BET test on the adsorptive material, are shown in Table 13, and include details on adsorbent weight, cross-section area, gas, equilibrium time and surface area.

BET results showed that chitin had a very high surface area ($4.67\text{m}^2/\text{g}$), comparable to the NAM material. Thus, it is expected to be advantageous for removing EE2 from aquatic solutions.

The surface area of the upgraded adsorptive system ENAM was expected to be a very high surface due to the combined large surface areas of NAM and chitin.

Table 13: Surface area for chitin and the upgraded adsorptive system (ENAM)

Types of adsorbent	Sample weight (g)	X sect. area $\text{\AA}^2/\text{mol}$.	Analysis gas	Time (h)	Area (m^2/g)
NAM	1.3422	16.2	Nitrogen	3	5.81
Chitin	0.139	16.2	Nitrogen	3	4.67
ENAM	As a combination between surface areas of NAM with chitin				Expected too high

An efficiency assessment (phase 3) of the formulated adsorptive system made from a mixture of NAM and chitin (ENAM) was conducted by a series of tests where different pH conditions were applied to find the best partitioning of EE2 from water. The results showed that the system had a very good EE2 removal efficiency (92%). To achieve the objective of 99% removal, a new system was proposed. This involved the development of a novel electro-adsorptive system (phase 4). It was assumed that this system, due to complexity of phenomena, affected both the removal target compound and adsorptive particles from aqueous solutions leading to generation of a clear effluent.

4.5. Results from phase 3: Experimental protocol - Quality assessment

The experimental protocol included possible combinations of parameters to reach the final conclusion. In phase 1, eight types of adsorbents were formulated; however, it was unknown which one was the best for the target compound adsorption. In phase 2, the upgraded adsorptive system was formulated, but its performance was unknown regarding EE2 removal. Therefore, in phase 3, the experimental protocol was designed to assess efficiency of the formulated adsorbents.

4.5.1. Stage 1: Sorption kinetics and equilibration time

Sorption kinetics and equilibration time for the partitioning of EE2 from aquatic environments were done using both types of new adsorptive materials made from softwood and hardwood (Figs. 31 and 32).

Based on a series of tests, material H1T1 (hardwood expose to 2-hour retention time) was found to be the most efficient. The maximum removal capacity from these tests was 47% under a pH of 7 as shown in Fig.32. EE2 removal under other conditions ranged from 17% to 44%; such low removal capacities could be due to the low dosage of the adsorbent (20g/L) or to the high initial concentration of EE2 (30mg/L), which may have induced competition of the EE2 molecule to reach the active sites present on the adsorbent surface. As revealed by these results, the second objective of this work was to understand the evaluation of the correlation between the eight formulated adsorbents with the maximum achievable partitioning of EE2 from aqueous solutions, considering the adsorptive material type and manufacturing conditions, such as effect of pyrolysis temperature effect and particle size. For example, a significant difference between 47% EE2 removal using H1T1 and H2T1 with 17% EE2 removal was found. This was confirmed by FTIR and TGA analyses (FTIR, A1-11 and A1-12, TGA, Table 9) which showed that H1T1 had a high amount of C-OH functional groups due to a high amount of lignin or/and a low thermal degradation of lignin (32.3%). Furthermore, when the particle size was higher ≤ 2 mm, which offers higher thermal degradation of lignin by heat, a lower number of functional groups and surface area was found. In addition, due to a hard access to advanced equipment and equipment sensitivity, limited repetition tests were conducted with not enough data for statistical analysis. Thus, experimental errors are displayed on all graphical representations and ranged from 5% to 10%.

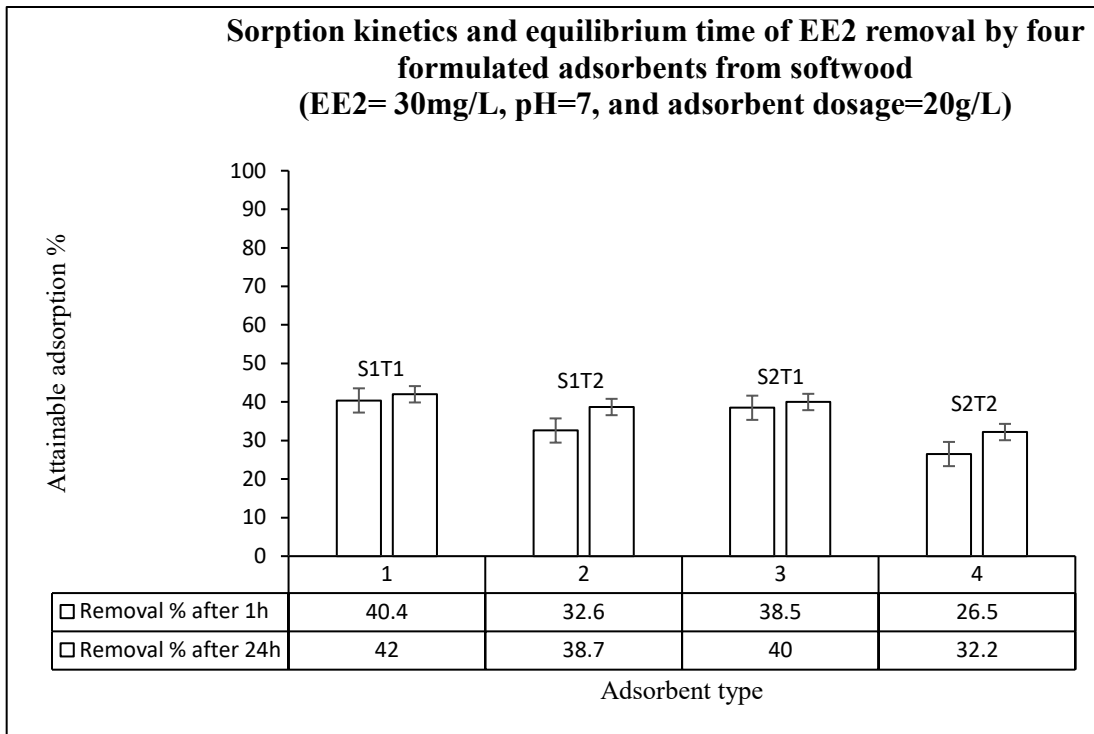


Figure 31: Sorption kinetics and equilibration time of EE2 removal by formulated adsorbents from softwood

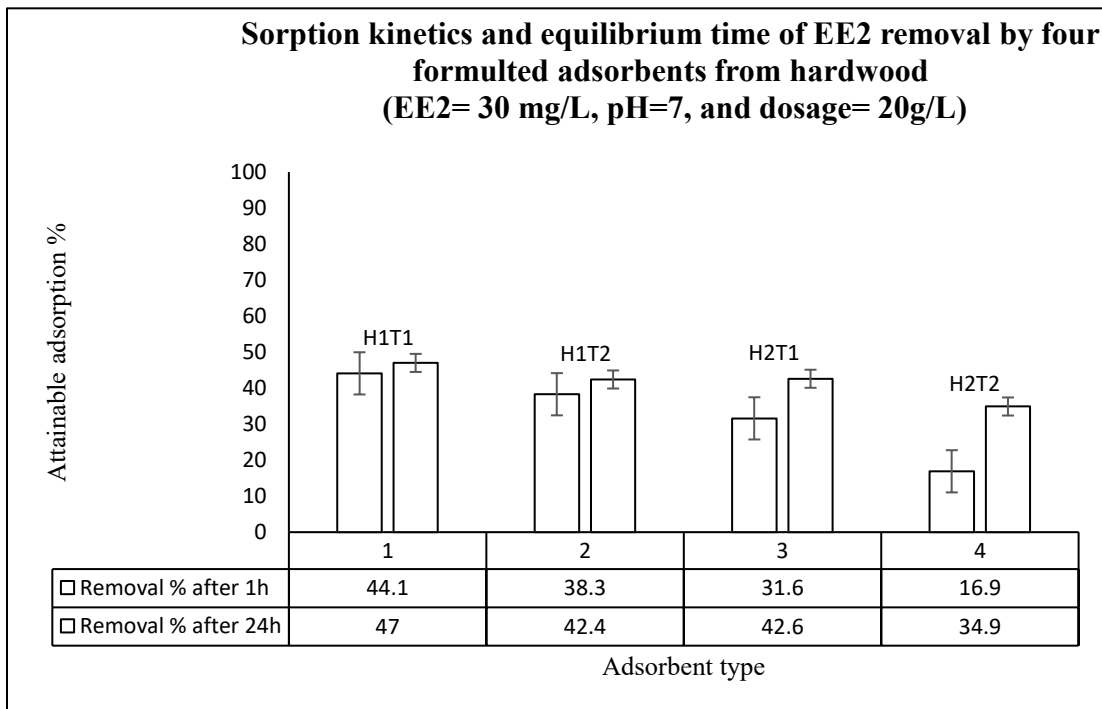


Figure 32: Sorption kinetics and equilibration time of EE2 removal by formulated adsorbents from hardwood

4.5.2. Stage 2: Sorption capacities

A series of tests was performed under constant conditions of pH =7, time =1h, and temperature = 25°C to assess the response of EE2 adsorption to change in its initial concentration, namely 30, 48, and 50 mg/L.

The results showed that H1T1 (hardwood material precursor with 1-hour exposure time to adsorption) had the highest adsorption capacity of 50% of EE2 removal when EE2 concentration in the aqueous solution was 50mg/L (Fig. 33). The increase in the removal capacity of EE2 from 47% (Fig. 32-EE2=30mg/L) to 50% (Fig. 33-EE2=50mg/L) was attributed to the presence of a higher amount of solute adsorbed to the solid phase at equilibrium compared to 30mg/L of EE2.

Isotherms models of EE2 adsorption were generated for the following formulated adsorbents: S1T1, S1T1, S2T1, S2T2, H1T1, H1T2, H2T1, and H2T2, to describe the adsorption distribution on their surfaces (Figs. 34- 41).

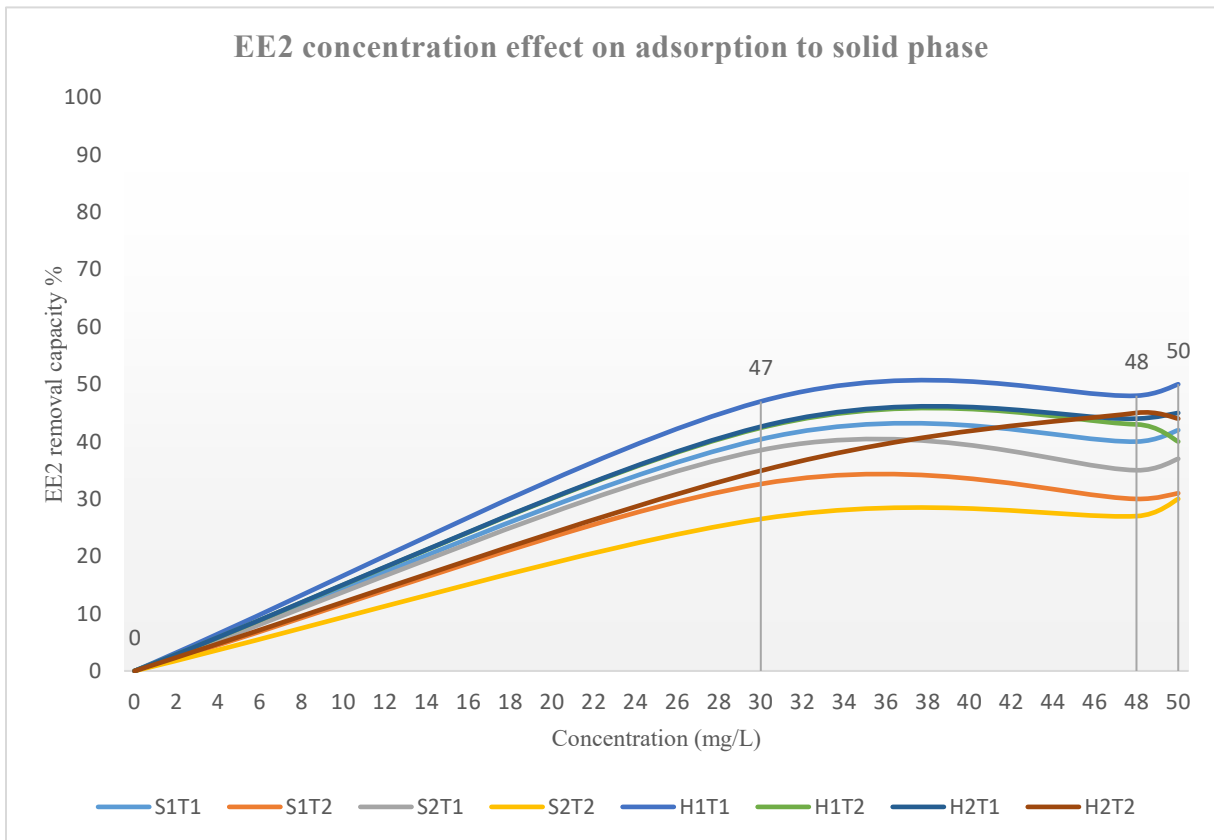


Figure 33: Adsorption capacity by eight formulated adsorbents

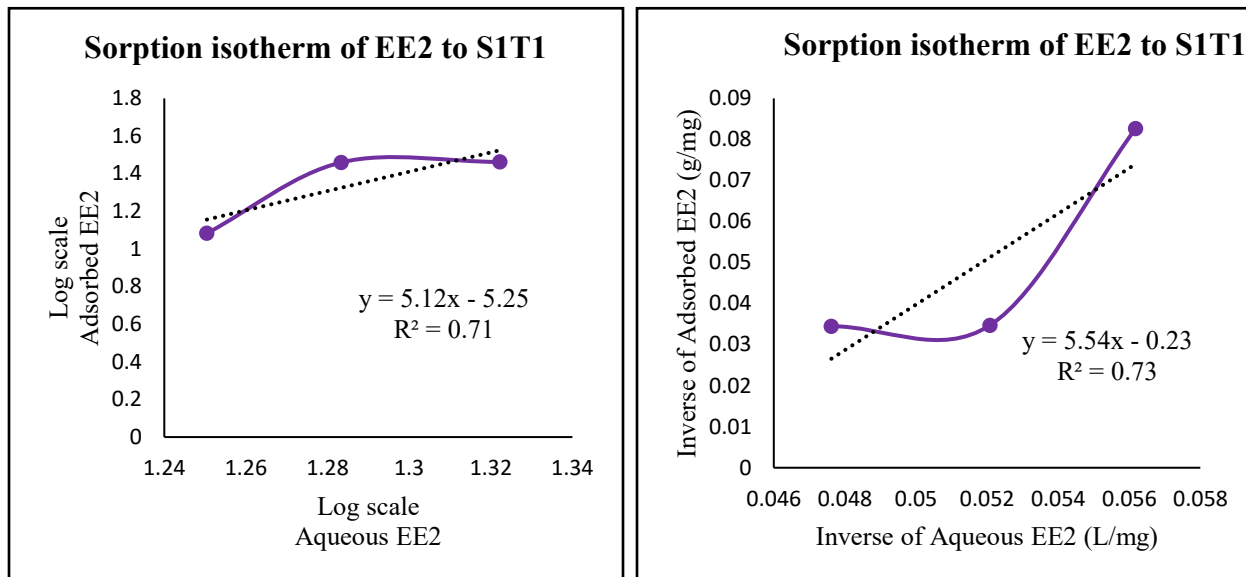


Figure 34: Freundlich and Langmuir isotherm models of EE2 sorption using S1T1

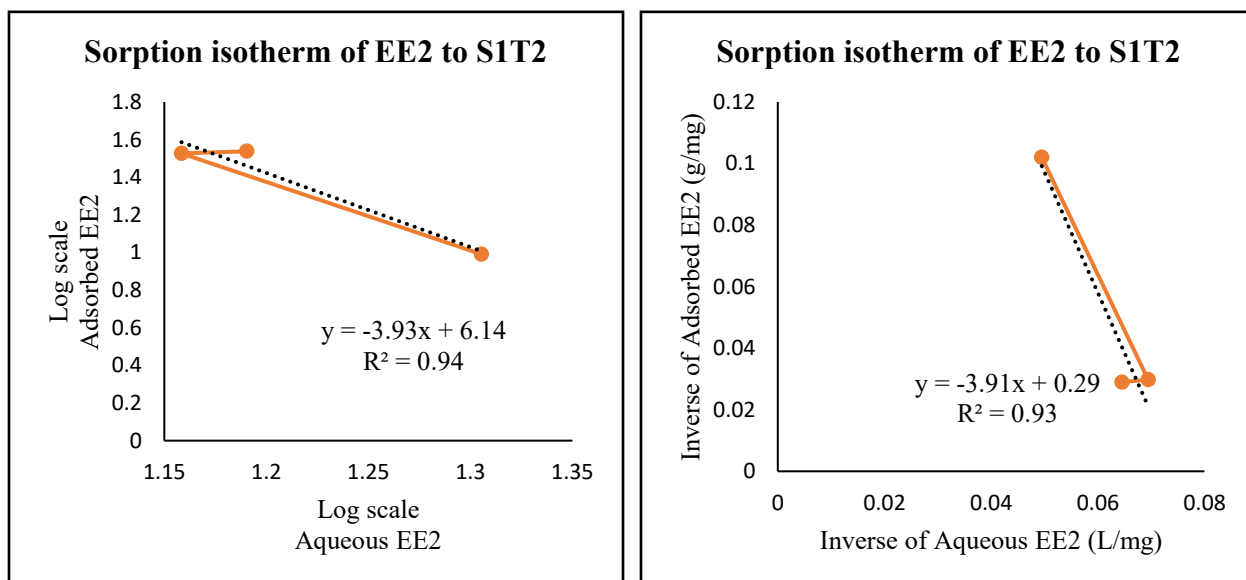


Figure 35: Freundlich and Langmuir isotherm models of EE2 sorption using S1T2

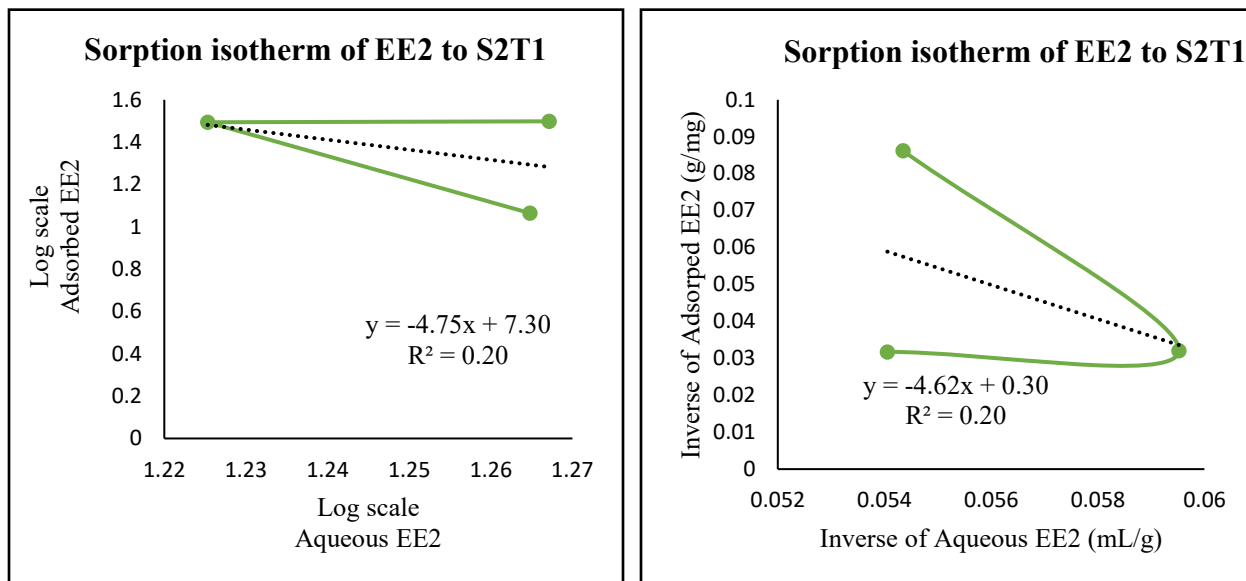


Figure 36: Freundlich and Langmuir isotherm models of EE2 sorption using S2T1

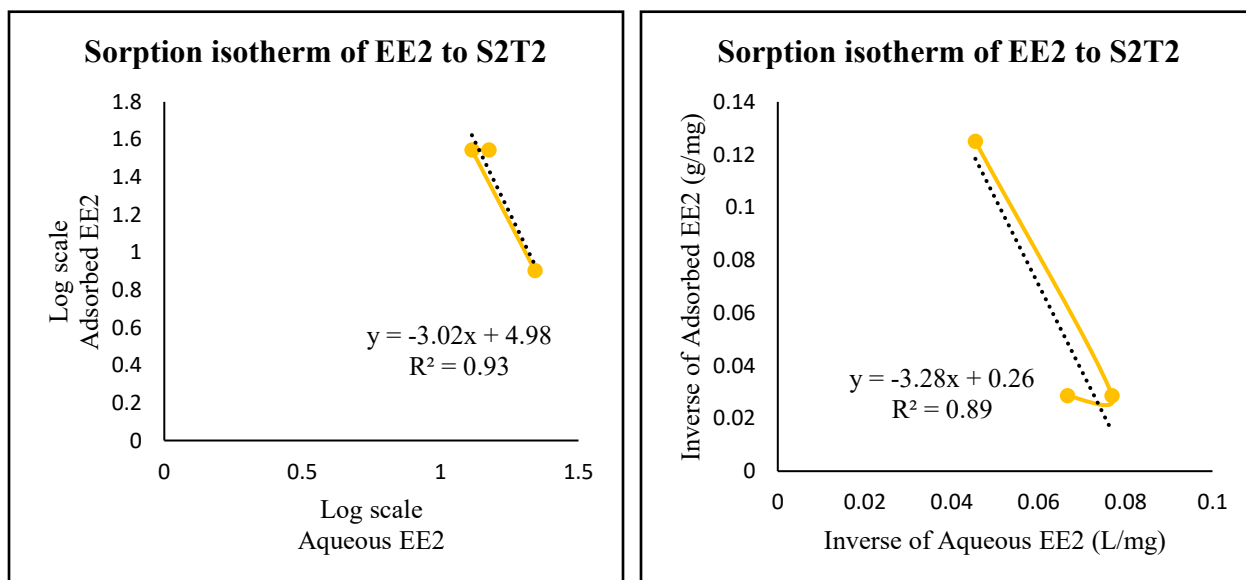


Figure 37: Freundlich and Langmuir isotherm models of EE2 sorption using S2T2

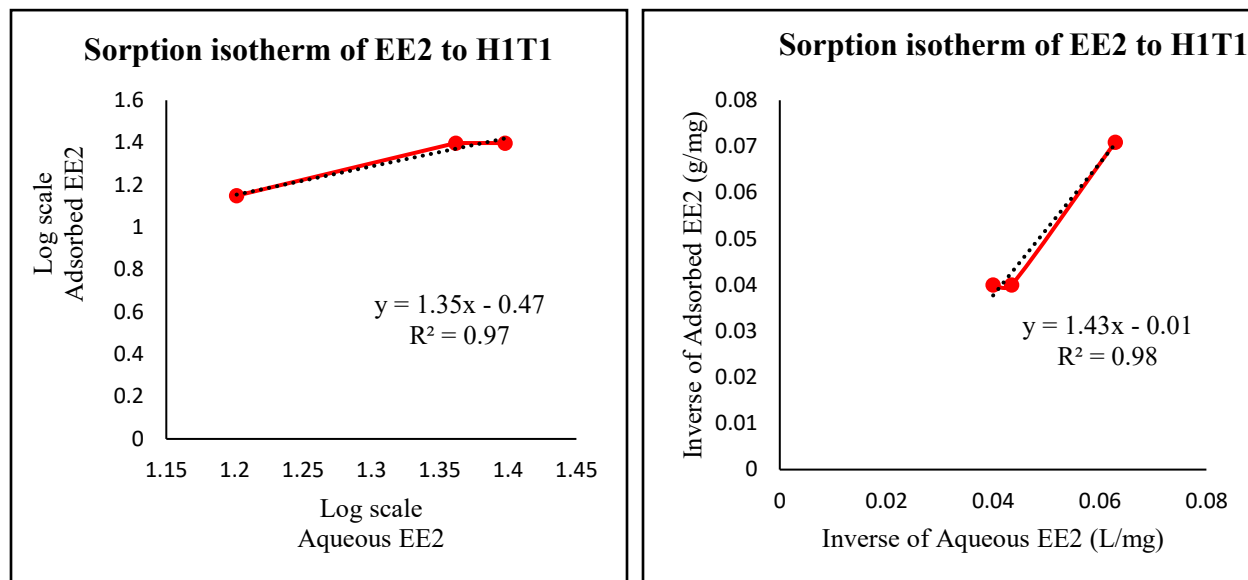


Figure 38: Freundlich and Langmuir isotherm models of EE2 sorption using H1T1

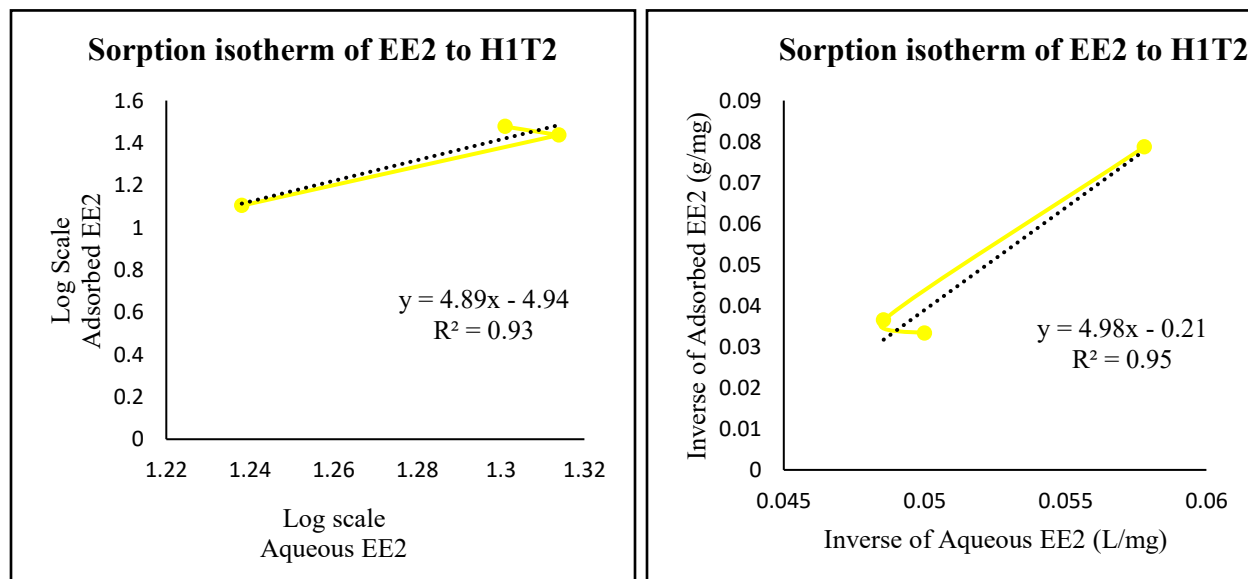


Figure 39: Freundlich and Langmuir isotherm models of EE2 sorption using H1T2

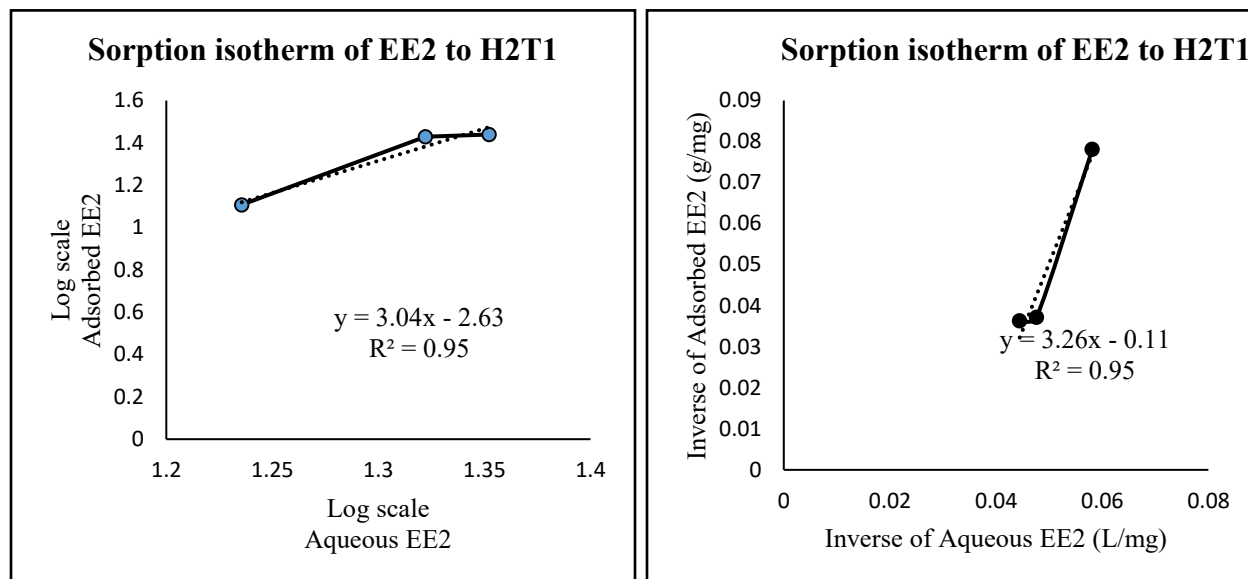


Figure 40: Freundlich and Langmuir isotherm models of EE2 sorption using H2T1

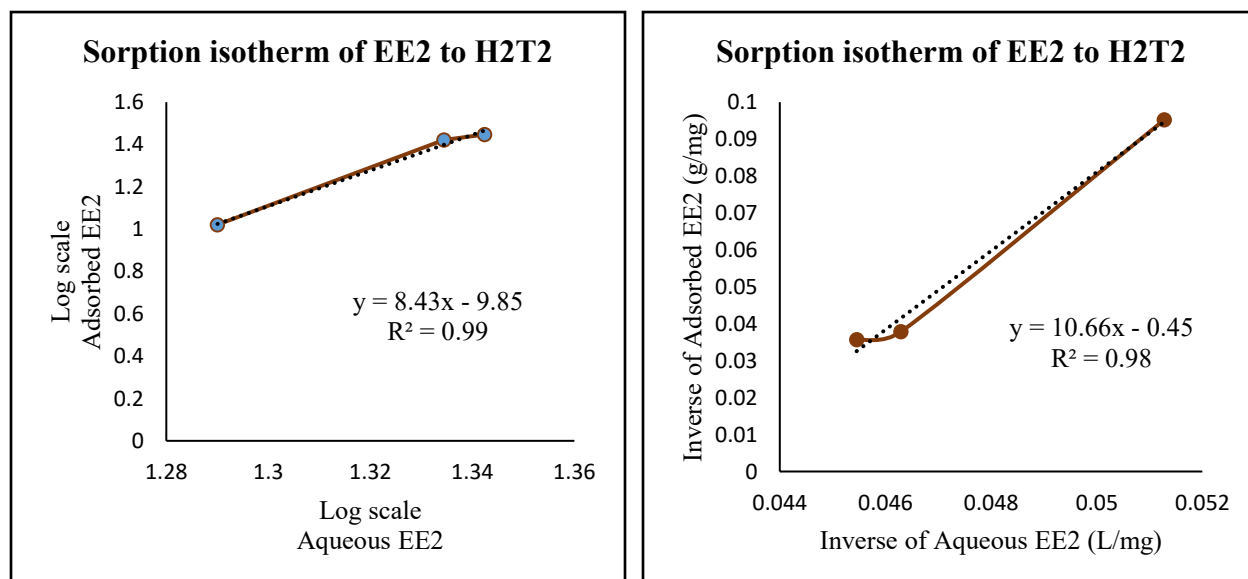


Figure 41: Freundlich and Langmuir isotherm models of EE2 sorption using H2T2

The study found that Freundlich and Langmuir isotherms were the best models describing the adsorption distribution on the surfaces of the formulated adsorbents. Freundlich represents non-uniform multilayer and heterogeneous adsorption distribution on the surfaces, whereas, Langmuir isotherm involves uniform monolayer adsorption distribution on the surfaces and removal of the interactive effects of the adsorbate molecules.

This study demonstrated that the best data fit of adsorbate EE2 mg/L to the formulated adsorbent H2T2 for both Freundlich and Langmuir isotherm models ($R^2=0.99$ and 0.98 , respectively) as shown in Fig. 41. However, that was not enough to infer that H2T2 was the best formulated adsorbent among the eight formulated adsorbents. For example, H1T1 showed better properties by FTIR and TGA analyses. In addition, H1T1 showed better adsorption capacity under equilibrium time, different concentrations, different pH, and as well displayed $R^2=0.97$ and 0.98 , respectively for Freundlich and Langmuir isotherm models. In addition, H2H2 consumed more energy during the pyrolysis process. Simultaneously, these models provide evidence that the formulated adsorbents have large surface areas with high active site densities, contrary to S2T1 which showed $R^2=0.20$ for Freundlich isotherm models.

4.5.3. Stage 3: PH effect

The pH values (2, 5, 7, and 10) of the aqueous environment affected the adsorption capacity of the adsorptive systems with respect to EE2 (Fig. 42). The zero charge values of the formulated adsorbents were measured before conducting the tests because they had a strong effect on the adsorption capacity. It was assumed that the surface charge of the formulated adsorbents could be negative if the pH was below the zero charge and positive if the pH was above the zero charge. The uptake of EE2 was highly related to the initial pH of the solution, which in turn influenced the surface properties of the adsorbent and ionization of the EE2. Under those circumstances, it was observed that the adsorption capacity increased when the aqueous pH increased. Among the eight formulated adsorbents, the highest removal capacity (82 %) was found in the case of H1T1 at pH= 7-10 while the lowest adsorption capacity (42-46%) was identified for S2T2 at pH= 7-10. The observed phenomenon can be attributed to the following reasons: 1. Adsorbent properties: i) Lower initial moisture content of H1T1; ii) Higher surface area of H1T1; iii) Higher active sites on the H1T1 surface; iv) Lower lignin degradation on H1T1 surface due to lower pyrolysis

temperature 600°C; or 2. EE2 behaviour in the aqueous environment: i) At pH ranging from 3 to 9, EE2 is essentially in non-dissociated form because of the pKa value of EE2 is 10.7; ii) The higher adsorption capacity at pH<2 may also be partially related to non-competition of H⁺ adsorption which increased the adsorption of EE2 on the adsorbent.

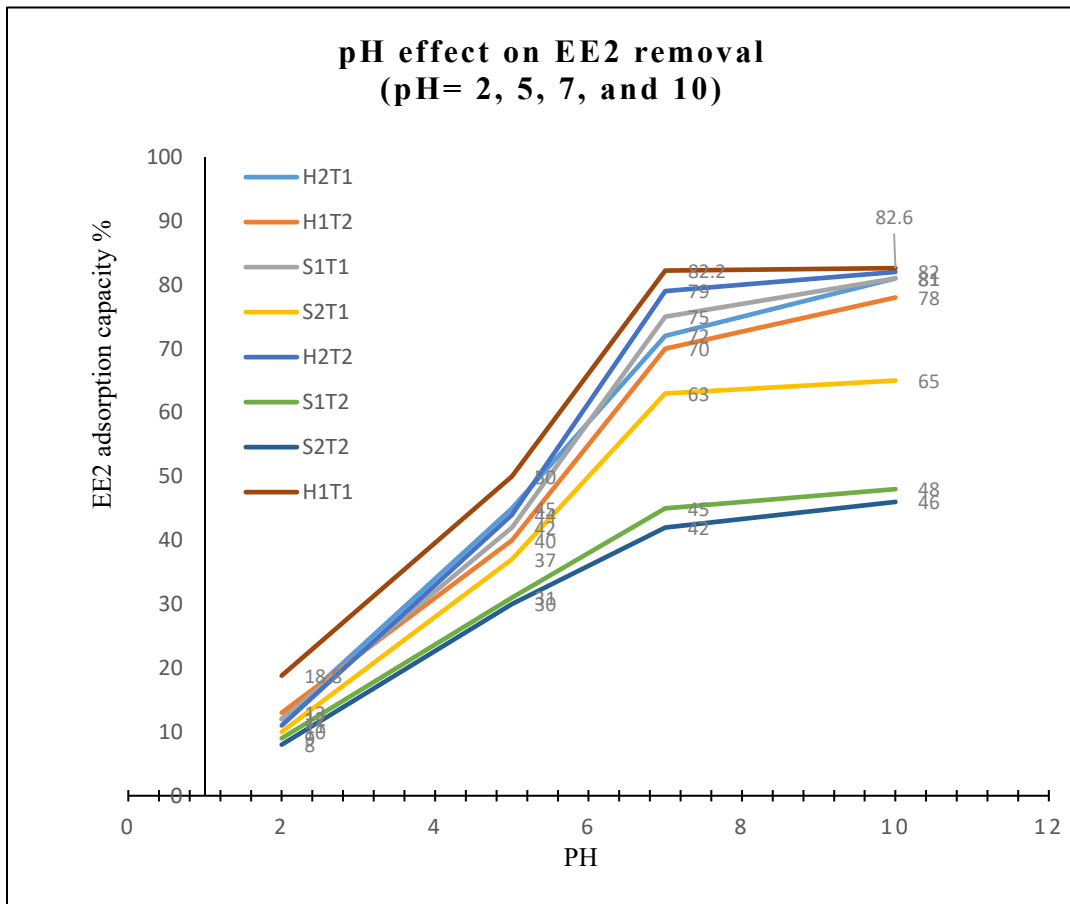


Figure 42: pH effect on EE2 adsorption capacity by eight formulated adsorbents

4.5.4. Results from pH effect on upgraded adsorption system (ENAM)

The results from phase 3 showed the maximum removal of EE2 at pH = 7-10 by 82% (43) using the best adsorptive sample (H1T1) produced from waste material (wood chips). However, the new material did not achieve the project objective, which was set as over 99% removal efficiency of EE2. Therefore, in phase 2, an upgrading of the system was designed by introducing another complementary waste material, chitin. It was hypothesized that it can enhance the adsorption of EE2 in aqueous system.

The application of a combination of both adsorptive materials resulted in an increase of the EE2 removal to 90% and 92% under pH 10 and 7, respectively (Fig. 43). This may be due to the large number of active sites present on the surface of chitin. However, at this point in time, the enhanced new adsorptive system did not achieve the objective of this work yet. It may be due to very fine particles of chitin, which were not completely removed from the aqueous solution after filtration. Therefore, another upgrading of the system was proposed to attain the research objective. An electrochemical method was designed and implemented to consolidate the adsorptive system in phase 4.

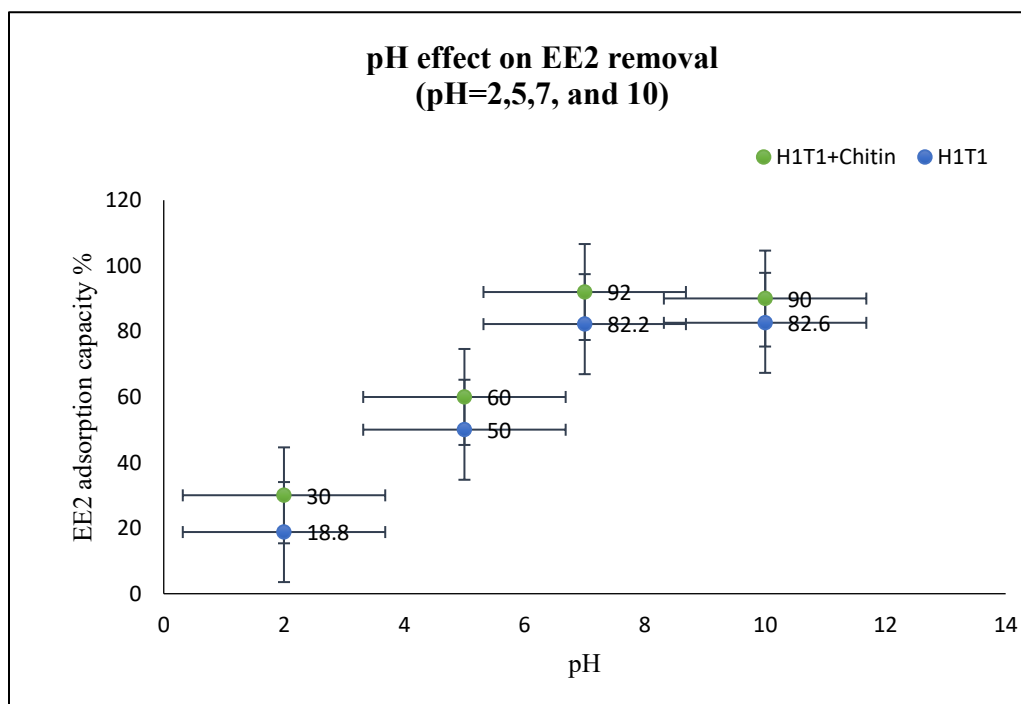


Figure 43: EE2 adsorption capacity by upgraded adsorptive system

4.6. Results from phase 4: Development of electro adsorptive system

Phase 4 of the study involved upgrading the technology dedicated to EE2 removal from aqueous solutions to an electro-adsorptive system in order to achieve the project objectives. Batch tests was conducted in an electrokinetic cell with retention time of 10 to 24 hours as shown in Fig. 44. After electrokinetic treatment, the remaining EE2 in the aqueous solution was scanned using UV-VIS spectrophotometers (Fig. 45).

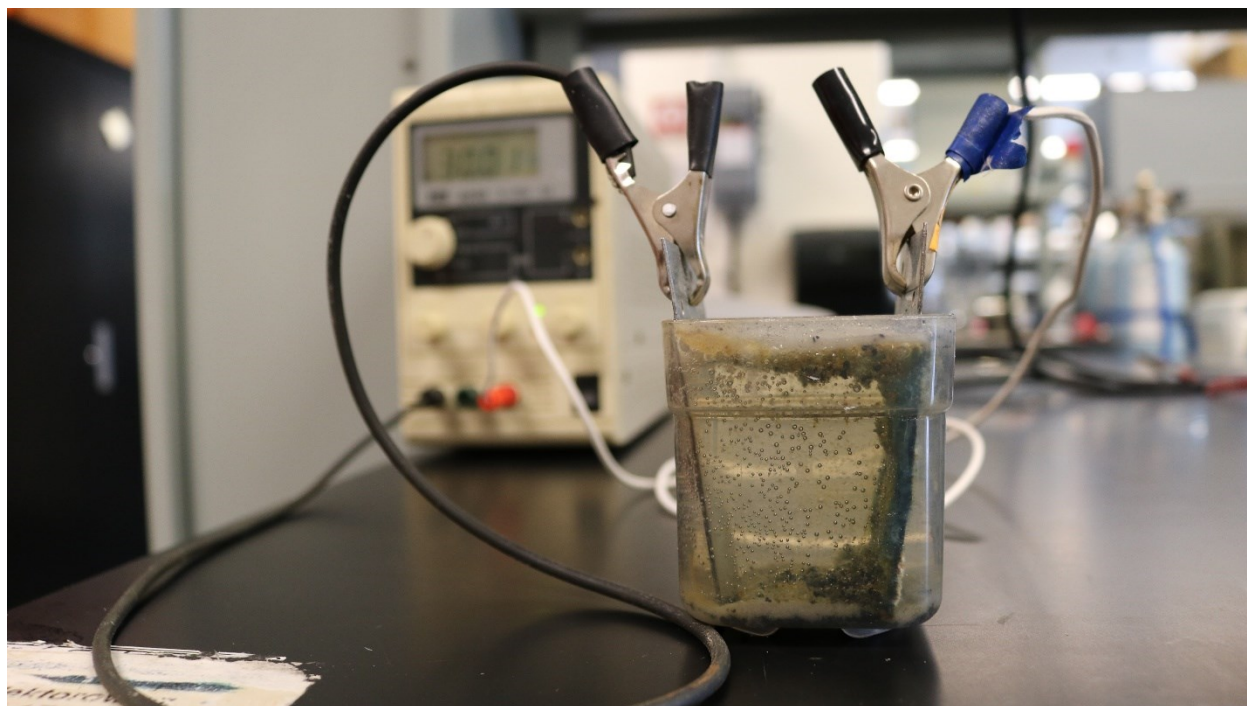


Figure 44: Electro-adsorptive system after 9h in EK by ENAM

The analytical results of the EE2 removal by electro-adsorptive system, which comprised of electrocoagulation and settling, were as follows:

- i) 99.99% EE2 removal (Fig. 46) using a natural adsorbent (chitin) made from the second new adsorptive material was achieved.
- ii) 91% EE2 removal (Fig. 47) using an adsorbent made from the first new adsorptive material (NAM) was attained.
- iii) 99.99% EE2 removal (Fig. 48) using an adsorbent made from enhanced new adsorptive material (ENAM) was possible.
- iv) Only 79% EE2 removal (Fig. 49) using a commercial activated carbon adsorbent (CACA) made from coconut shell was measured (Siemens, wastes, activated carbon, type: AC830C, net wt.: 551-Bs, lot no.: 20879-1). The difference in these results can be attributed to possible changes induced by the electro-adsorptive system.

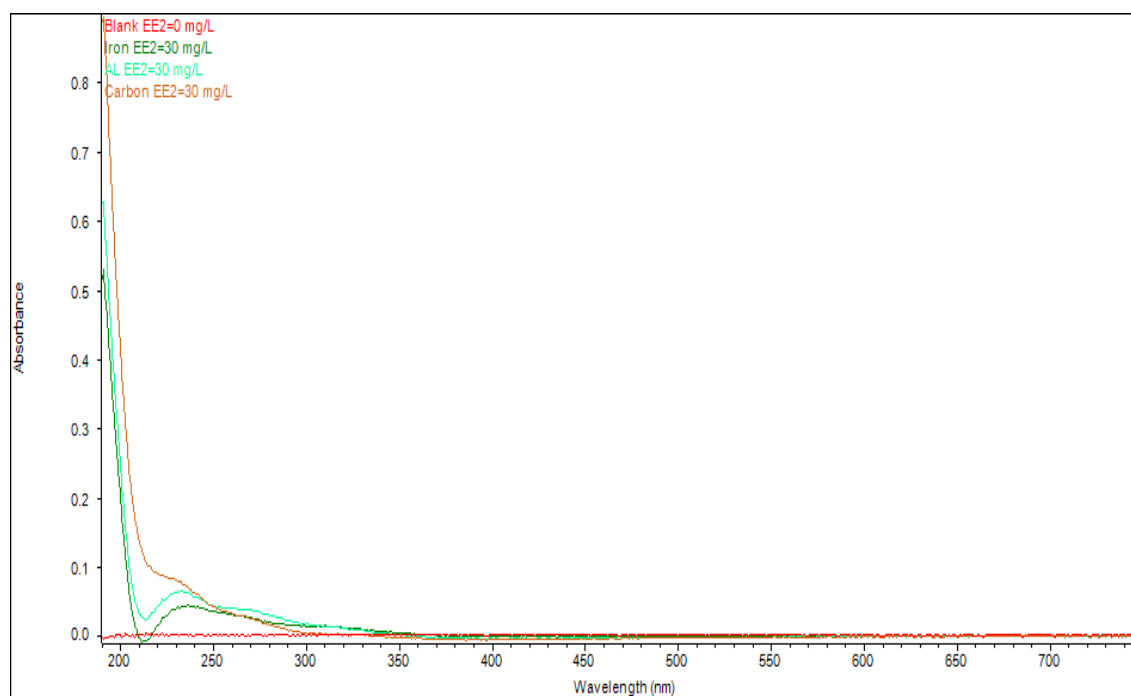


Figure 45: Scanned aqueous solution using UV-VIS Spectrophotometers after EE2 removal by Iron-Iron, Iron-Al, and Iron-C cells

4.6.1. Investigation of electro adsorptive system conditions

This section investigates the conditions involved in the electro-adsorptive system. Batch experiments were performed under stable condition of pH=7, EE2 concentration of 30mg/L, and adsorbent dosage of 20g/L with changing electrokinetic cell configurations, voltage applied, and adsorbent type in the system.

4.6.1.1. Electro adsorptive system by chitin - Impact of electrokinetic cell configurations

Three types of electrokinetic cell configurations were studied to optimize electro-adsorptive system. Three-electrode systems with a low DC voltage gradient were tested. To maintain the sustainability of the system, simple and non-expensive materials were used as electrodes. The distance between the electrodes was also maximized to 5cm. The following combinations of electrokinetic (EK) cells were tested: i) Iron: Iron (Fe); ii) Iron: Aluminum (Al); iii) Iron: Carbon (C). The EK cells were connected to a power supply using two cables transmitting a voltage of up to 60V. In order to increase cost effectiveness, a low voltage of 1V/cm was applied.

During the electro-coagulation process in each configuration, the following mechanisms were observed: i) Coagulation of colloidal materials in the aqueous solution; ii) Settling of coagulated flocs; iii) Oxidation of the adsorbent surfaces at the anode; iv) Potential oxidation of EE2, which due to the applied voltage, might have been insignificant. The collected samples were analyzed with respect EE2 removal. The results of the analytical test showed that 99.99% of EE2 was removed regardless of the electrodes types, which are indicative of flexibility in electrode use.

A comparison of the results is provided in Fig. 46; it shows the removal percentage of suspended particles of used adsorbent (chitin) obtained from each EK cell configuration, where the anode material was changed and the cathode was kept as iron. After 10 h, samples were collected from the system for analysis. After filtration, it was found that 5.5% particles remained suspended in the EK cell solution with the Iron: Iron configuration, as well as 6.2% and 9.0% for configurations Iron: Aluminum, and Iron: Carbon, respectively.

The remaining particles in the solution may be attributed to: i) Very fine size of some flocs (or non-affected by EC particles), which were unable to settle by gravitation; ii) Electrostatic forces

which were not sufficiently affected by the EK configuration, and which preserved suspension at certain level in the aqueous solution. It was deduced that using iron for both electrodes would be useful to increase suspended particle removal of the adsorbents as shown in Fig. 46.

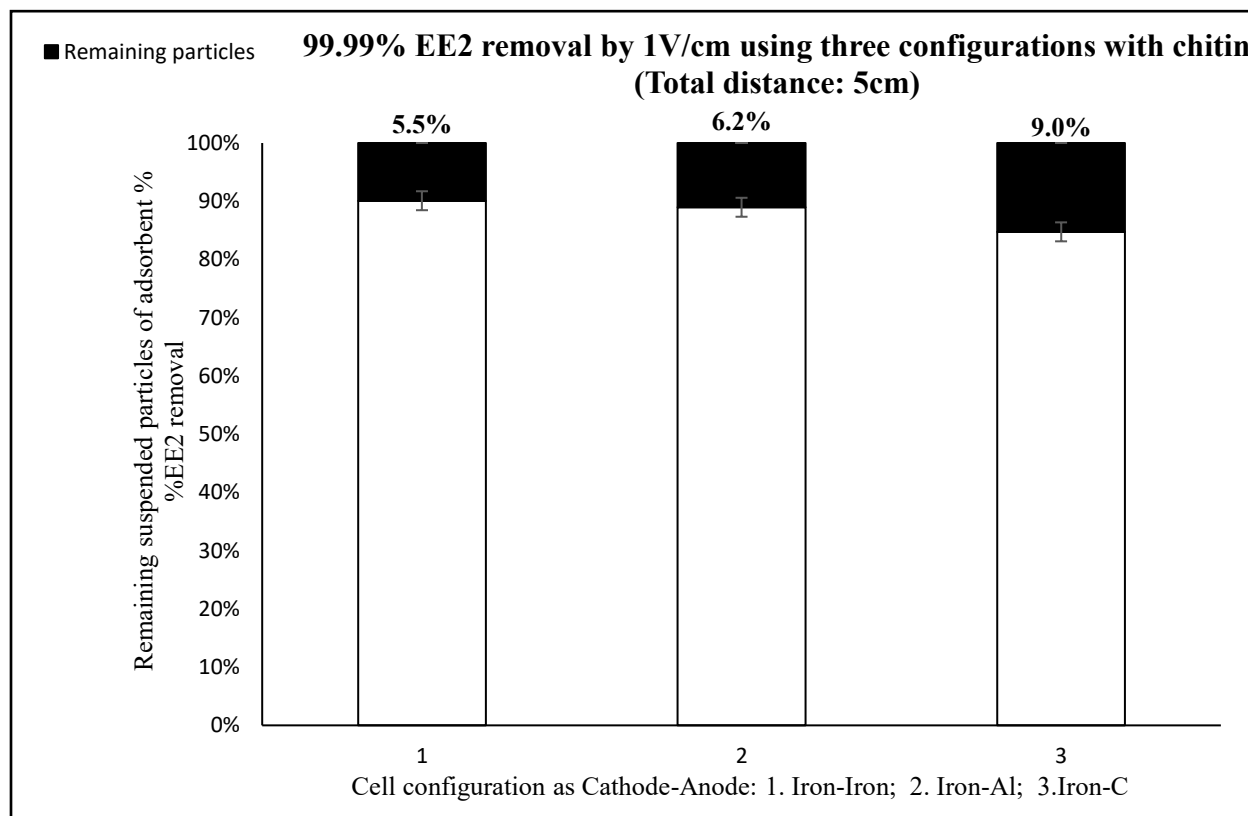


Figure 46: Electrokietic configuration's effect on removal% of EE2 and suspended particles of chitin

4.6.1.2. Investigation of best conditions for electro adsorptive system: voltage and adsorbents

An investigation of possible conditions that may enhance the performance of the electro-adsorptive system was conducted. After determining the best cathode material among the three EK cell configurations, the electro-adsorptive system was studied by changing the adsorptive material and voltage.

✓ **Electro - adsorptive system by the best formulated adsorbent (NAM)**

In this section, the best adsorbent made from the new adsorptive material (H1T1) was produced by pyrolysis of hardwood at 600°C with particle size $\leq 1\text{mm}$. This material showed the best adsorptive properties in phase 1 and phase 2. Thus, this type of adsorbent was tested using electrocoagulation (EC). The applied conditions were as follows: i) Both electrodes were made from iron; ii) Distance between the electrodes was kept 5cm; iii) Three supplied voltages were targeted 10, 15, and 20V; iv) EE2 concentration was 30mg/L; v) Adsorbent dosage was 20g/L; vi) pH =7; vii) Operating time of the system was 10h; however, it was noticed that most suspended particles of the adsorbent settled during the shorter time (7h) and under the low voltage (up to 20V) due to their unique surface properties beside their large size.

✚ This test showed a promising results regarding the removal of suspended particles of the adsorbent (Fig. 47) with 91% removal of the EE2.

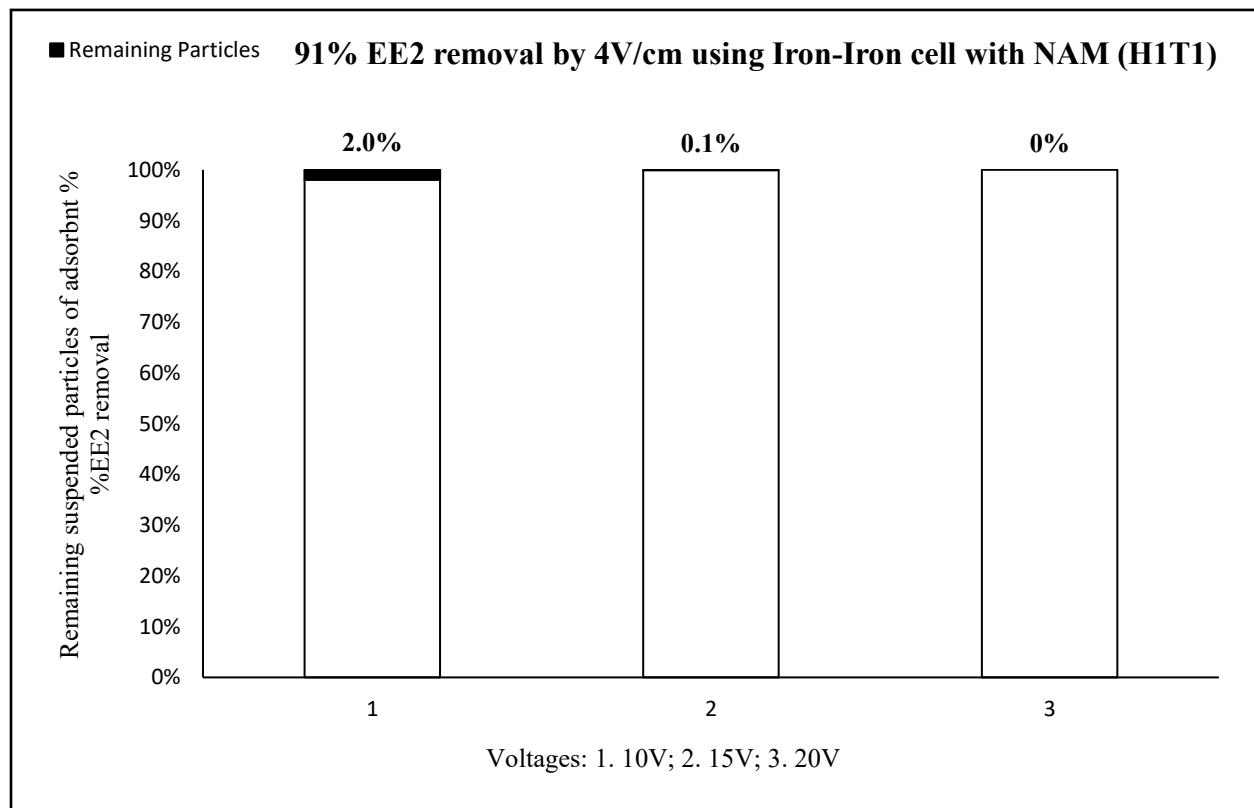


Figure 47: Removal% of EE2 and suspended particles of NAM (H1T1) in Iron-Iron EK cell

✓ **Electro - adsorptive system by upgraded adsorptive system**

To enhance the adsorbent performance and to increase cost-effectiveness, the adsorbent was modified with a new adsorptive material generated from fishery waste. The main purpose of this enhancement was to increase the number of functional groups on the adsorbent surface (i.e. create more active sites on the surface). In this case, chitin was the choice for the adsorbent enhancement.

The applied conditions for the electrocoagulation test using ENAM were as follows: i) EK cell used electrodes made of iron; ii) Distance between the electrodes 5cm; iii) Four supplied voltages 10, 15, 20, and 30V; iv) EE2 concentration of 30 mg/L; v) Adsorbent dosage of 20g/L; vi) Enhancement percentage NAM: Chitin 20:80; vii) pH=7; viii) Operating time was 10h.

The following mechanisms were involved in this test: i) Electrocoagulation; ii) Settling of big adsorbent particles (measured by microns); iii) Floatation of nanoparticles of an adsorbent; iv) Oxidation at the anode; v) Deposition on electrodes. It was assumed that these key mechanisms may enhance the cost-effectiveness, optimise time consumption, and improve the water quality.

✚ The results showed 99.99% of EE2 removal from the aqueous solution. Only a negligible amount of the adsorbent suspended particles remained in the aqueous solution at the highest applied voltage (30V) as shown in Fig. 48. In this case, the project objective was achieved.

The results showed that such waste enhancement material (chitin) was an ideal choice to improve the adsorbent properties of the media. However, it is preferred to be used as an enhancer rather than individually because it is difficult to coagulate.

The designed electro-adsorptive system using ENAM represents a promising technology for contaminated water treatment because of improvement of water quality with respect to EE2 removal and probably for other pharmaceutical compounds.

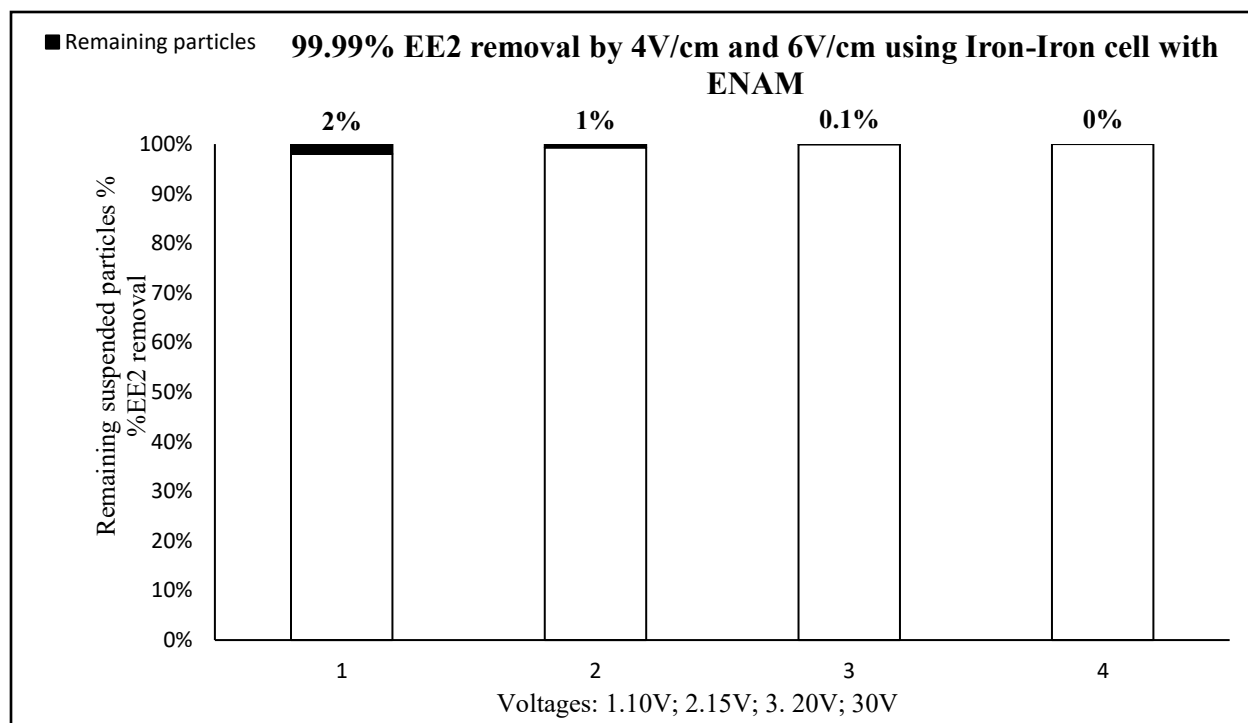


Figure 48: Removal% of EE2 and suspended particles of ENAM in Iron-Iron EK cell

4.7. Results from phase 5: Electro adsorptive system - Comparison

In this chapter, results of a sequence of actions were explained qualitatively and quantitatively to unravel the advantages and disadvantages of the adsorptive system for EE2 removal from the aqueous solution. A comparison was also established between the formulated adsorptive systems with a commercially available adsorptive system.

The formulated adsorptive system was designed from NAM mixed with chitin (ENAM) while the commercial adsorptive system (Commercial Activated Carbon Adsorbent (CACA)) was made from coconut shells (Siemens, westates, activated carbon, type: AC830C, net wt.: 551-Bs, lot no.: 20879-1).

Electrocoagulation tests were performed using ENAM and CACA under the following conditions: i) Electrodes made from Iron: Iron; ii) Distance between the electrodes 5cm; iii) Three supplied voltages: 10, 15, 20, and 30V; iv) EE2 concentration = 30mg/L; v) Adsorbent dosage = 20g/L; vi) pH=7; vii) Operating time = 10h.

It was observed that the following mechanisms were involved in the removal process: i) Coagulation of colloidal suspensions; ii) Settling of flocs (measured by micron); iii) Suspension of Nano adsorbent particles produced from the surface of the commercial adsorbent due to poor adsorbent quality.

✚ The results from the analytical tests were as follows: i) 79% of EE2 removal from the aqueous solution was achieved; ii. 0.8% of the adsorbent material remained as suspended particles at the highest applied voltage (30V) as shown in Fig. 49.

It seems that this CACA is not a suitable matrix for use in electro-adsorptive system due to its low removal capacity under high voltage. It was also found that the CACA produced a black soluble waste layer, which affected the quality of the aqueous solution. The produced waste could be attributed to the surface treatment since CACA is expected to be treated with some types of polymer, which can easily dissolve under an electrical field. Moreover, the EE2 removal capacity was low due to the presence of a lower number of active sites on the surface. Thus, CACA can be considered as a low cost-effective material due to its low manufacturing quality.

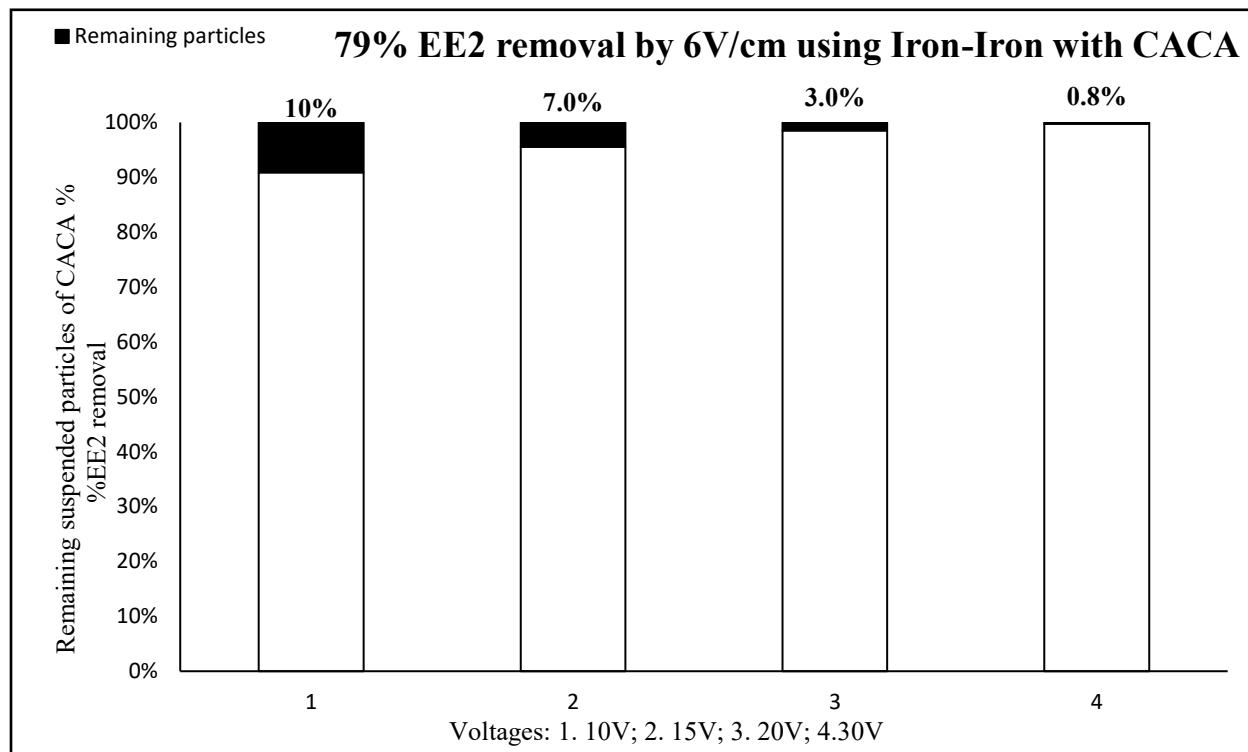


Figure 49: Removal% of EE2 and suspended particles of CACA in Iron-Iron EK cell

Moreover, the SEM images with respect to porosity are strongly consistent with the final results of EE2 removal; an adsorbent with large pores has lower number of active sites on the surface. A number of non-uniform pores was present on the surface of commercial CACA which significantly reduced the surface area and number of active sites. Adding chitin to the CACA enhanced the surface area and active site density. Although there was an improvement, other issues such as the formation of a black soluble waste layer reduced the attractiveness of the CACA system. In addition, its low removal capacity under high operating conditions compounded the problem. Fig. 50 shows the SEM images of CACA taken after electrokinetic (EK) process.

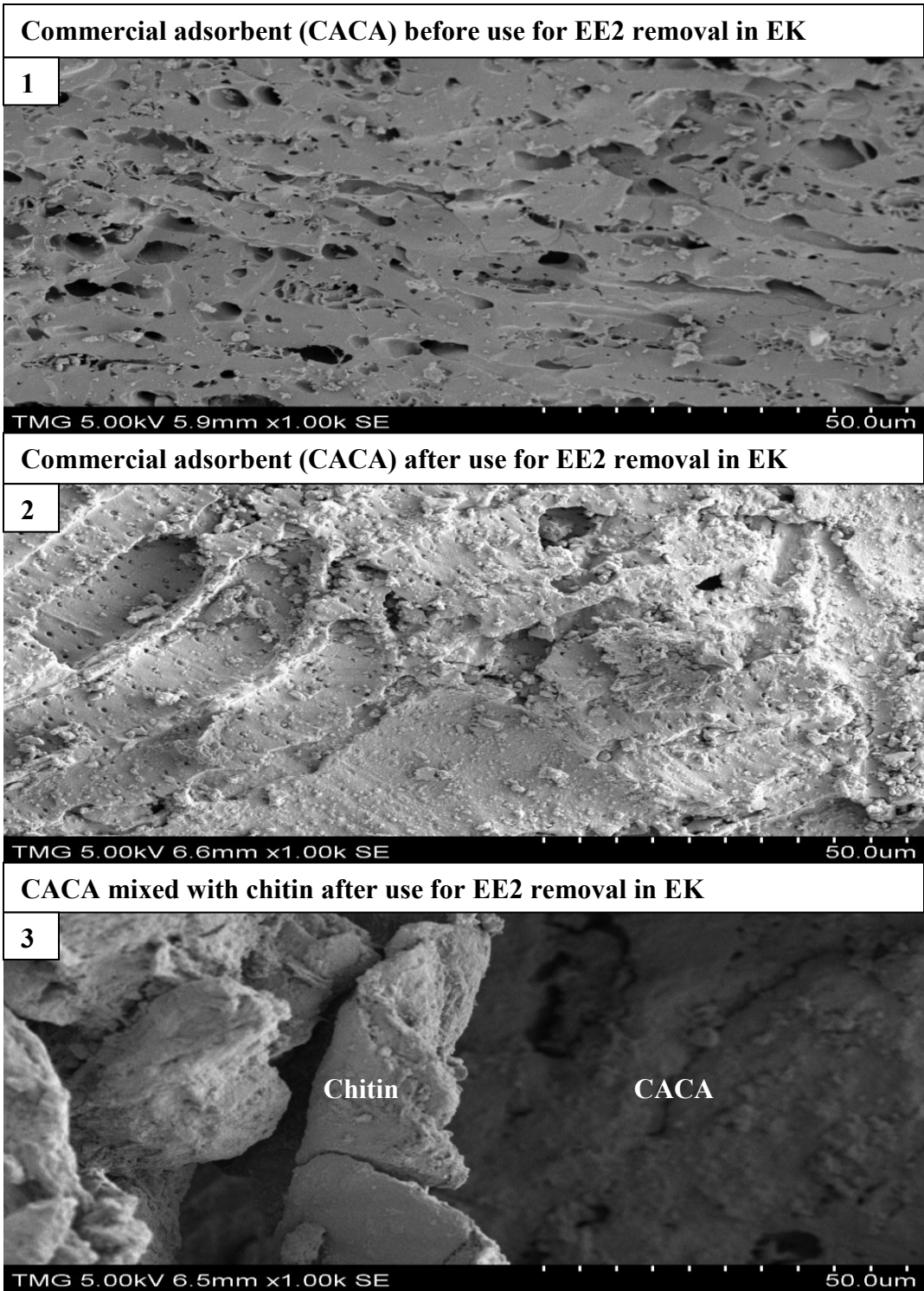


Figure 50: SEM images of CACA before and after its use in EK cell

In addition to the images shown in Fig. 50, SEM images were captured for chitin (Fig. 51-1 and 2), NAM (Fig. 52-1 and 2), and ENAM (Fig. 52-3) before and after application of the electrical

field. The SEM images in Fig. 52-2 show how the electro-coagulating products and pharmaceutical contaminants coated the adsorbents (advantage), while Fig. 51-2 shows how the adsorbent has been affected by the applied electrical field. The electrical field induced damage in the thin layers on the adsorbent surface (disadvantage). Thus, adding chitin to NAM enhanced the active surface to improve the removal capacity while preserving undamaged surface layer (Fig.52-3). This is advantageous in cases where the adsorbent is expected to be reused several times. Electro-damaged surface of chitin can have advantage since this can render the surface more porous and generate additional active surfaces. The images also revealed two mechanisms involved in the EE2 removal process: first- a physical mechanism due to the EE2 accumulation and electro-coagulation precipitation, and second- a chemical mechanism leading to the formation of chemical bonding on the adsorbent surface by EE2.

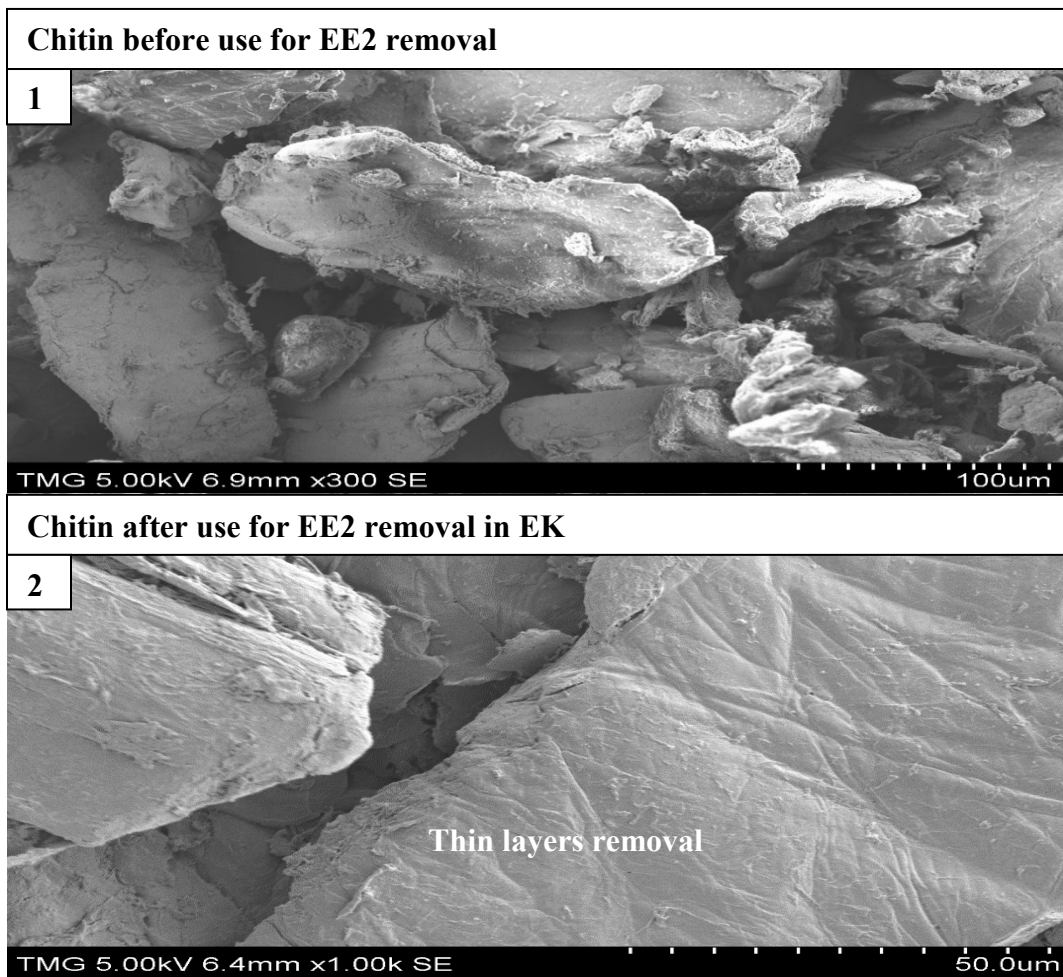


Figure 51: SEM images of chitin before and after its use in EK cell

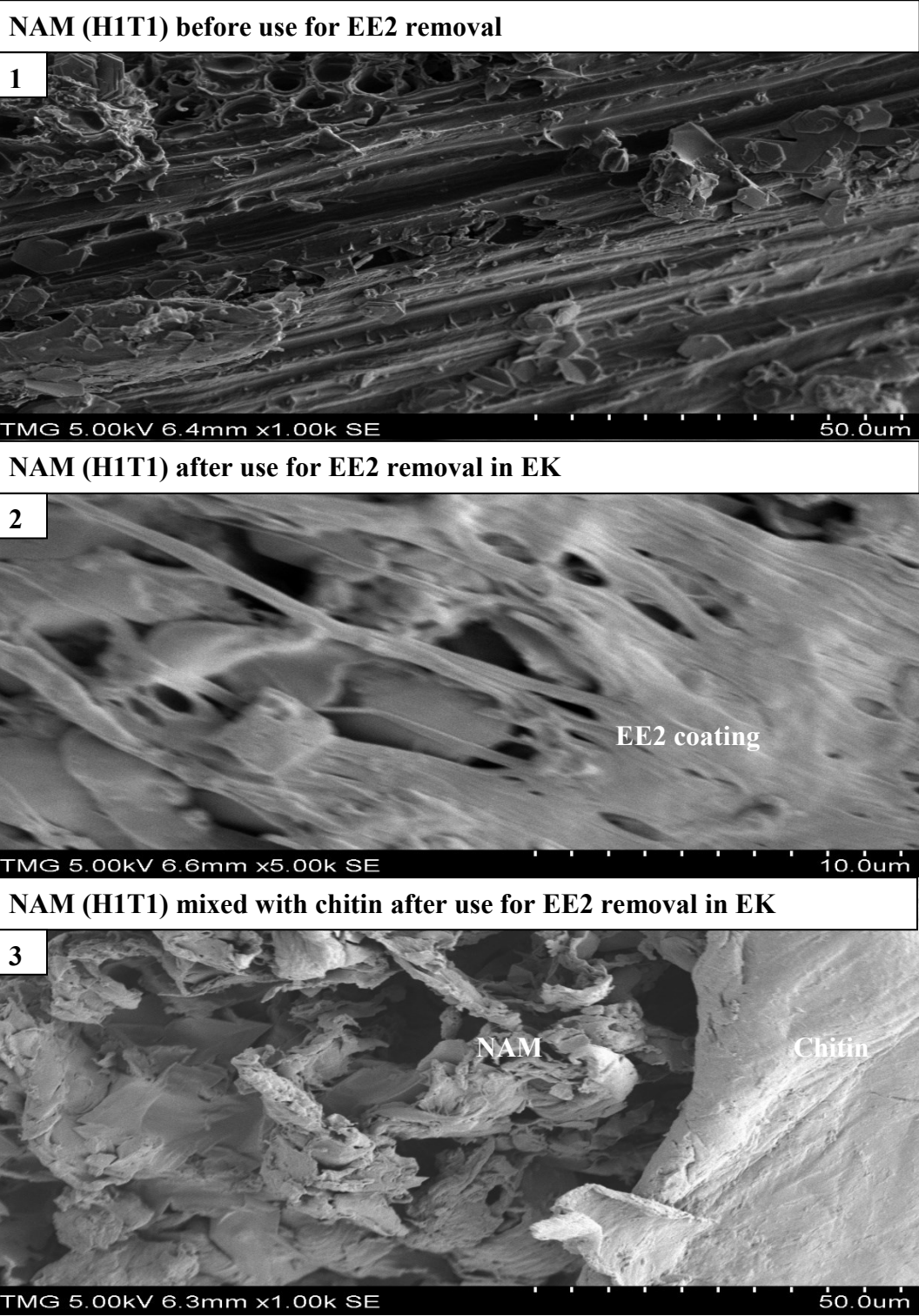


Figure 52: SEM images of NAM and ENAM before and after their use in EK cell

4.8. Results from phase 6: Cost effectiveness increase and energy saving

This section includes results from: 1. Materials distribution optimization model; 2. Energy saving during electro-adsorptive system production.

➤ Materials distribution optimization model - Cost effectiveness of delivered materials

Simulating the proposed materials distribution model in phase 6 using MATLAB (code in appendix 2) by the optimal roundtrip for visiting 20 locations (e.g. cities). MATLAB codes are shown in Appendix 2. The results showed that before simulation, the roundtrip for visiting one city required 4.6 km and 92 km if 20 visits are required. The optimisation showed a useful model aiming at reducing the total roundtrip distance to 10 km.

➤ Energy saving optimization model - Tasks combination

It was assumed to complete a given collection of tasks on a single process that can accommodate one job at a time as shown in Table 14.

In this section, a table model was created to solve an energy problem (Table 14). As an example, the manufacturing of a material at lab-scale was considered. Table 14 shows the total required time of the manufacturing procedure for the formulated adsorbents by pyrolysis (Fig. 12, stage 3). This approach has been useful to solve energy saving problem because it helped to reduce the total required time of manufacturing from 80h to 20h. This approach helped to save energy of the entire work by a factor of 1/3.

Table 14: Required time for each single task under ideal conditions

Time (hour)	Pyrolysis = 600°C				Pyrolysis = 800°C				Total Required Time	Optimal time
	Task 1	Task 2	Task 3	Task 4	Task 5	Task 6	Task 7	Task 8		
Process time p_i	1	1	1	1	1	1	1	1	8	2
Release time r_i	8	8	8	8	8	8	8	8	64	16
Due time d_i	8	8	8	8	8	8	8	8	64	16
Scheduled start x_i	9	9	9	9	9	9	9	9	72	18
Completion time ($x_i + p_i$)	10	10	10	10	10	10	10	10	80	20
Lateness ($x_i + p_i - d_i$)	2	2	2	2	2	2	2	2	16	4

Legend: Ideal conditions mean the equipment is ready to use.

Release time is a preparation time before and after using the equipment.

Due time is regular work hours for institution (e.g. university).

Scheduled start is a consumed time to finish a sample.

Furthermore, using chitin without pre-treatment for enhancement of NAM helped to save energy and cost by the following procedure:

The proposed pre-treatment procedure of chitin was assumed by subjecting chitin to heat in order to deacetylate its surface functional groups and convert it to chitosan. Then chitin should be immersed in the sodium hydroxide solution (NaOH) for 1-2h at room temperature at a ratio of 1:15-solid: liquid. The resulting samples should be kept in a freezer for 24h at -83°C, and then, transferred to an oven at 155°C. The reaction also required agitation at 250rpm for 8h. Finally, the mixture should be filtered.

➤ **Energy saving optimization approach - Electro adsorptive system**

To increase cost-effectiveness, performance of the adsorbent was improved by using 20g/L. A low adsorbent dosage of 20g/L was used throughout the course of this research to fully remove EE2 from aqueous solutions. This dosage was a useful criterion since it helped to precisely evaluate the optimum properties of the adsorbents, such as surface area.

In addition, applying a low voltage (10, 15, 20, 30 V/cm) to the electro-adsorptive system for total EE2 removal and suspended particles contributed to save energy.

The results showed 99.99% of EE2 removal from the aqueous solution and the presence of a negligible amount of adsorbent suspended particles (ENAM) in the aqueous phase at the highest applied voltage (30V) in the electro-adsorptive system. In this case, the project objective was achieved. Under similar conditions, the results showed 79% of EE2 removal from the aqueous solution and 0.8% residual adsorbent suspended particles for the CACA system at the highest applied voltage (30V) in the electro-adsorptive system. As a comparison between the two types of adsorbent, the total energy savings are shown in Table 15. The formulated electro-adsorptive system helped to save energy by 21% at 5V/cm as compared to the CACA system.

Table 15: Energy saving optimization model by electro-adsorptive systems

Initial conditions	ENAM				CACA				Results under similar conditions		Total energy using CACA
	ENAM	CACA	ENAM	CACA	ENAM	CACA	ENAM	CACA			
removal % of EE2	99.99%				79%				99.99%	79%	21%
Applied Voltage	10	15	20	30	10	15	20	30	30	30	Unknown
Remaining particles%	2	1	0.1	0	10	7	3	0.8	0%	0.8%	0.8%
Required energy	5V/ 1% to				5V/ 3% to				Optimal	100 - 79= 21% and 0.8%	By 21%+ 0.8% 100% removal

Chapter 5: Final conclusion, contributions, and future work

5.1. Final conclusion

This research study demonstrated that estrogenic compounds in wastewater treatment effluents present an elevated risk for both environment and population, thus a new technological approach might be developed urgently to remove estrogenic compounds from wastewater treatment effluents due to their serious health effects.

This research permitted to develop an electro-adsorptive system for pharmaceutical products' removal from aqueous solutions. The system can be applied in water purification facilities or to polish effluents generated by the wastewater treatment plants. This research focused on 17 α -ethynylestradiol (EE2) as a representative of pharmaceuticals since this compound in water might be a precursor of many important endocrine impairments in living organisms. To agree with sustainable development principles, adsorptive materials were generated based on wasted residues from forestry and fishery only. The results showed that hardwood residues expressed better adsorptive properties than softwood residues. They had better distribution of porosity, surface area and better response to thermal treatment proven by FTIR, BET and TGA, respectively, and UV-VIS. Then, technological parameters of manufacturing process were developed focusing mainly on hardwood residues. The process undergoing: i) Shredding of primary material, ii) Drying, iii) Treating under 600°C in absence of air, iv) Activating with phosphoric acid (H₃PO₄), v) Neutralizing, was able to generate new adsorptive material (NAM) having excellent adsorptive properties, comparable to commercial activated carbon. Subsequently, NAM demonstrated the capability of EE2 removal by 82% at pH= 7 to 10.

Adsorption phenomena it seems to reduce adequately EDCs in aquatic environment. For example, adsorbent derived from a waste softwood showed a maximum adsorption capacity of 42% for EDC (EE2), whereas, adsorbent derived from a waste hardwood showed a maximum adsorption capacity of 47% for EDC (EE2). These primary results of this test discovered that adsorbent derived from the waste hardwood has more active sites on the surface than AC derived from the waste softwood. Thus, it was seen that development this type of adsorbent might be a good option to increase a cost- effectiveness. Based on the literature review, there is no study yet showed the

removal EE2 using a natural waste resource in mixture with AC which might show a higher adsorption capacity.

It was also concluded that chitosan and chitin (primary material for chitosan) do not express significant differences in the adsorptive process. Subsequently, chitin which did not required a costly pre-treatment, was applied. A combination of two adsorbents: chitin as advanced adsorptive material and NAM was permitted to achieve the removal of EE2 by 92%.

In this study, the natural waste resource called chitin was a good choice to enhance EE2 removal from an aquatic environment. Chitin was mixed with formulated adsorbent to increase adsorbent functional groups on the surface. The obtained results of this test showed that 92% of EE2 was removed which is perfect, but it is still far away from the expectation. Therefore, Electro-adsorptive system made from a combination of AC-chitin and electrocoagulation system was the option to reach this research objective. In subsequent phase of this study, it was proven that by combining ENAM with electrical field in electrokinetic (EK) reactor, the removal of EE2 from aqueous solution can reach 99.99%. The study showed that configuration of electrodes Fe-Fe is much better than other system of cathode-anode, e.g. Fe-Al or Fe-carbon. The developed electro-adsorptive system permitted to remove EE2 from the solution through several paths: i) Adsorption into micro-pores of activated NAM; ii) Adsorption to chitin organic surface; iii) electrocoagulation; iv) Settling/floating; v) Oxidation through radicals produced on electrodes. This system showed 99.99% of EE2 removal from the aqueous solution.

In addition, the individual electro-adsorptive system made from ENAM-electrocoagulation system was compared with CACA-electrocoagulation to contribute to knowledge about properties and behaviours of both system under similar conditions. It was found the synthesized system from NAM-chitin and electrocoagulation was much better than a commercial system made CACA-electrocoagulation in both cases (properties and removal). Theoretically, the performance of formulated adsorptive systems was compared with another adsorptive system in previous works which showed 95.3% E2 removal by a bone char [215]. It was expected a high performance of formulated adsorptive systems under similar conditions in previous works (low concentration of E2 from 5.0–9.0 mg L⁻¹ and the high adsorbent dosage of 50g L⁻¹).

5.2. Contributions

The main purpose of this work is to provide a sustainable solution for the removal of a target compound (EE2) from water and WWTP effluent. The following factors would be taken in consideration to achieve the sustainability of the process:

➤ Development of:

- 1) New Material from waste woodchips.
- 2) Enhanced New Material from waste woodchips and waste seafood carapace.
- 3) Advanced engineered approach to formulate an adsorptive system.
- 4) New an electro-adsorptive system where the electrical field changed properties of absorptive materials, increased EE2 removal capacity, and increased suspended adsorbent particles removal.
- 5) Removal method of the suspended particle of an adsorbent to achieve maximum extraction of adsorbent particles.

➤ Contributions of:

- 1) Compare between two types of new adsorptive materials in response to the change in manufacturing conditions, for example, pyrolysis, particle size.
- 2) Knowledge about the properties and behaviours of new materials, considering both manufacturing process and application of generated products into environmental engineering.
 - Wood residues properties: Hardwood residues expressed better adsorptive properties than softwood residues.
 - Adsorptive ability of combination of various systems: HIT1-S2T2, chitin, ENAM, CACA, and electrical field.

- Properties and behaviours of new materials based on TGA, FTIR, BET, and SEM.
- 3) Optimize energy consumption during manufacturing process of new materials by decreasing time and temperature.
- Chitin without pre-treatment for enhancement of NAM.
 - Combining multiple tasks in one task.
 - 20g/L as a low dosage of adsorbent to fully remove EE2 from an aqueous solution.
- 4) Define the best technological conditions.
- Fe-Fe electrodes configuration
 - Adsorptive surface area
 - Adsorptive surface functional groups
 - Adsorptive compounds
 - Enhancement of adsorptive capability.
- 5) Knowledge about properties and behaviours of the suspended adsorbent particles under different applied voltages in the electrocoagulation process, considering the involved removal mechanisms regarding to adsorbent surface properties.
- Electrocoagulation process of adsorptive materials under various EK configurations.
- 6) Designing a novel electro-adsorptive system to remove EE2 and suspended particles of adsorbents from an aqueous solution.

➤ **Advantages of formulated system (the electro adsorptive system):**

- 1) High cost-effectiveness.
- 2) High removal capacity.
- 3) System flexibility to remove a large number of contaminations from an aqueous solution regardless their concentration level (Table 4).
- 4) System processes combination, such as adsorption, deposition, and oxidation which are able to change contaminant properties from a non-removable to removable contaminant.
- 5) Reusable adsorbents by chemical treatments.

5.3. Future work

Too many ideas come to the mind for the future research work, such as using different type of a waste material, focusing on new removal phenomena, and applying different conditions...etc. However, one of the best ideas comes to the mind is to repeat this research work with establishing a comparison based on adsorbents made from two different natural waste materials called chitin and chitosan to understand a difference between these two waste materials, which are driven from the same source. One of them named chitin is already used in this study. Meanwhile, the verification of the electro adsorptive system quality can be done by following:

- 1) Scaling up and verified electro adsorptive system at a large scale.
- 2) Assessment the cost effectiveness at a pilot scale.
- 3) Energy saving model extension by applying large scale conditions.
- 4) Designing electro adsorptive system with at large scale which fitting to continue flow conditions.
- 5) Testing electro-adsorptive system directly on effluent.
- 6) Establishing a comparison based on adsorbents made from two different natural waste materials called chitin and chitosan to understand a difference between these two waste materials, which are driven from the same source.
- 7) Changing a polymer properties (chitin) using new manufacturing conditions.

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Appendix 1 - Additional results

A1.1. Preliminary results

For cost and energy saving, a preliminary test was made based on widely available and unexpensive products, such as paracetamol (PCM).

The test was very useful to generate an experimental procedure to test targeted compound removal (EE2) from an aqueous solution using formulated adsorbents.

At pH 7 and PCM concentration=100mg/L, the obtained results of this test showed 99.99% PCM removal from the aqueous solution using 20g/L of a formulated adsorbent (Fig. A1-1).

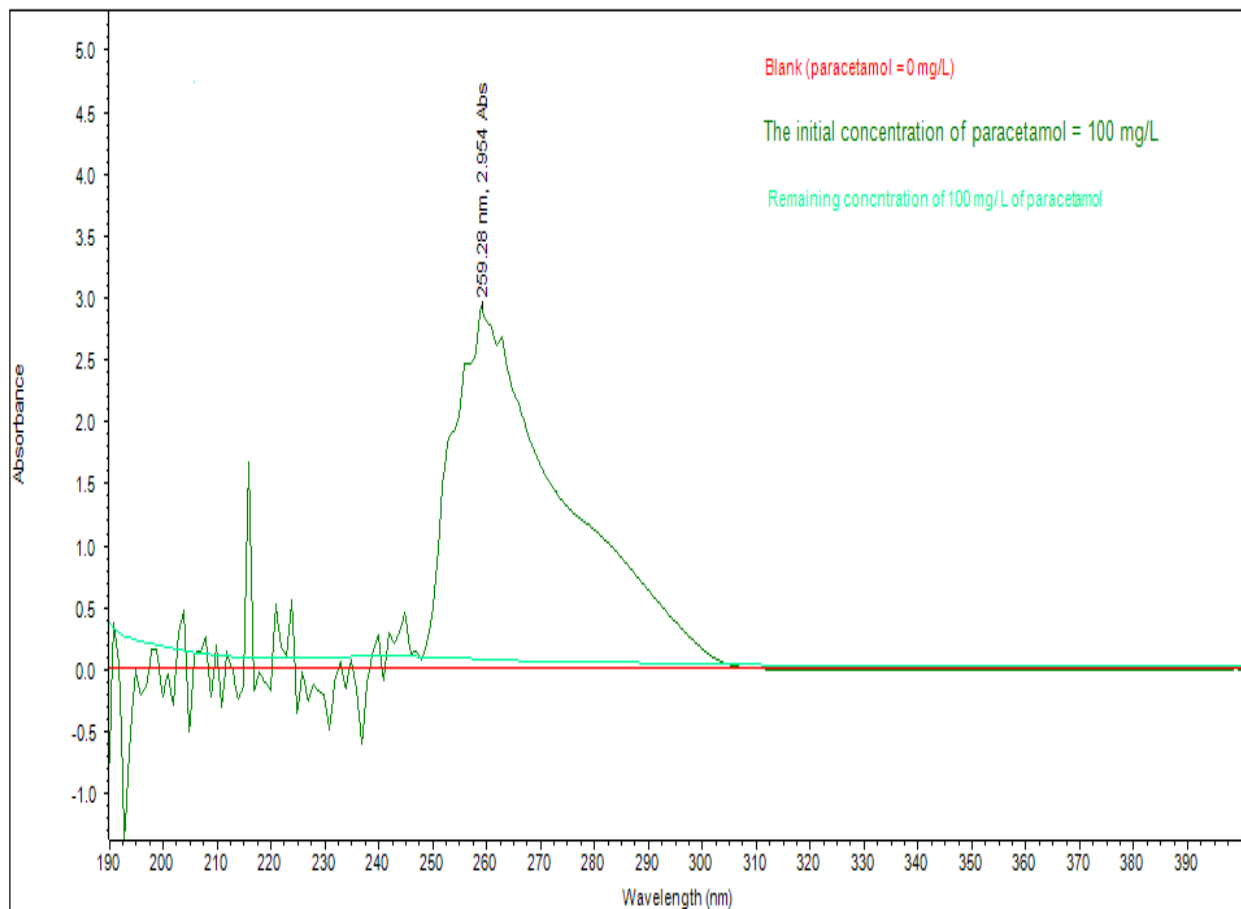


Figure A1-1: 99.99% PCM removal from an aqueous solution using a formulated adsorbent

A1.2. Final results

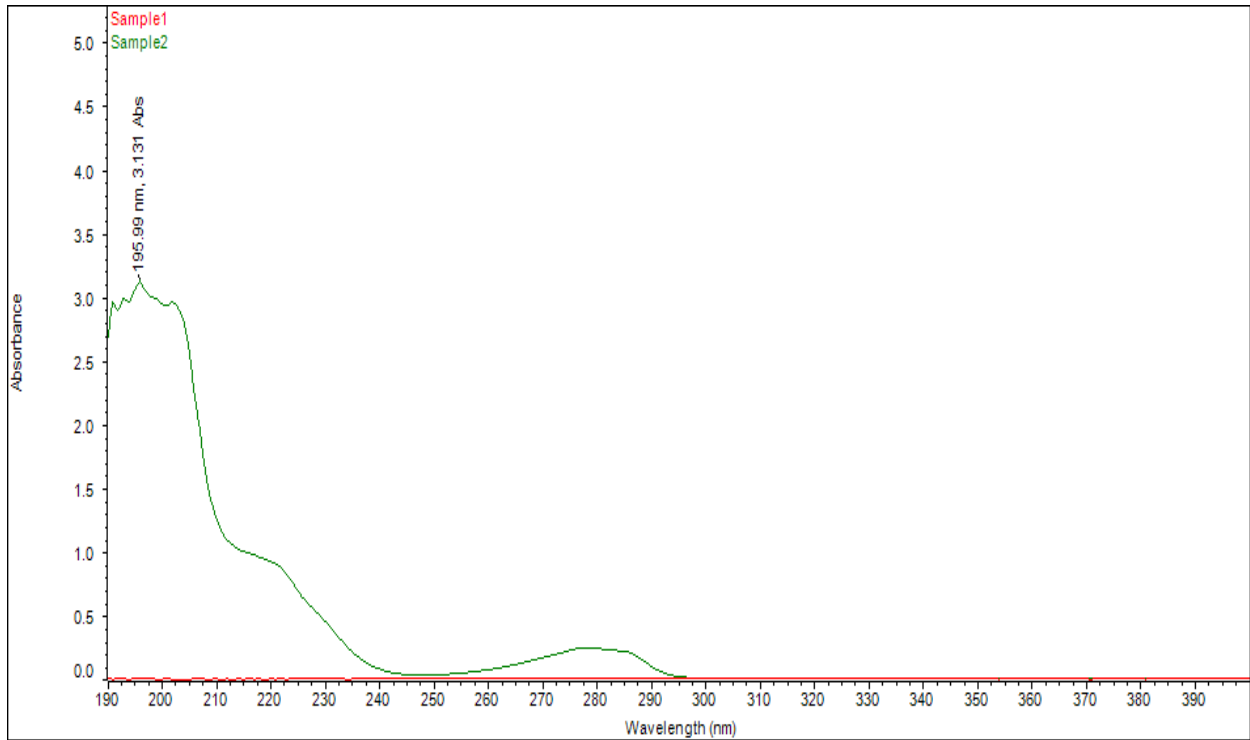


Figure A1-2: Peak of 200mg/L EE2 in the aqueous solution

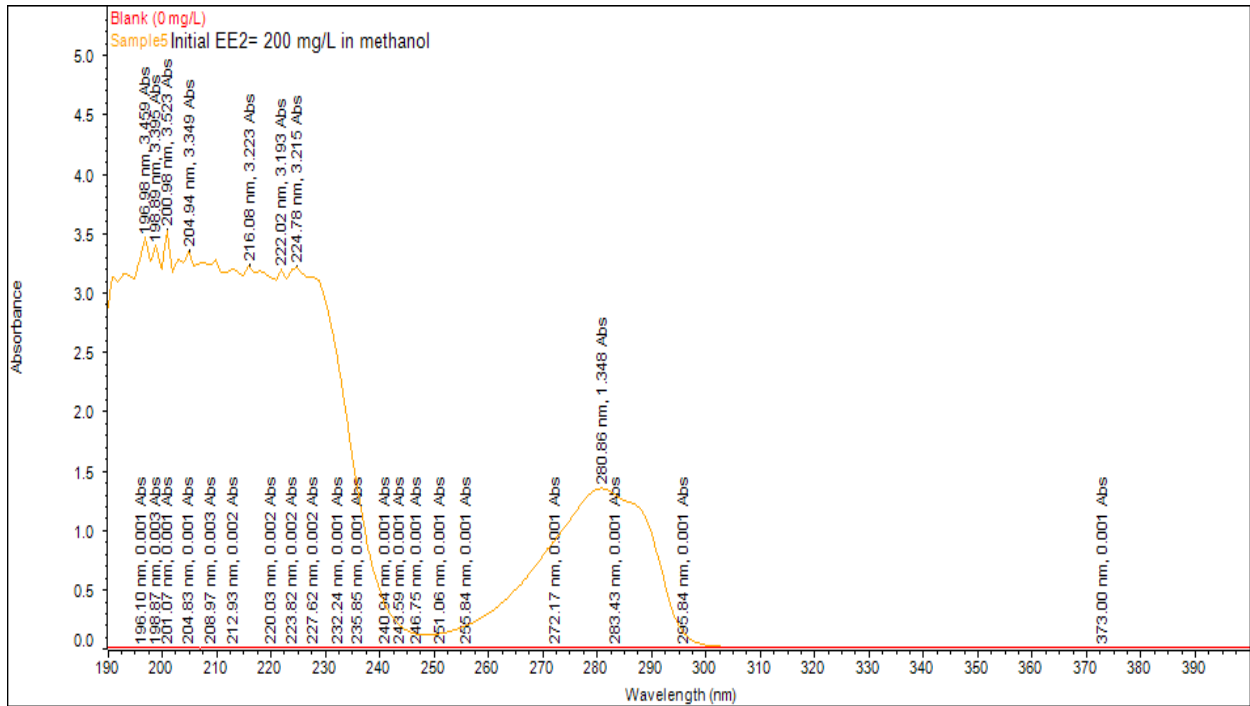


Figure A1-3: Peak of 200mg/L EE2 in methanol

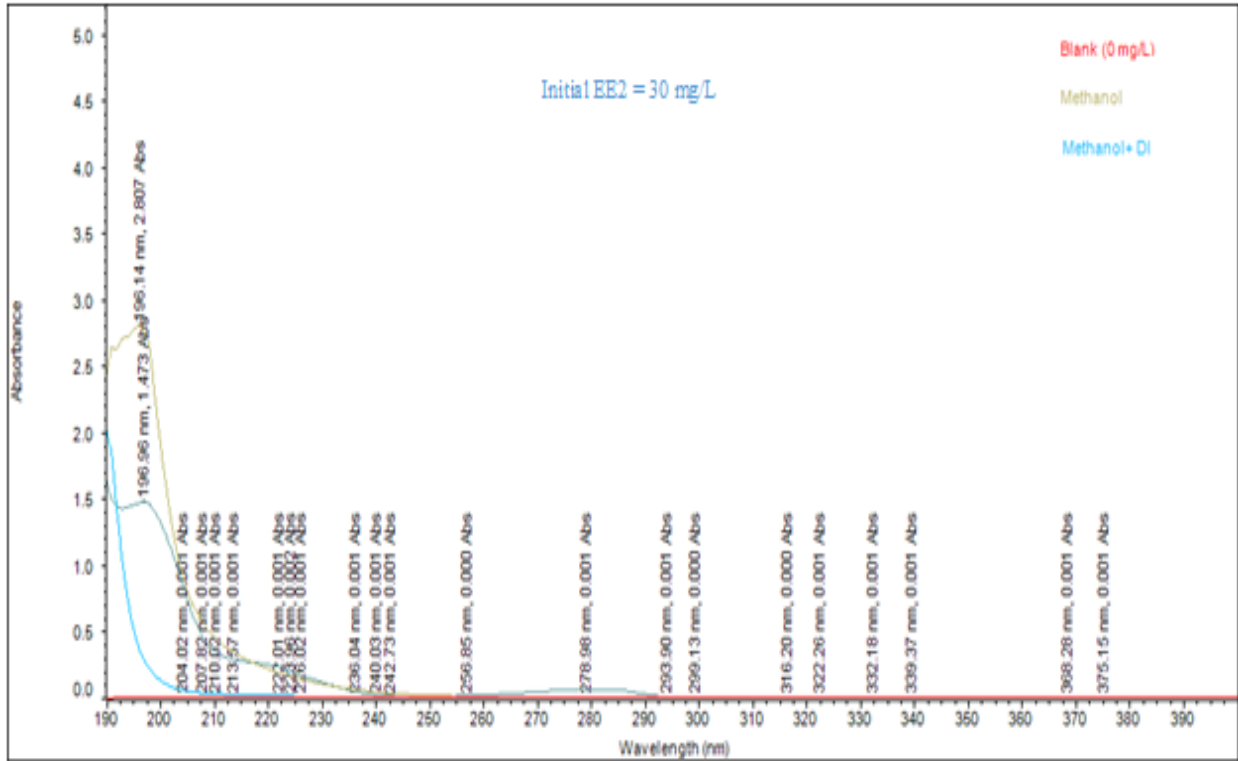


Figure A1-4: Peak of 30mg/L EE2 in the aqueous solution

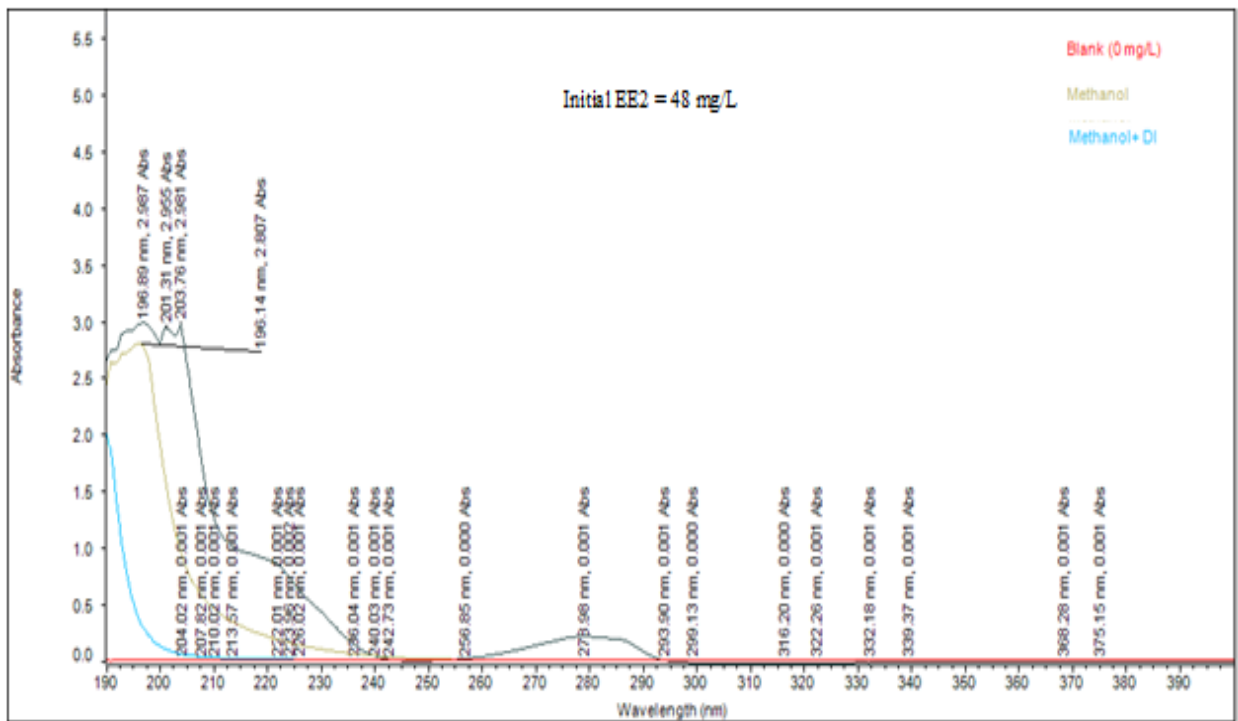


Figure A1-5: Peak of 48mg/L EE2 in the aqueous solution

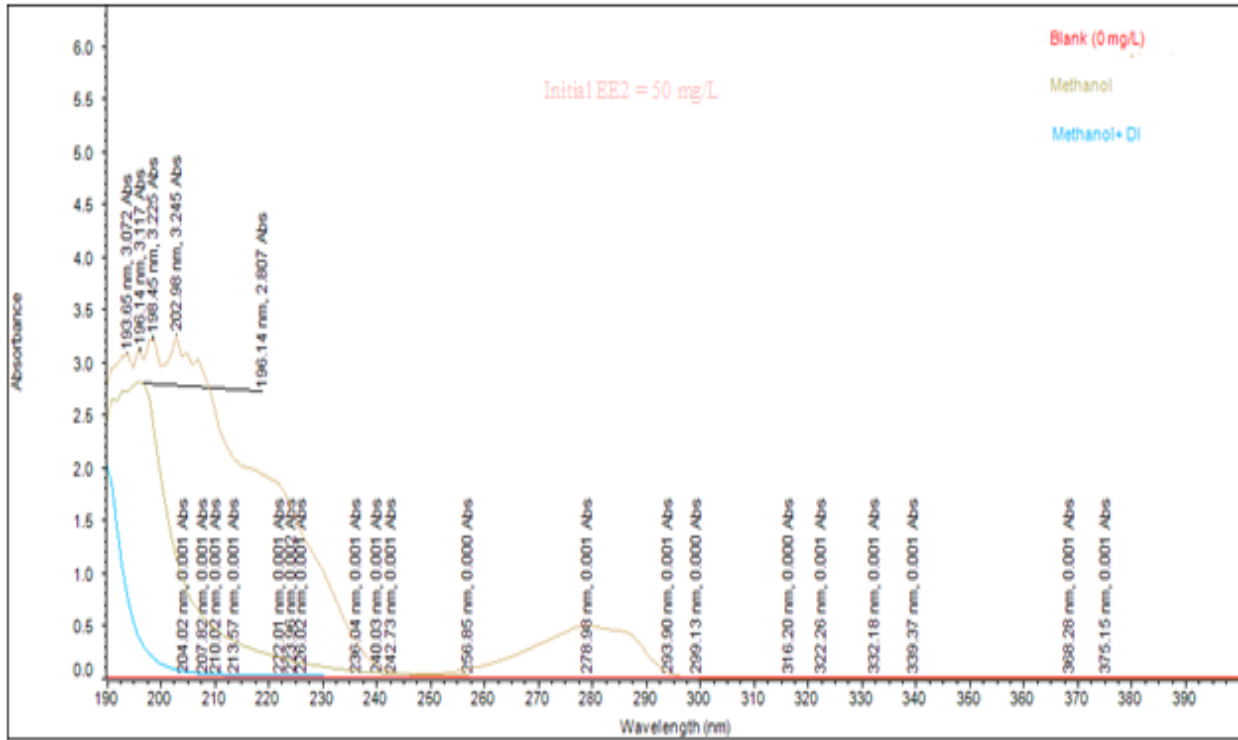


Figure A1-6: Peak of 50mg/L EE2 in the aqueous solution

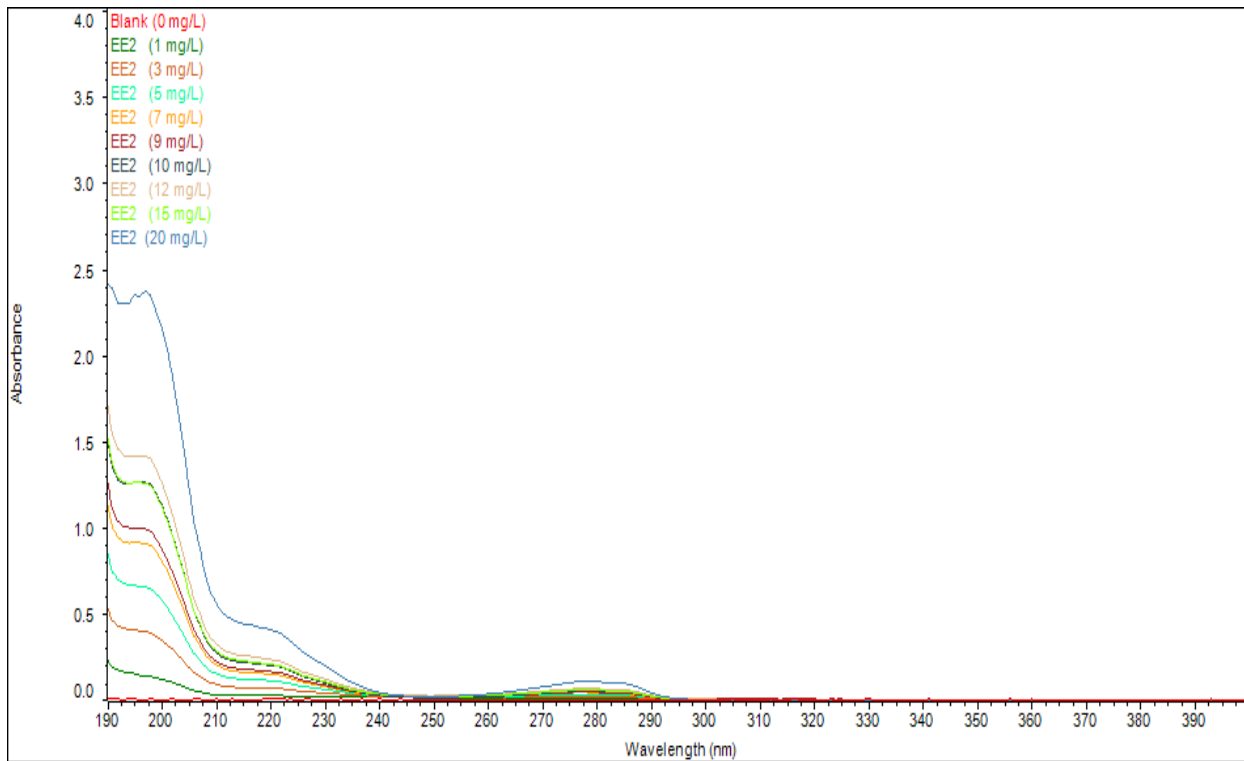


Figure A1-7: Peaks of blank and standard solution

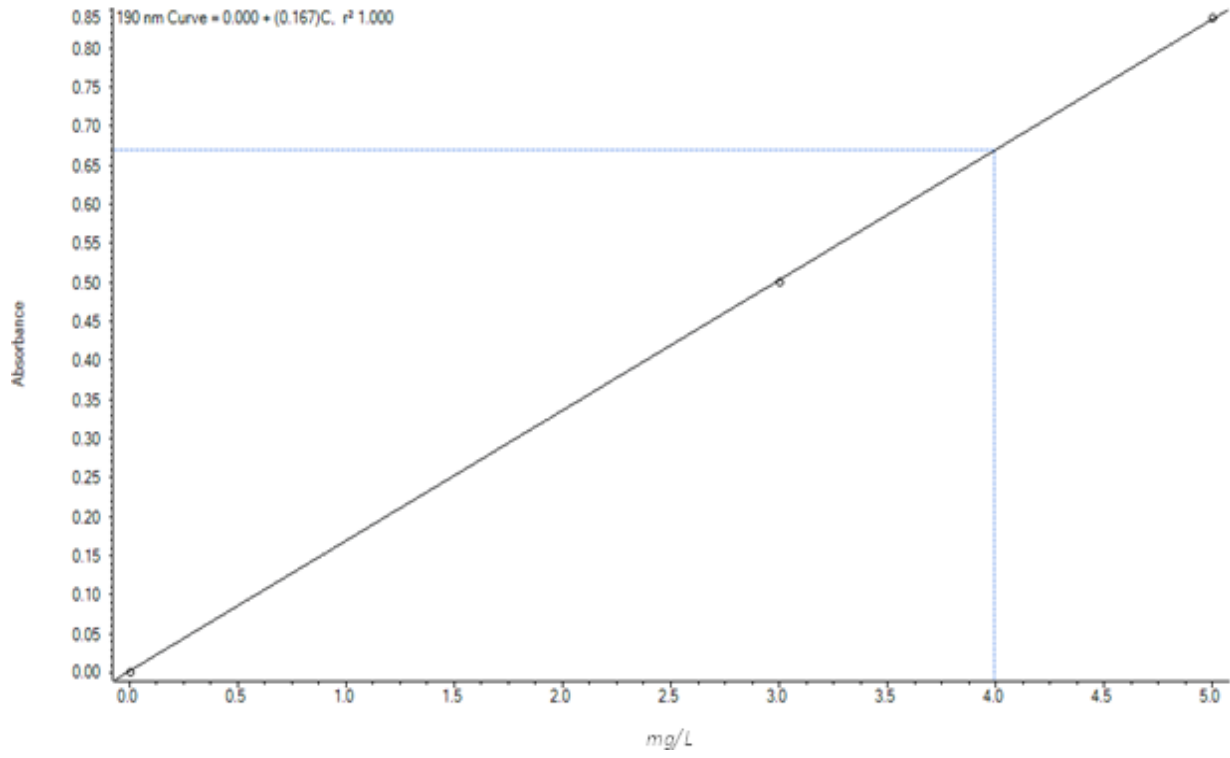


Figure A1-8: Calibration curve of remaining concentration measurements

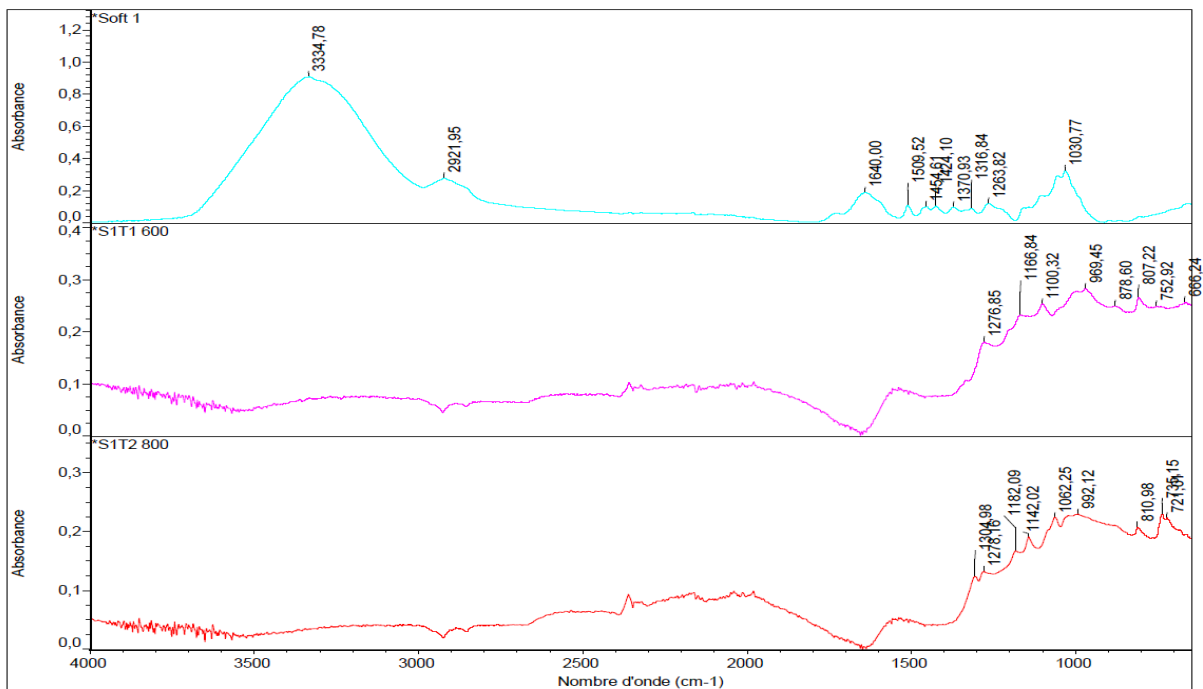


Figure A1-9: FTIR spectra of the raw softwood and formulated adsorbents at 600°C and 800°C with particle size $\leq 1\text{mm}$

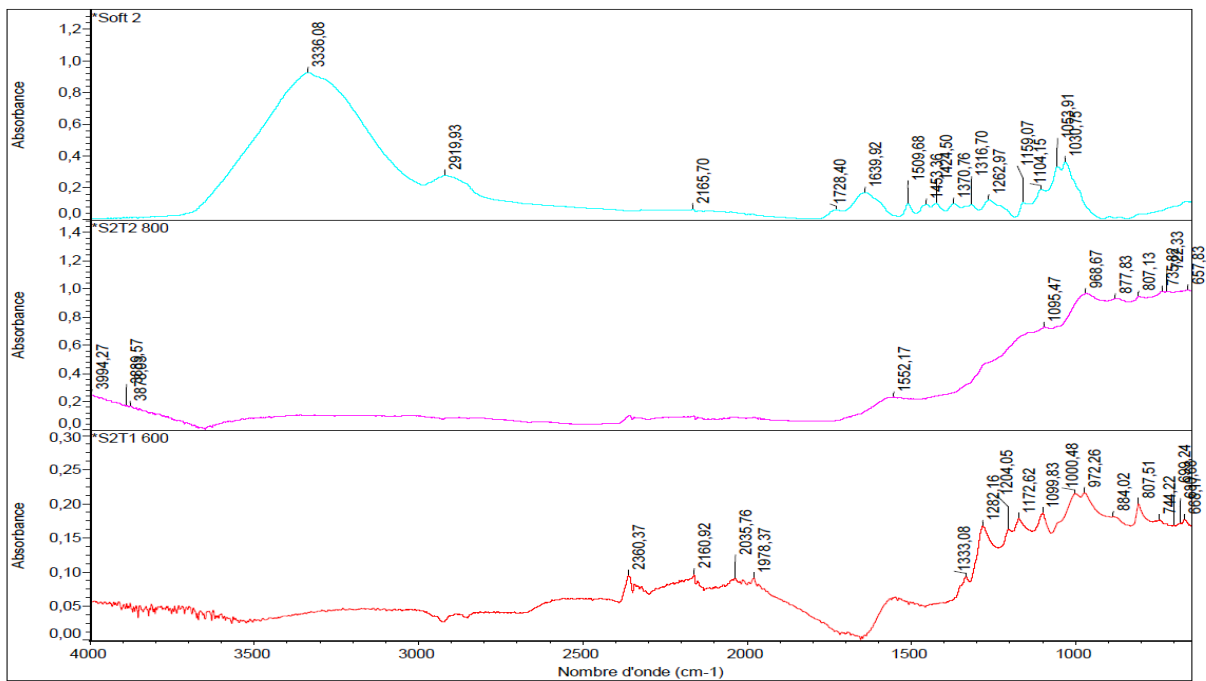


Figure A1-10: FTIR spectra of the raw softwood and formulated adsorbents at 600°C and 800°C with particle size $\leq 2\text{mm}$

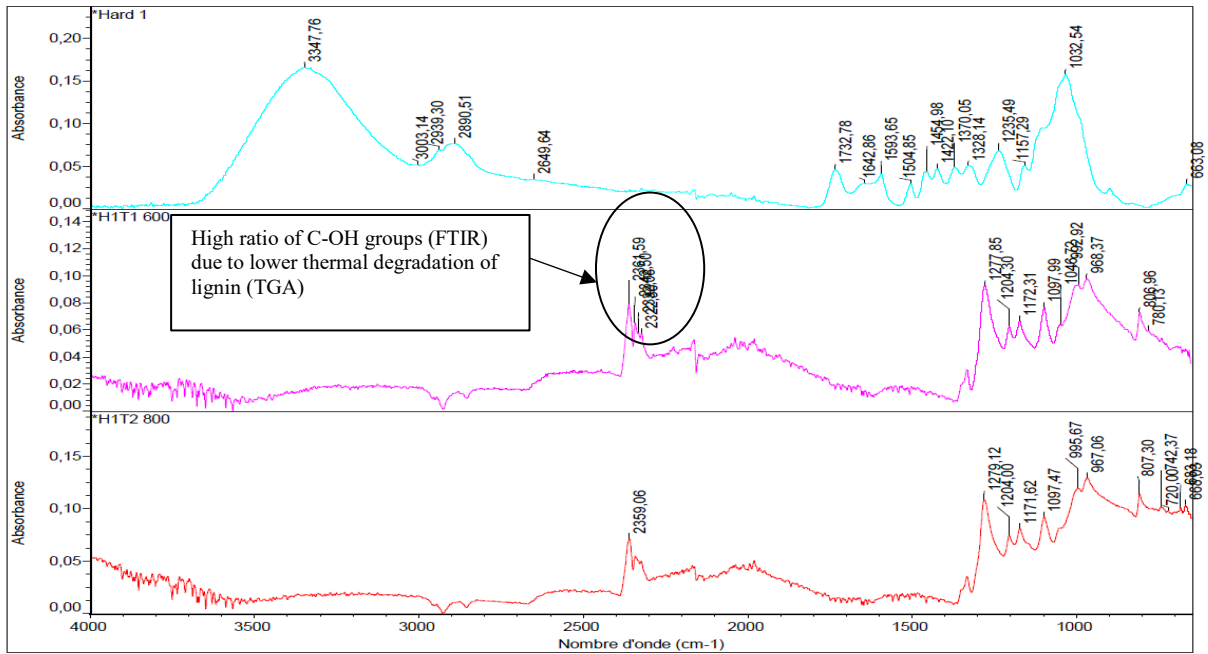


Figure A1-11: FTIR spectra of the raw hardwood and formulated adsorbents at 600°C and 800°C with particle size $\leq 1\text{mm}$

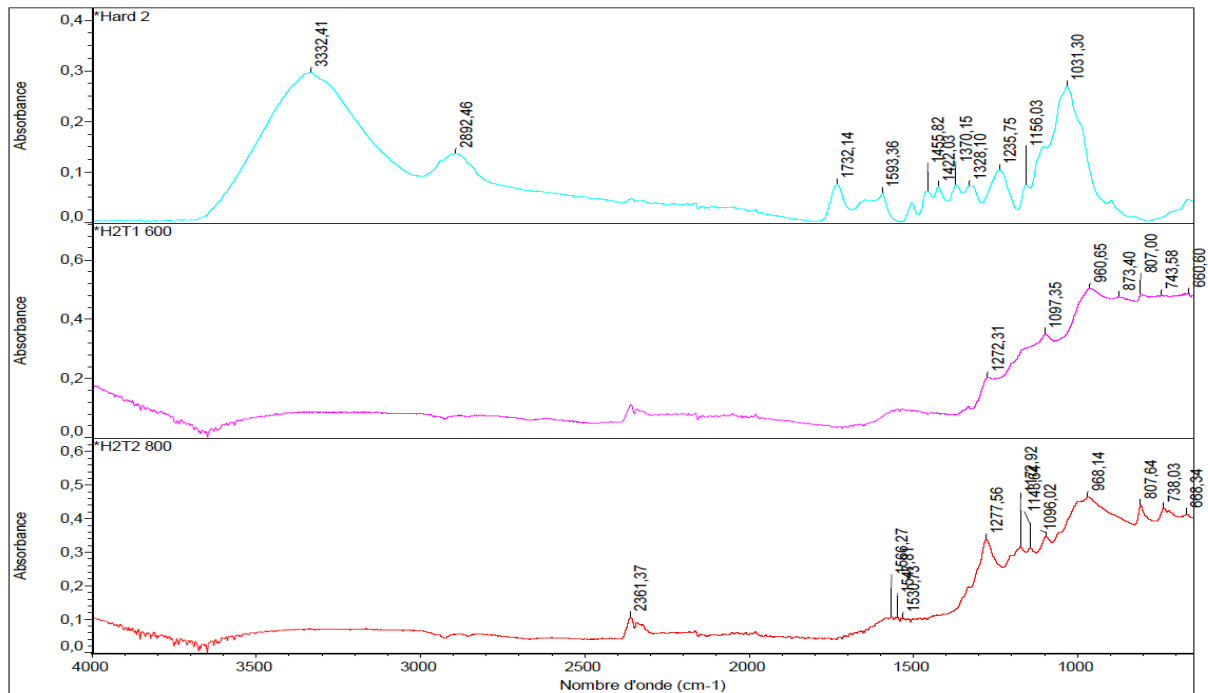


Figure A1-12: FTIR spectra of the raw hardwood and formulated adsorbents at 600°C and 800°C with particle size $\leq 2\text{mm}$

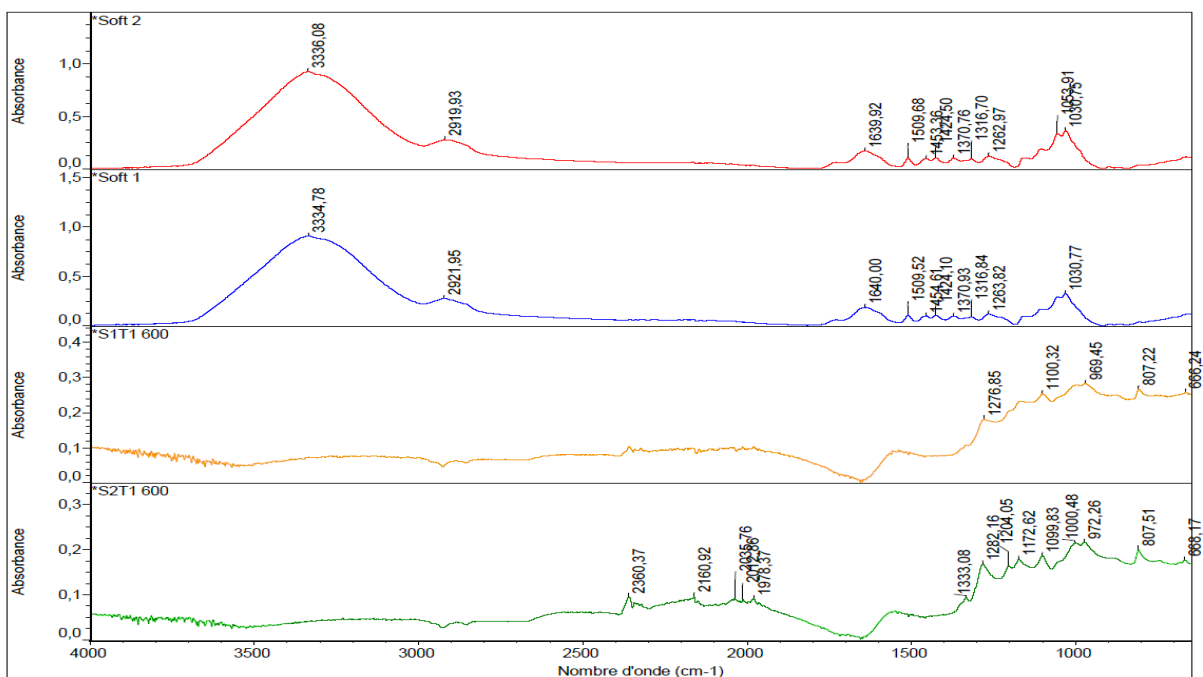


Figure A1-13: FTIR spectra of the raw softwood and formulated adsorbents at 600°C with particle size $\leq 1\text{mm}$ and $\leq 2\text{mm}$

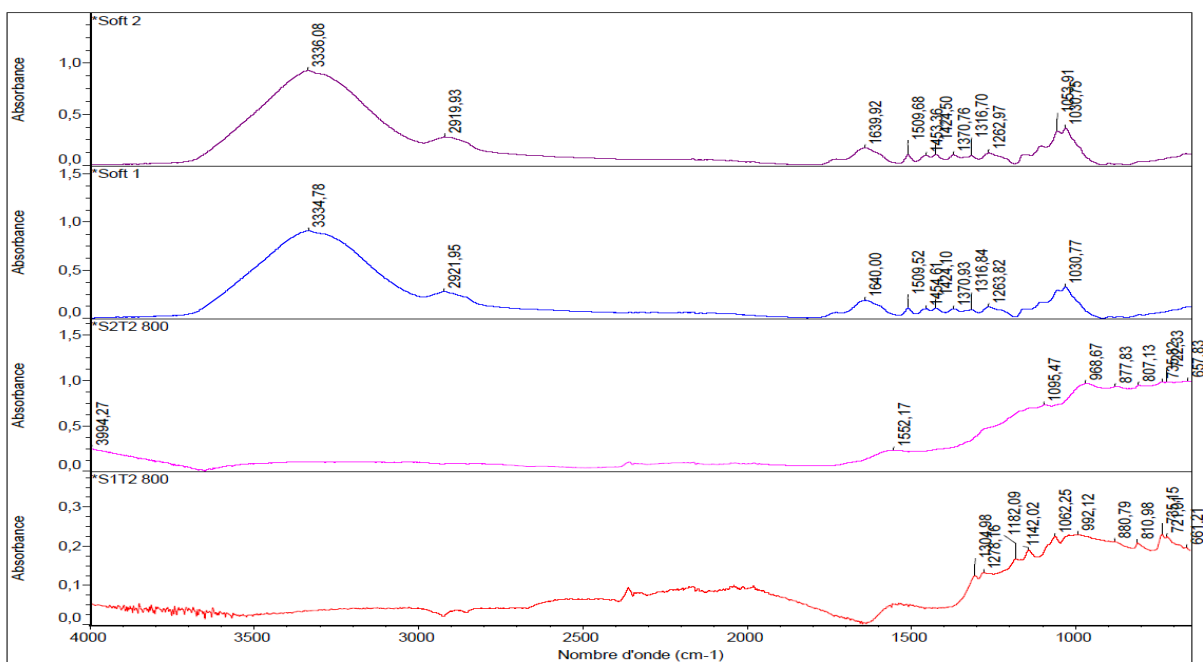


Figure A1-14: FTIR spectra of the raw softwood and formulated adsorbents at 800°C with particle size $\leq 1\text{mm}$ and $\leq 2\text{mm}$

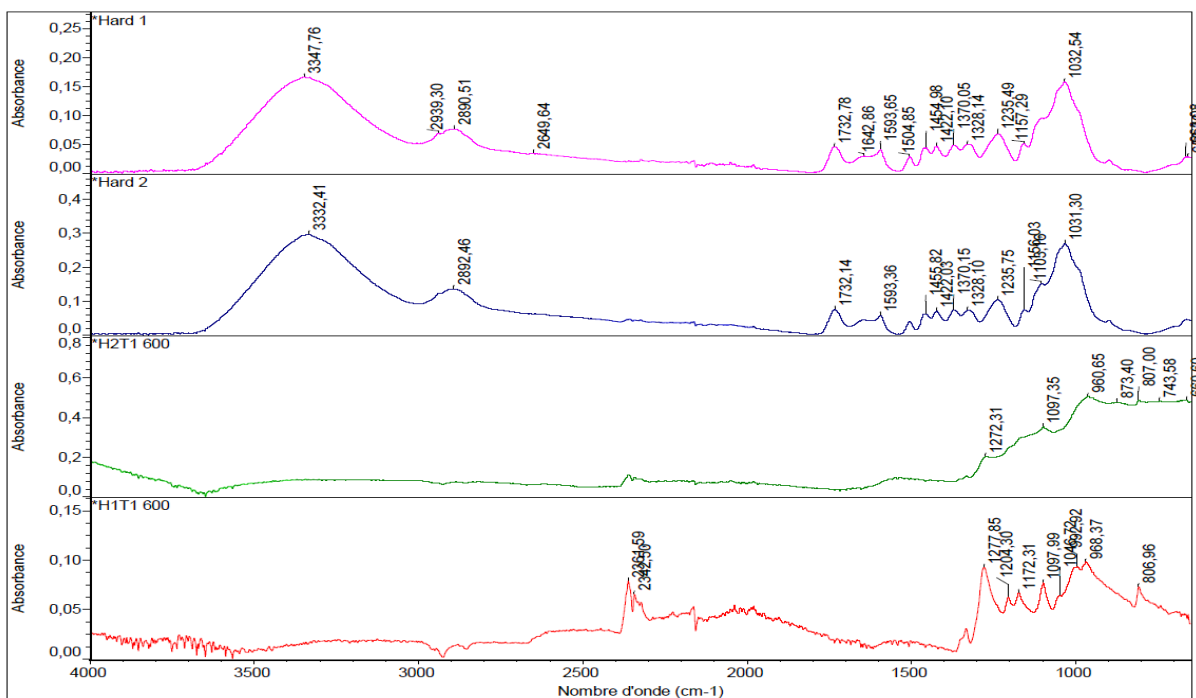


Figure A1-15: FTIR spectra of the raw hardwood and formulated adsorbents at 600°C with two particle size $\leq 1\text{mm}$ and $\leq 2\text{mm}$

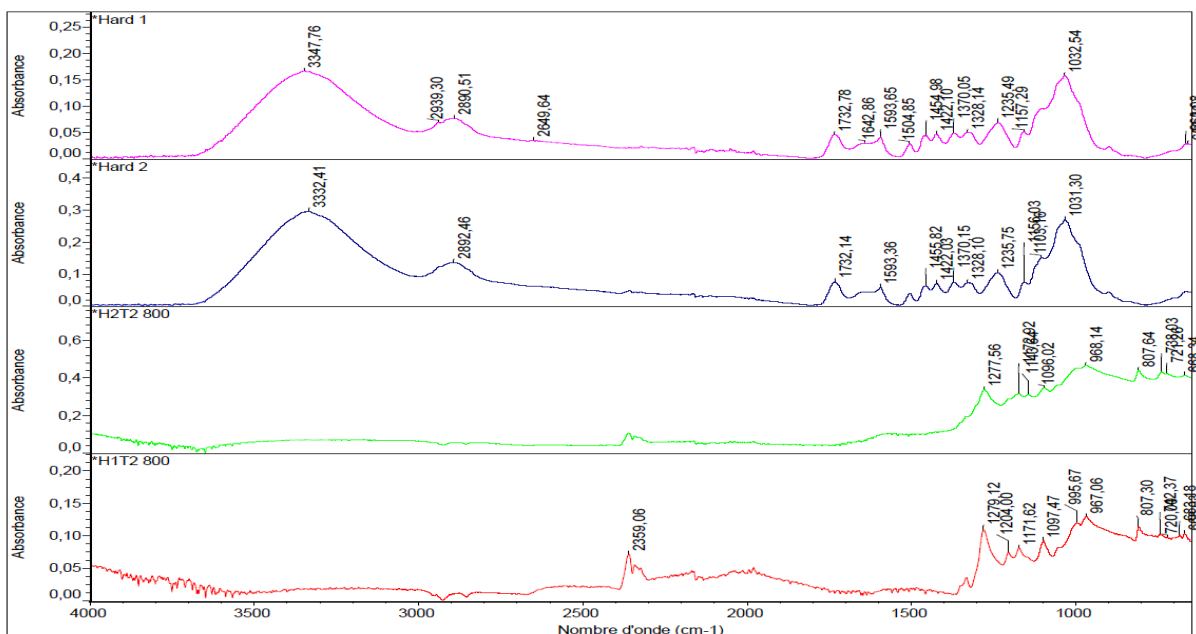


Figure A1-16: FTIR spectra of the raw hardwood and formulated adsorbents at 800°C with particle size $\leq 1\text{mm}$ and $\leq 2\text{mm}$

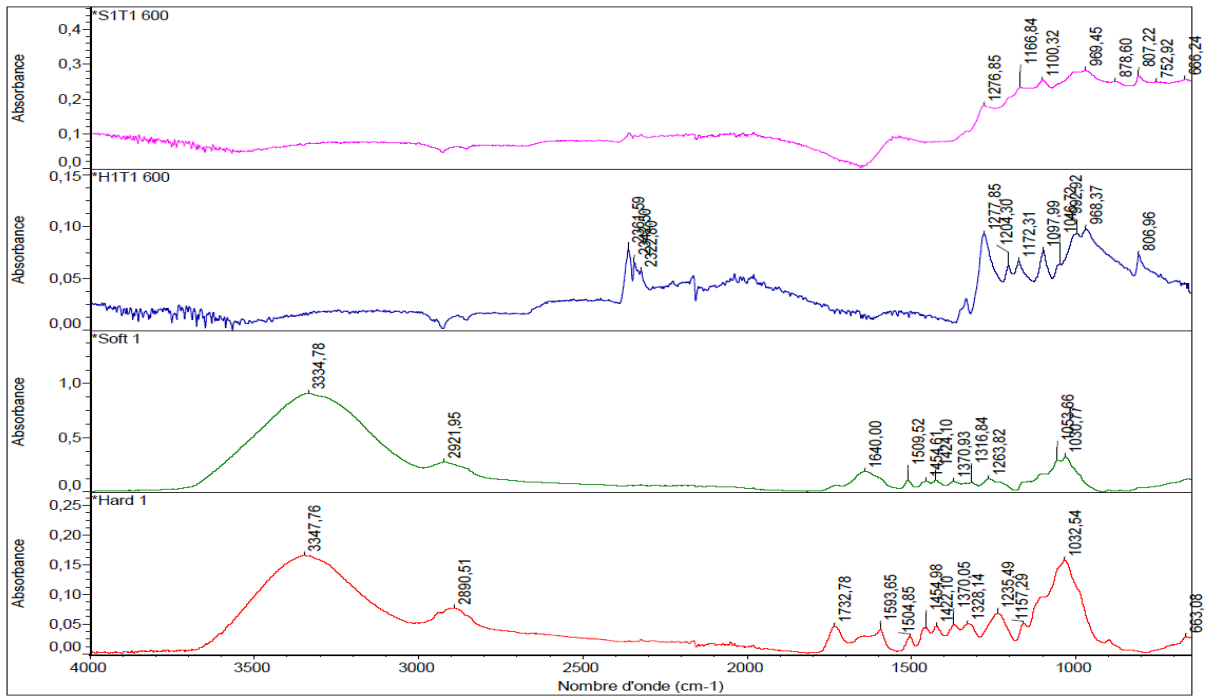


Figure A1-17: FTIR spectra of the raw softwood and hardwood and formulated adsorbents at 600 °C with similar particle size ≤1mm

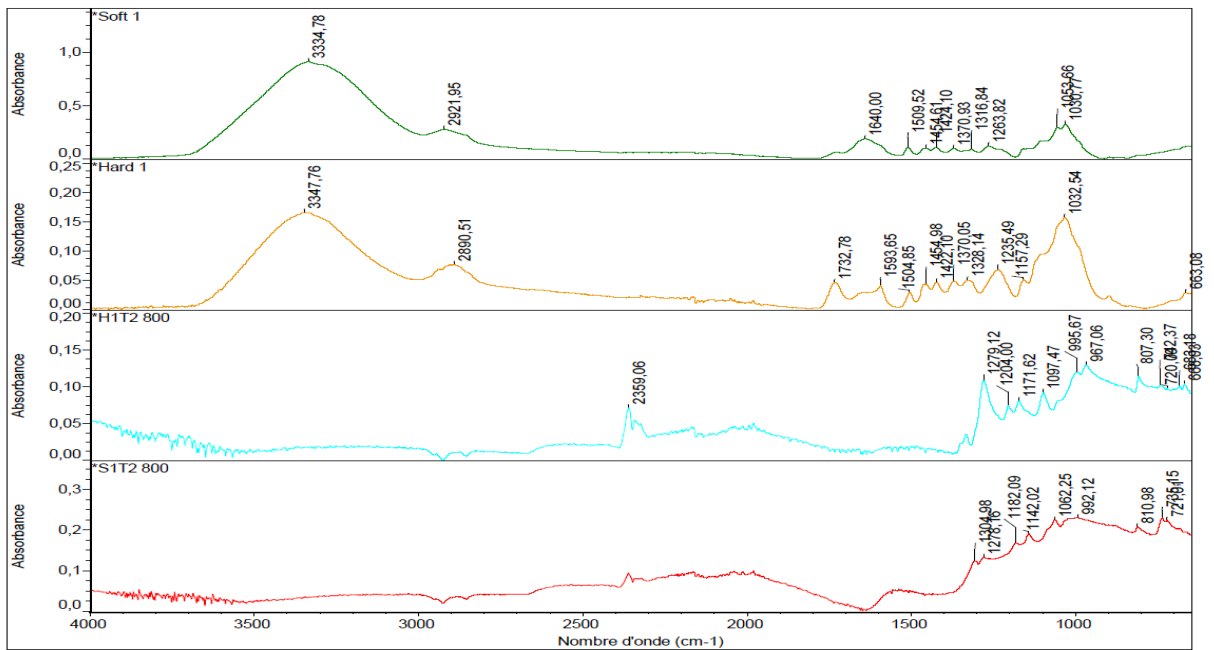


Figure A1-18: FTIR spectra of the raw softwood and hardwood and formulated adsorbents at 800 °C with similar particle size ≤1mm

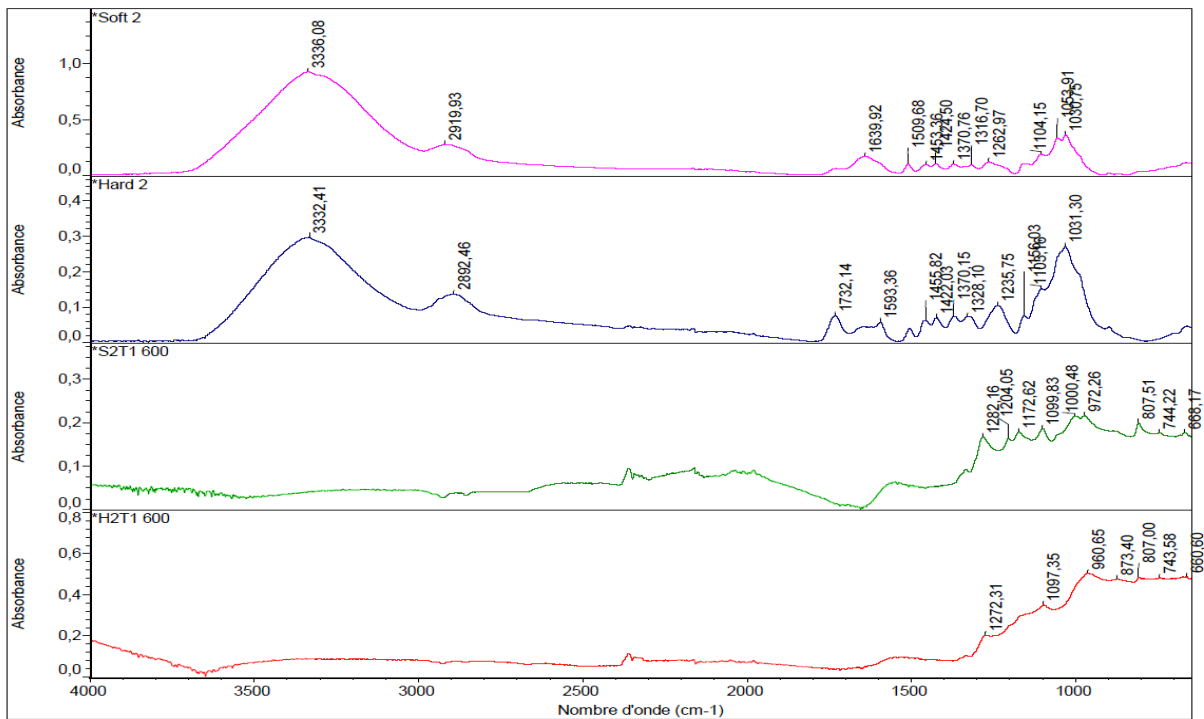


Figure A1-19: FTIR spectra of the raw softwood and hardwood and formulated adsorbents at 600°C with similar particle size $\leq 2\text{mm}$

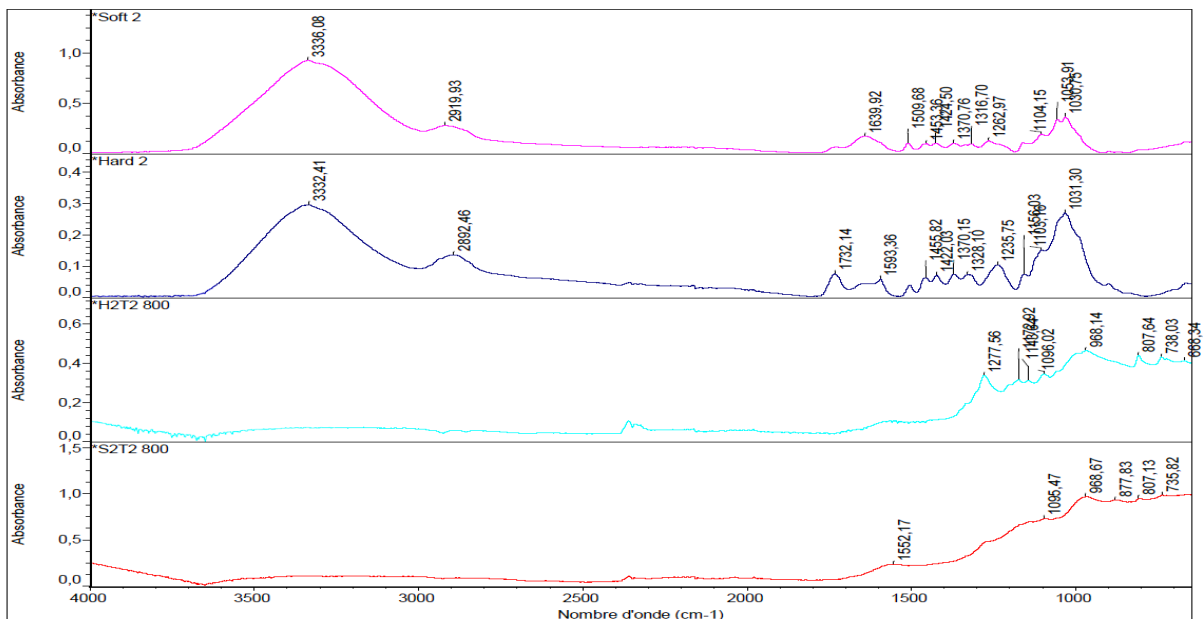


Figure A1-20: FTIR spectra of the raw softwood and hardwood and formulated adsorbents at 800°C with similar particle size $\leq 2\text{mm}$

11/15/2018

Quantachrome Instruments
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb 1 for Windows 1.53

File name: C:\QCdata\PhysData\HASSAN_SAMPLE1
Sample ID: Hassan_sample1 bet
Comments:
Operator: Gwenael
Analysis gas: Nitrogen
Adsorbate (DRP): Nitrogen
Outgas Temp: 300.0 °C
P/Po tolerance: 3
Station #: 1

Sample name: NAM

Description:
Sample weight: 1.3422 g
X sect. area: 16.2 Å²/molec
Bath Temp.: 77.30
Outgas Time: 48.0 hrs
Equil. time: 3
PC sw. version: 1.53
Non-ideality: 6.58e-05
Analysis Time: 106.5 min
End of run: 11/15/2018 11:20
TempComp: On

A ● BF —

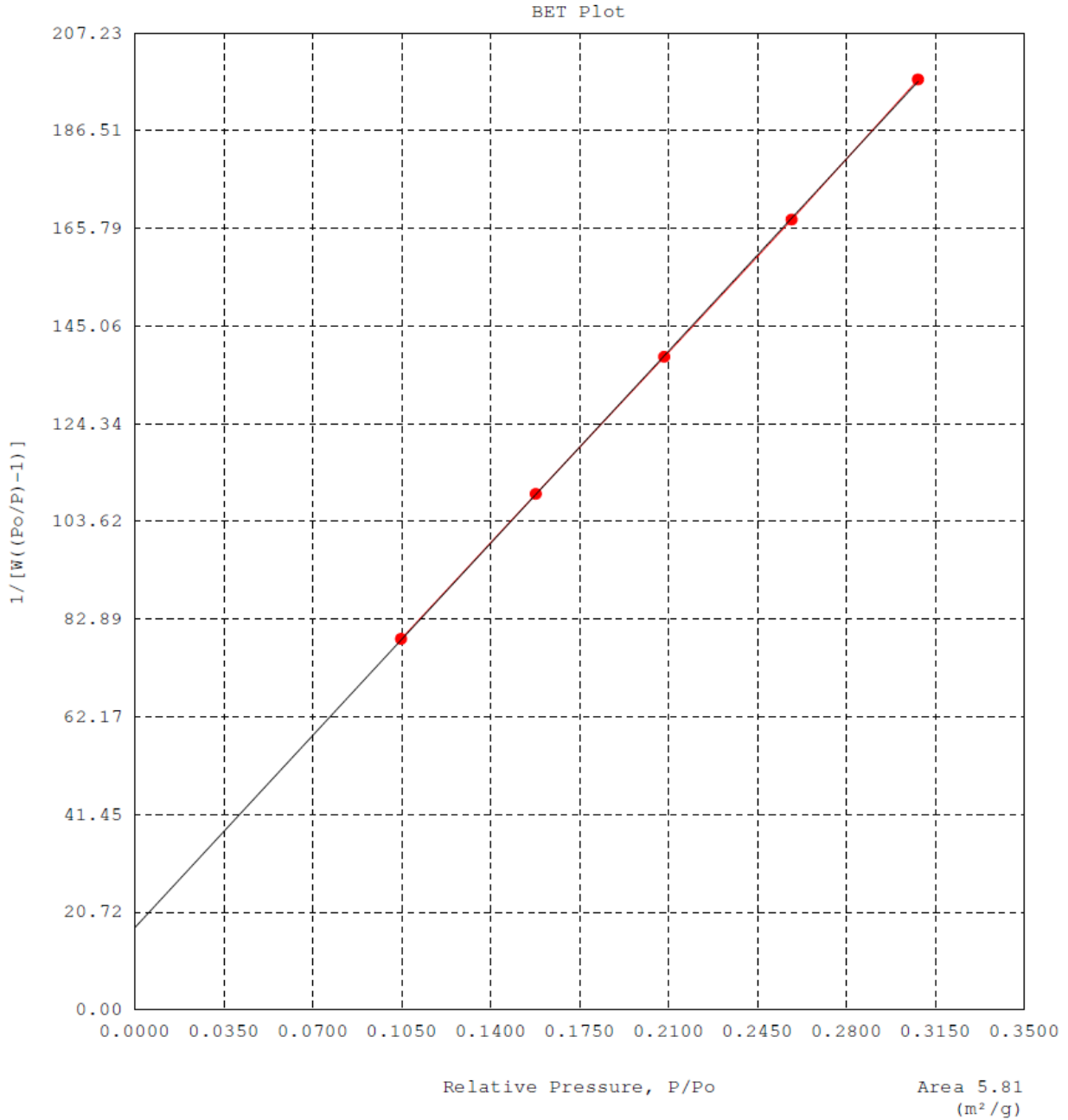


Figure A1-21: Brunauer Emmett Teller plot (BET) for NAM

11/15/2018

Quantachrome Instruments
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb 1 for Windows 1.53

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Sample ID: Hassan_sample1 bet
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Analysis gas: Nitrogen
Adsorbate (DRP): Nitrogen
Outgas Temp: 300.0 °C
P/Po tolerance: 3
Station #: 1

Description: **Sample name: NAM**

Sample weight: 1.3422 g
X sect. area: 16.2 Å²/molec
Bath Temp.: 77.30
Outgas Time: 48.0 hrs
Equil. time: 3
PC sw. version: 1.53
Non-ideality: 6.58e-05
Analysis Time: 106.5 min
End of run: 11/15/2018 11:20
TempComp: On

A ●—

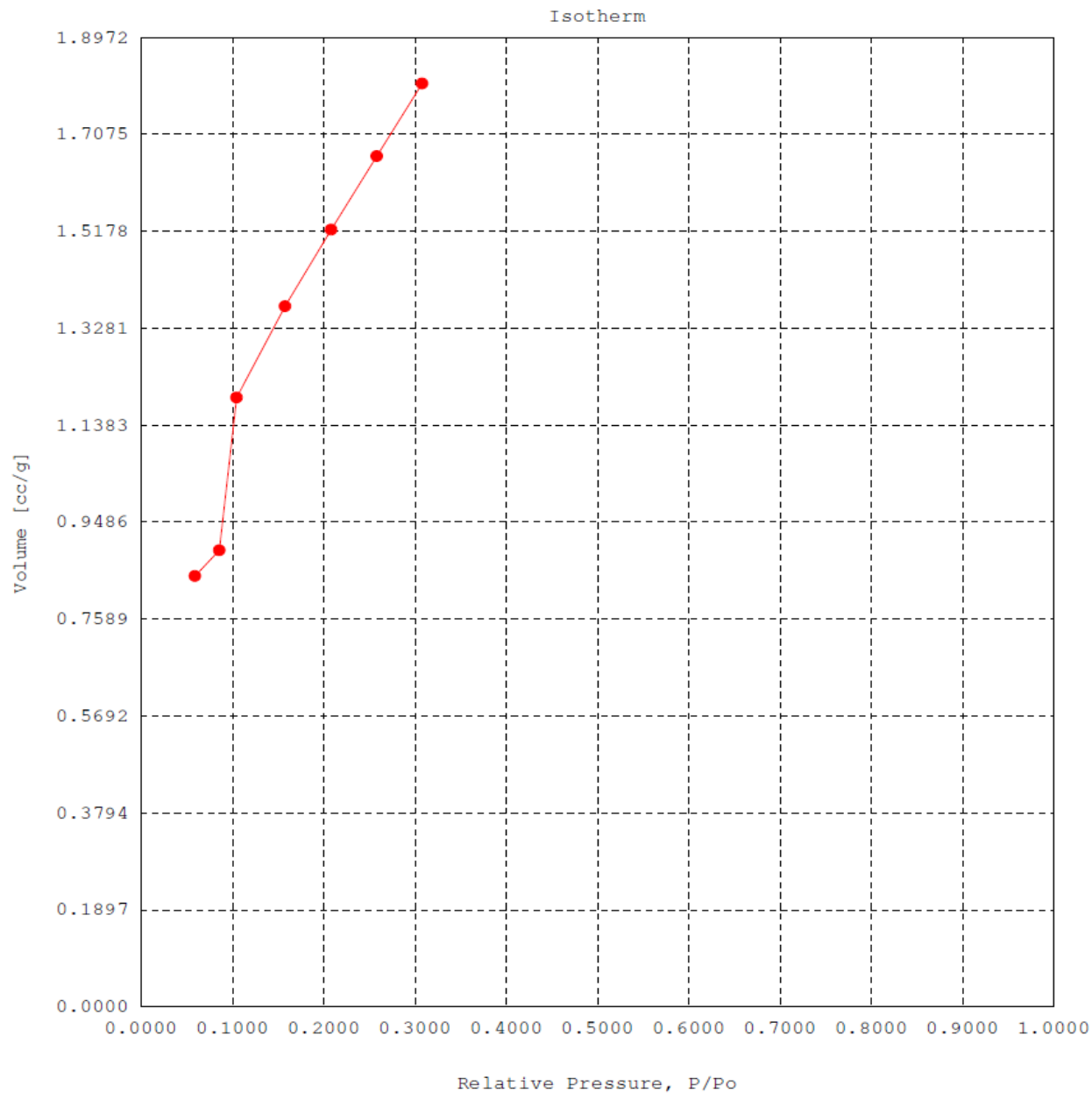


Figure A1-22: Brunauer Emmett Teller isotherm (BET) for NAM

09/27/2018

Quantachrome Instruments
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb 1 for Windows 1.53

File name: C:\QCdata\PhysData\ENMA.raw
Sample ID: Description:
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Operator: Gwenael
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Adsorbate (DRP): Nitrogen
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P/Po tolerance: 3
Station #: 1

Sample name: Chitin

Sample weight: 0.139 g
X sect. area: 16.2 Å²/molec
Bath Temp.: 77.30
Outgas Time: 3.0 hrs
Equil. time: 3
PC sw. version: 1.53
Non-ideality: 6.58e-05
Analysis Time: 95.9 min
End of run: 09/27/2018 14:18
TempComp: On

A ● BF —

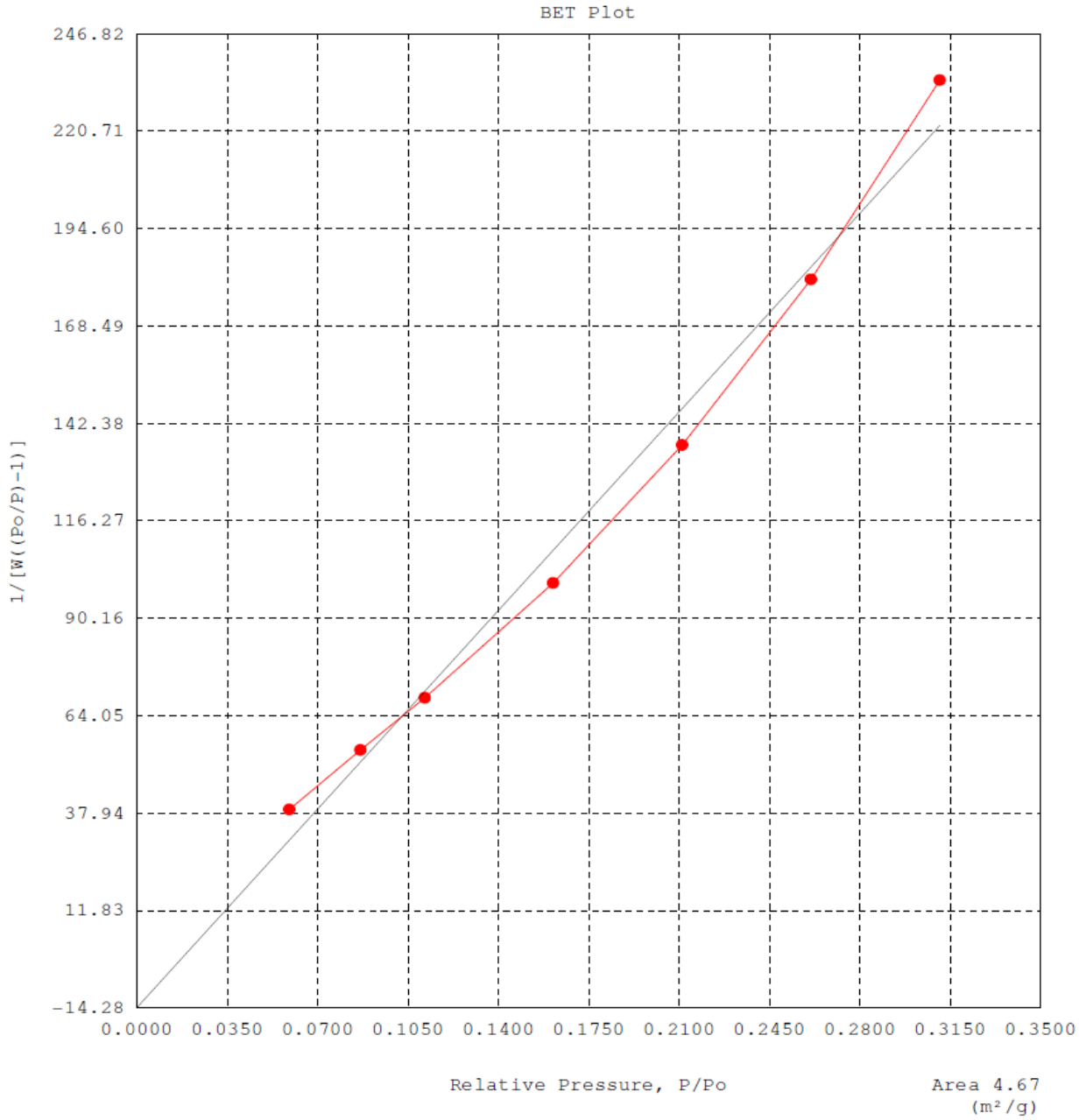


Figure A1-23: Brunauer Emmett Teller plot (BET) for chitin

09/27/2018

Quantachrome Instruments
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb 1 for Windows 1.53

File name:	C:\QCdata\PhysData\ENMA.raw	Sample name: Chitin			
Sample ID:	Description:				
Comments:					
Operator:	Gwenael	Sample weight:	0.139 g		
Analysis gas:	Nitrogen	X sect. area:	16.2 Å ² /molec	Non-ideality:	6.58e-05
Adsorbate (DRP):	Nitrogen	Bath Temp.:	77.30	Analysis Time:	95.9 min
Outgas Temp:	200.0 °C	Outgas Time:	3.0 hrs	End of run:	09/27/2018 14:18
P/Po tolerance:	3	Equil. time:	3	TempComp:	On
Station #:	1	PC sw. version:	1.53		

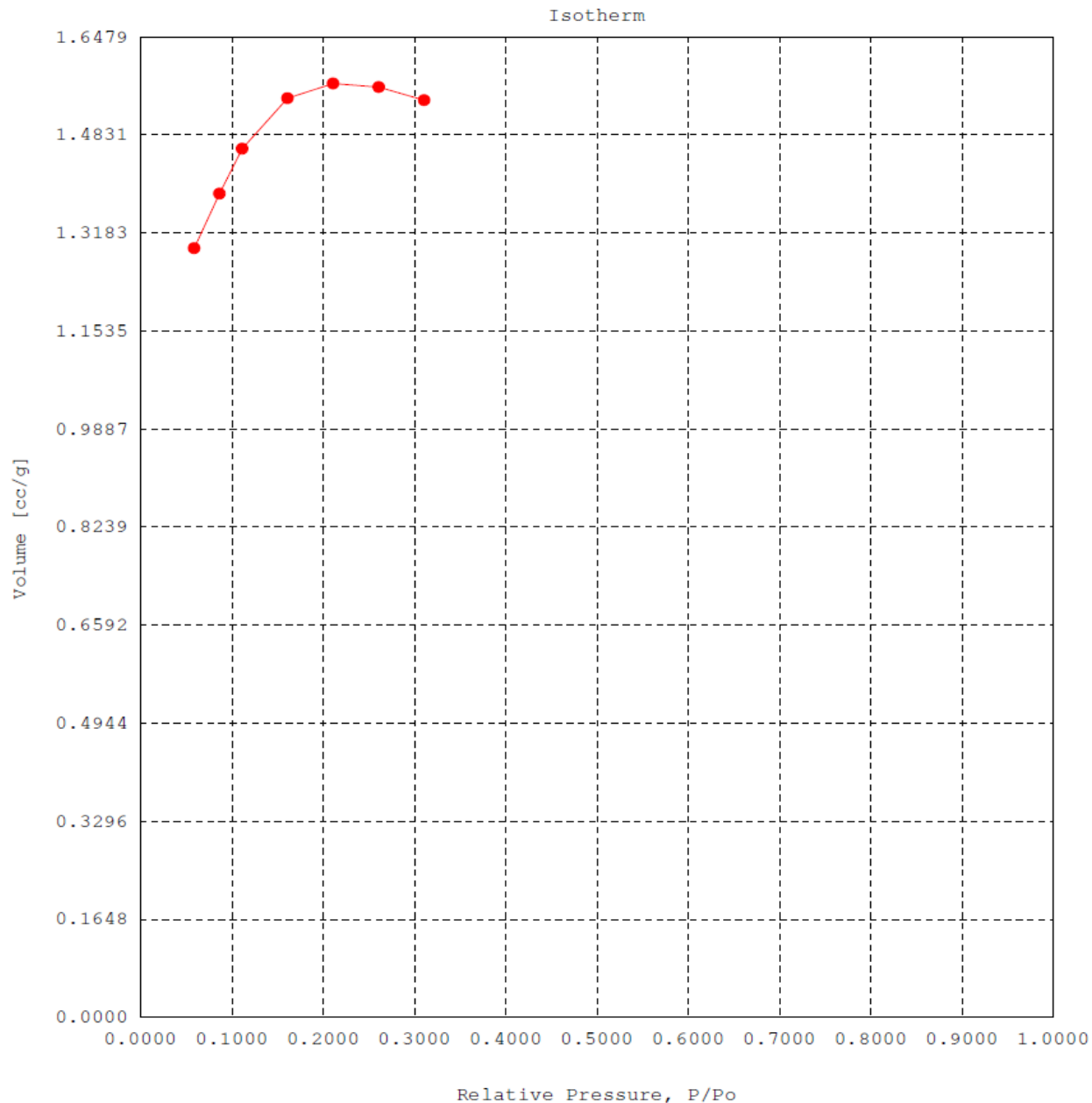
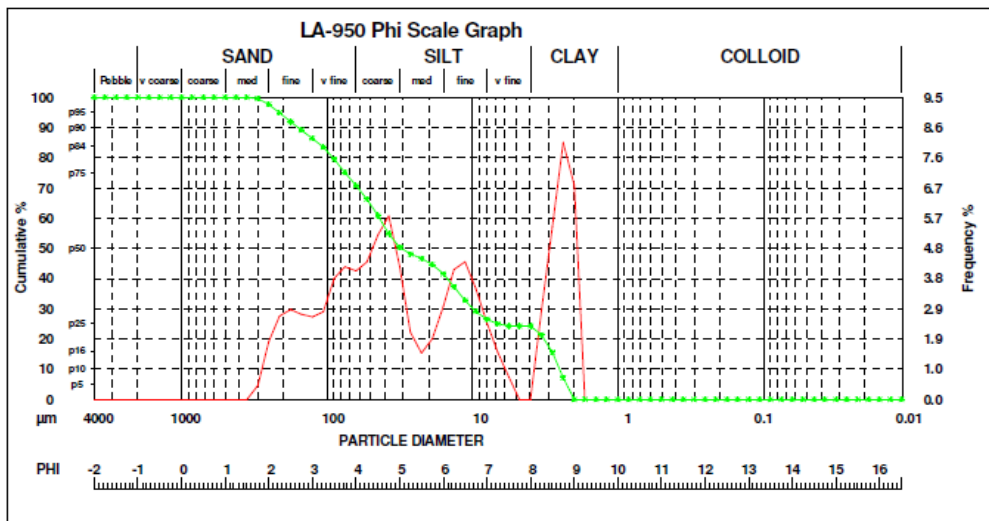


Figure A1-24: Brunauer Emmett Teller isotherm (BET) for chitin

HORIBA Laser Scattering Particle Size Distribution Analyzer LA-950

Sample Name	: 1UM STD	Median Size	: 30.66066(μm)
ID#	: 201808311413902	Mean Size	: 54.21790(μm)
Data Name	: 201808311413902	Variance	: 4440.6(μm ²)
Transmittance(R)	: 97.4(%)	Std.Dev.	: 66.6375(μm)
Transmittance(B)	: 98.3(%)	Mode Size	: 2.4260(μm)
Circulation Speed	: 6	Span	: OFF
Agitation Speed	: 4	Geo.Mean Size	: 22.1474(μm)
Ultra Sonic	: OFF	Geo.Variance	: 2.6678(μm ²)
Form of Distribution	: Manual	Skewness	: 1.7329
Distribution Base	: Area	Kurtosis	: 5.5142
Material	: STD	Diameter on Cumulative %	: (1)5.000 (%) - 2.2244(μm)
Source	: HORIBA		: (9)90.00 (%) - 157.0602(μm)
Sample Number	: 1		
Test or Assay. Number	: 1		
Refractive Index (R)	: Antonio_Mina_test[Quartz(1.440 - 0.100i),Water(1.333)]		
Refractive Index (B)	: Antonio_Mina_test[Quartz(1.440 - 0.100i),Water(1.333)]		



	Diameter				Diameter			Diameter				Diameter		
	Diameter	PHI	MILS	Microns	Frequency	Frequency	CUMULATIVE	Diameter	PHI	MILS	Microns	Frequency	Frequency	CUMULATIVE
F PEBBLE	5	-2.00	157.48	4000.00	0.00	0.00	100.00	V FINE SILT	8.00	0.15	3.28	2.89	0.00	24.21
	6	-1.75	132.42	3363.59	0.00	0.00	100.00		8.50	0.11	2.76	5.72	0.00	15.60
	7	-1.50	111.36	2828.43	0.00	0.00	100.00		8.75	0.09	2.52	8.51	0.00	7.09
FINE PEBBLE	10	-1.00	78.74	2000.00	0.00	0.00	100.00		9.00	0.08	1.95	7.09	0.00	0.00
	12	-0.75	66.21	1681.79	0.00	0.00	100.00		9.25	0.06	1.64	0.00	0.00	0.00
	14	-0.50	55.68	1414.21	0.00	0.00	100.00		9.50	0.05	1.38	0.00	0.00	0.00
V CRS SAND	16	-0.25	46.82	1189.21	0.00	0.00	100.00	CLAY	9.75	0.05	1.16	0.00	0.00	0.00
	20	0.25	33.11	840.90	0.00	0.00	100.00		10.00	0.04	0.99	0.00	0.00	24.21
	25	0.50	27.84	707.11	0.00	0.00	100.00		10.25	0.03	0.82	0.00	0.00	0.00
CRS SAND	30	0.75	23.41	594.60	0.00	0.00	100.00		10.50	0.02	0.69	0.00	0.00	0.00
	35	1.00	19.69	500.00	0.00	0.00	100.00		10.75	0.02	0.58	0.00	0.00	0.00
	40	1.25	16.55	420.45	0.00	0.00	100.00		11.00	0.02	0.49	0.00	0.00	0.00
	45	1.50	13.92	363.55	0.00	0.00	100.00		11.25	0.02	0.41	0.00	0.00	0.00
	50	1.75	11.70	297.30	0.45	0.45	99.55		11.50	0.01	0.35	0.00	0.00	0.00
MED SAND	60	2.00	9.84	250.00	1.90	2.36	97.64		11.75	0.01	0.29	0.00	0.00	0.00
	70	2.25	8.28	210.22	2.76	3.22	94.88		12.00	0.01	0.24	0.00	0.00	0.00
	80	2.50	6.96	176.78	2.97	3.94	91.92		12.25	0.01	0.21	0.00	0.00	0.00
	100	2.75	5.85	148.65	2.81	4.75	89.11		12.50	0.01	0.17	0.00	0.00	0.00
FINE SAND	120	3.00	4.92	125.00	2.73	5.48	86.38		12.75	0.01	0.15	0.00	0.00	0.00
	140	3.25	4.14	105.11	2.91	6.39	83.47		13.00	0.00	0.12	0.00	0.00	0.00
	170	3.50	3.48	88.39	4.01	7.40	79.47		13.25	0.00	0.10	0.00	0.00	0.00
V FINE SAND	200	3.75	2.93	74.33	4.39	8.79	75.08		13.50	0.00	0.09	0.00	0.00	0.00
	230	4.00	2.46	62.50	4.25	10.04	70.83		13.75	0.00	0.07	0.00	0.00	0.00
	270	4.25	2.07	52.56	4.54	11.58	66.29		14.00	0.00	0.06	0.00	0.00	0.00
	325	4.50	1.74	44.19	5.44	13.02	60.84		14.25	0.00	0.05	0.00	0.00	0.00
	400	4.75	1.46	37.18	6.07	14.09	54.77		14.50	0.00	0.04	0.00	0.00	0.00
CRS SILT	450	5.00	1.23	31.25	4.41	20.46	50.36		14.75	0.00	0.04	0.00	0.00	0.00
	500	5.25	1.03	26.28	2.21	22.67	48.15		15.00	0.00	0.03	0.00	0.00	0.00
	635	5.50	0.87	22.10	1.53	24.20	46.62		15.25	0.00	0.03	0.00	0.00	0.00
	5.75	0.73	18.58	2.00	8.83	26.20	44.61		15.50	0.00	0.02	0.00	0.00	0.00
MED SILT	6.00	0.62	15.63	3.08	8.83	31.28	41.54		15.75	0.00	0.02	0.00	0.00	0.00
	6.25	0.52	13.14	4.29	37.25	35.99	37.25		16.00	0.00	0.02	0.00	0.00	0.00
	6.50	0.43	11.05	4.55	32.69	31.54	32.69		16.25	0.00	0.01	0.00	0.00	0.00
	6.75	0.37	9.29	3.66	29.03	27.88	29.03	COLLOID	16.50	0.00	0.01	0.00	0.00	0.00
FINE SILT	7.00	0.31	7.81	2.53	15.03	25.35	25.35							
	7.25	0.26	6.57	1.56	24.95	23.79	24.95							
	7.50	0.22	5.53	0.74	24.21	22.05	24.21							
	7.75	0.18	4.65	0.00	24.21	20.30	24.21							

Figure A1-25: Particle sizes analysis of chitin

Appendix 2 - Mat Lab code using simulating annealing

```

input locations = [20 location];
% function f = plot locations (input locations)
% PLOT locations
% PLOT locations (input locations) plots the location of locations from the argument
% inputlocations. Inputlocations argument has 2 rows and n columns, where n is
% the number of locations. Apart from the location the symmetric route is also
% plotted.
shg
temp_1 = plot(inputlocations (1,:),inputlocations(2,:),'b*');
set(temp_1,'erasemode','none');
temp_2 = line(inputlocations(1,:),inputlocations(2,:),'Marker','*');
set(temp_2,'color','g');
x = [inputlocations(1,1) inputlocations(1,length(inputlocations))];
y = [inputlocations(2,1) inputlocations(2,length(inputlocations))];
x1 = 10*round(max(inputlocations(1,:))/10);
y1 = 10*round(max(inputlocations(2,:))/10);
if x1 == 0
    x1 = 1;
end
if y1 == 0
    y1 = 1;
end
axis ([0 x1 0 y1]);
temp_3 = line(x,y);
set(temp_3,'color','k');
dist = distance(inputlocations);
distance_print = sprintf('The roundtrip length for %d locations is % 4.6km
(inputlocations)',dist)%d means integer and not double;
text (x1/15,1.05*y1, distance_print,'fontweight','bold');
drawnow;
% end
function d = distance(inputlocations)
% DISTANCE
% d = DISTANCE (inputlocations) calculates the distance between n locations as
% required in a Traveling Salesman Problem. The input argument has two rows
% and n columns, where n is the number of locations and each column represent
% the coordinate of the corresponding location.
d = 0;
for n = 1: length(inputlocations)
    if n == length(inputlocations)
        d = d + norm(inputlocations(:,n) - inputlocations(:,1));
    else
        d = d + norm(inputlocations(:,n) - inputlocations(:,n+1));
    end
end

```