

**DESIGN AND OPTIMIZATION OF MEMBRANE
FILTRATION AND ACTIVATED CARBON PROCESSES
FOR INDUSTRIAL WASTEWATER TREATMENT BASED
ON ADVANCED AND COMPREHENSIVE ANALYTICAL
CHARACTERISATION METHODOLOGIES**

SALMAN ALIZADEH KORDKANDI, B.Sc., M.Sc.

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of the Requirements for the Degree Master of Applied Science

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METHODOLOGIES

AUTHOR: SALMAN ALIZADEH KORDKANDI, B.Sc. (UNIVERSITY
OF TABRIZ), M.Sc. (SAHAND UNIVERSITY OF TECHNOLOGY)

SUPERVISOR: Dr. DAVID LATULIPPE

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Lay Abstract

Aevitas is an industrial wastewater treatment plant, which is situated at City of Brantford. Every day, this plant receives about 15 trucks of mixture of wastewaters from many different industries. The input wastewater into the plant should be treated and meet the environmental standard so that it can be discharged into municipal wastewater plant. Currently, the maximum allowable chemical oxygen demand (COD) for discharging the treated wastewater from Aevitas to municipal wastewater treatment plant is 600 ppm. Despite the fact, the current system in Aevitas is not efficient to meet this criterion. Thus, we strive to design efficient processes to overcome the problem. To this end, 75 samples were collected from Aevitas to observe the kind of chemicals that are the source of COD and then, two processes including activated carbon adsorption and membrane filtration were used for further reduction of COD. Although activated carbon can reduce the COD, the limited adsorption capacity was a major concern for its long-term application, especially if the COD of influent wastewater is higher than 2000 ppm. Membrane filtration was used as an alternative for activated carbon and the results showed that membrane could reduce the COD below 600 in the 48% of the cases.

Abstract

Aevitas is an industrial wastewater treatment plant that receives about 300 m³/day of mixture of wastewater from different industries. Chemical oxygen demand of higher 600 ppm and the variety of the chemical constitution of industrial wastewater are two significant problems on Aevitas. Therefore, there is a strong need for developing advanced analytical techniques that can identify the specific compounds that are the source of COD. During 10 months, about 75 industrial samples were characterised using a battery of tests including GC/MS, COD, TOC, and pH to identify the chemicals that are main source of COD in the industrial wastewaters. Results showed that the COD of 87% of 75 provided samples from Aevitas plant were higher than 600.

At the first step of process design, activated carbon was used to eliminate the identified organic chemicals from the wastewaters. The maximum and minimum of COD removal (depends on the chemical composition) of the wastewaters were obtained as 94 and 24%, respectively. Moreover, the amount of COD and TOC that can be adsorbed on the surface of 1 gram of the activated carbon were 25 and 7 mg, respectively. Although activated carbon is capable to reduce the COD, its capacity of adsorption is limited. To overcome this problem an alternative process, membrane filtration was applied for COD removal.

Two types of crossflow NF (NF270, NF90, NFX, NFW, NFS, TS80, XN45, and SXN2_L) and RO (BW60 and TW30) membranes in two modules of spiral wound and flat sheet were used. The filtration results of 11 different industrial wastewaters showed that NF90, TS80, NFX, and NFS were effective in COD removal. However, in terms of output flux NFX and NFS flat sheet were better than others were. Similar to the activated carbon process, the COD removal in filtration process was between 30 and 90%. The obtained results can be used to scale up the membrane filtration process at Aevitas.

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1. Introduction and Background

In any kind of wastewater treatment, two methods of handling are used for processing the pollutants, one is water in liquid form, (which is the main constituent of the wastewater) and the other method is attributed to the solid part or the sludge which has been dispensed in the water. In addition, there are several kinds of wastewater including municipal wastewater (i.e. from schools, offices, residential buildings, and so forth), industrial wastewater (i.e. textile, brewery, leather, automotive, and so forth), and storm water (i.e. rainwater) [1]. The wastewaters must be treated before being discharged to the natural environment for several reasons [2]:

- To prevent suspended solid from discharge back to the natural environment.
- To prevent aquatic system and wildlife from potential hazardous chemicals.
- Human health concern.
- To recycle the water for the matter of water scarcity.

The wastewater must be characterized before choosing the treatment technique. Generally, three categories of characterization, physical (i.e. color, odor, temperature, turbidity and so on), chemical (i.e. organic compounds, nutrients and dissolved solids), and biological (i.e. bacteria, viruses, and parasites) are investigated. High amount of organic carbon is one of the major concern that has been at the center of attention due to the cause of oxygen depletion in aquatic system. The organic compounds that are existed in the industrial wastewater have some common and significant properties:

- Some of them are combustible.
- Their boiling or melting points are not high
- Less soluble in water
- Are available in high molecular weight (Mw)

- Almost forms the main component of food for aquatic existents.

There are several sources for production of organic chemicals, natural (i.e. vegetable, natural oil, cellulose, and starch), synthetic (plastic, rubber, and polymer), and biotechnology (alcohols, antibiotic, and organic acid). When the organic compounds are discharged into the environment, depending on their physiochemical properties, different rates of degradation are observed. Microorganisms can easily degrade organic compounds like alcohol, organic acid, and starch. However, on the other hands, non-biodegradable organic compounds like Polycyclic Aromatic Hydrocarbons (PAHs) have a toxic effect on aquatic system in some cases where it has been exposed to the microorganism. Since the treatment of the PAHs (i.e. biocide, industrial waste, cellulose, and phenol) is difficult in the natural environment, they stay in ecosystem for a long time. Increasing the amount of organic compounds in water carries many undesirable effects on ecosystem. For example, producing Trihalomethane (a carcinogenic chemical) as a result of oxygen depletion can be occurred at high concentration of organic matter in water. Although the amount of total organic carbon (TOC) can be measured accurately by TOC analyzer as a parameter for defining the quality of water, two other criteria named Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) are also common to express the quality of water too. However, most of the industrial wastewaters contain toxic chemicals, and thus BOD cannot be a proper criterion to express the quality of the effluent.

1.1. Single source industrial wastewater properties

Despite the fact that Canada is one of the most successful countries in waste reclamation, about 411 million litres of wastewater still needs to be treated before being discharged to the natural environment [3]. The standard for discharging an industrial wastewater depends upon the guidelines endorsed by the regional government or local cities. Factors influencing

these rules are the availability of the water source and the infrastructure for shipping of the wastewater into the treatment plant. The quantity and quality of the industrial wastewater depend on the industries that produce the wastewater. Mining, food, petroleum, pigment, beverage, pulp and paper, tanning, oil, and textile industries can be considered as the main sources of wastewater in Canada [4]. In most cases, organic matter makes up to 70% of the solid portion of wastewater.

For example, in food industry, several processes are used to produce the final product and the type of products affects the composition of output wastewater from this industry. Although the applied processes can influence the final product, there are some common features among the wastewater from food industries [5] which have been listed as below:

- High amounts of proteins and fats and carbohydrates[6]
- A bioprocess can be used to eliminate the organic matters and the nitrogen simultaneously [7]
- Most of the time, the ratio of the main substrate such as carbon, nitrogen, and phosphorous is not balanced for biodegradation processes [8]. For example, the wastewater from potato processing industry contains high amount of starch, which is an added source of organic carbon. For biodegradation of the organic carbon by bacteria, sources of phosphorous and nitrogen should be added to the bioprocess to keep the treatment efficient.

The wastewater from food industries are the output of three main applications; 1) transportation, 2) cleaning, and 3) processing. To treat these industrial wastewaters several consecutive processes including sedimentation, flocculation, coagulation, and oxidation are needed to reduce the COD to an acceptable level. For example, to treat wastewater from

slaughterhouse or French fries processing, a grease separation from the water can be of great help for the next treatment steps. In addition, in the brewery industry, most of the volume of the water is spent on the cleaning of the barley and usually every 100 kg of barley produce about 700 litre of wastewater, which contains both fibres, minerals, and proteins. Although the composition of an industrial food wastewater is non-toxic, its volume and COD is relatively high [9]. The following table is provided to show the characteristics of an industrial food wastewater. Several papers published their results regarding the industrial food wastewater treatment.

Table 1. Characteristic of food industrial wastewater [10].

Industry	TS (ppm)	TP (ppm)	TN (ppm)	BOD (ppm)	COD (ppm)
Flour and Soybean	-	3	50	600-4000	1000-8000
Palm oil mill	40	-	750	25	50
Sugar-beet processing	6100	2.7	10	-	6600
Dairy	1100-1600	-	-	800-1000	1400-2500
Corn milling	650	125	174	300	4850
Potato chips	5000	100	250	5000	6000
Baker's yeast	600	3	275	-	6100
Winery	150-200	40-60	310-410	-	18000-21000
Dairy	250-2750	-	10-90	650-6250	400-15200
Cheese dairy	1600-3900	60-100	400-700	-	23000-40000
Olive mill	75500	60-100	400-700	-	130100
Cassava starch	830	90	525	6300	10500

For example, in a study conducted by Béatrice, reverse osmosis (RO) membrane has been used for treating dairy industry wastewater [11]. For tracking the treatment efficiency of the RO process, two parameters, TOC, and conductivity of the samples were measured. The calculation of their results indicated that 540 m² of RO membrane is required to treat 100 m³ of wastewater per day with 95% water recovery [11]. Membrane processing technology with a flux of around 11 Lh⁻¹ m⁻² was used for the treatment of that wastewater and the content of TOC in the permeate sample of the filtration was measured as 7 ppm while the conductivity dropped down to 50 μScm⁻¹ [12].

Automotive industry is another industry that needs high volume of water. The water in this industry is used for rinsing different parts of the cars which need to be coated or finished [13]. These type of wastewaters contain high amounts of oil and grease[14], hence, the concentration of the organic chemicals in the wastewater is high, especially oily-based compounds. The oil generally forms an unstable emulsion, oily wastewater emulsion or a totally immiscible mixture [15]. While the oil content can be separated from an immiscible mixture or unstable emulsion by physiochemical treatments, the oily wastewater emulsion cannot be easily separated using conventional techniques due to the presence of surfactants, which form a solution/emulsion with very small drops in micro size. In an effort made by Bo Lai et.al coagulation-flocculation process was used for COD removal from automobile manufacturing industrial wastewater [16]. The initial COD of 1222 was undergone treatment process and after 30 min of reaction the COD dropped down to about 120 [16]. An ultrafiltration flat sheet membrane has been used for metal, COD, and BOD removal from automobile manufacturing wastewater [17].

The wastewater from textile and dye manufacturing industries have different influences on natural environment. Since several processes (i.e. wool and cotton) are involved in fibre

finishing and preparation, a variety of compounds are expected to be in the wastewater. The important sources of pollution in textile wastewater are from scouring, mercerizing, bleaching, dyeing, printing, and carbonization. Some of the produced pollutants during the process are toxic and some of them damage the environment aesthetic. Analysis of the composition of textile wastewater showed that the main cause of colour in the wastewater are some azo bond, aniline, hydroquinone and naphthol chemicals, which are fluorescent organic compounds. The following Table shows the characterisation of dyeing wastewater that have been taken from seven different industries.

Table 2. Characteristic of seven textile wastewaters which have been used for manufacturing different types of textile material [18].

Parameters	Category						
	1	2	3	4	5	6	7
BOD ₅ /COD	0.2	0.29	0.35	0.54	0.35	0.3	0.31
BOD ₅ (ppm)	6000	300	350	650	350	300	250
COD (ppm)	8000	1040	1000	1200	1000	1000	800
Oil and Grease (ppm)	5500	-	-	14	53	-	-
TSS (ppm)	8000	130	200	300	300	120	75
Phenol (ppm)	1.5	0.5	-	0.04	0.24	0.13	0.12
Colour (ADMI)	2000	1000	-	325	400	600	600
PH	8	7	10	10	8	8	11
Temp. (°C)	28	62	21	37	39	20	38
Water usage (1 kg ⁻¹)	36	33	13	113	150	69	150

Long Wu et.al made an effort to modify activated carbon via non-thermal plasma to improve the adsorption of cupric ions [19]. The results revealed that adsorption capacity of modified activated carbon improved by 150% relative to the pristine activated carbon [19]. In another work the bamboo based activated carbon has been synthesized for adsorption of phenol and pharmaceuticals with the amine-functionalized magnetic group [20]. In a study by Tawfik et. al. a developed model on phenol adsorption process showed that the maximum

adsorption capacity of activated carbon was 18.12 mg per gram of activated carbon modified by diethylenetriamine [21].

In steel and iron wastewater treatment process a significant amount of acid, dust, oil and grease should be removed as the casting in blast furnaces involves these pollutants [22]. During the finishing process coke ovens needs the most volume of the water for cooling down the temperature of hot coke and the oven. Normally 0.4 L of water is need to produce 1 kg of coke, however, many toxic contaminants including cyanides, ammonia, phenol, and thiocyanate will be added into the water. Although the amount of soluble COD is not a matter of concern in this wastewater, the concentration of very toxic chemicals is higher than the standard range.

1.2. Multi-source time-varying industrial wastewater properties

As mentioned in the previous section most of the works that have been done in this area are the industrial wastewater treatment from only one source of wastewater production and the pollutants in them are somehow predictable. While the challenges of multi-sources industrial wastewater treatment is the introducing a versatile technique to remove the high amount chemical pollutants so that the wastewater (after treatment) can be discharged into municipal wastewater treatment plant. Principally, there are two options for eliminating these pollutants, first one is using on-site treatment package and the other one is shipping the wastewater from industrial site to a central plant for further treatment [1]. Each option has its merits and demerits, however, offsite treatment owing to the low cost of facility establishment in terms of the volume of the wastewater being treated, planning, and operations are more favourable for multi-source industrial wastewater treatment [23]. The difficult task is to find the best match treatment for each wastewater with a different chemical composition. To construct an effective treatment plant, a comprehensive

characterisation of input industrial wastewater is significant. Knowing the source of the wastewater is helpful to have an idea about the majority of the chemicals that have been released in the output wastewater from industries, however, for some reasons the information from all industries is not available [24, 25]. In such occasions, a comprehensive analytical method should be developed to clarify the composition of the mixture. Mixing different wastewaters also needs a high level of safety as some chemicals might react when they are mixed. To assess and reduce the risk of any undesirable action, those industries that are potential to produce hazardous or explosive chemicals should be determined and their wastewater should be carried via different trucks. The produced wastewater from organic chemical manufacturing plant could be a good example for mixture of different wastewater as it includes many chemicals.

Table 3. Characteristic of a typical chemical manufacturing wastewater containing a wide range of organic chemicals[1, 26].

Product	BOD (ppm)	COD (ppm)	TSS (ppm)
Phthalic acid anhydride and maleic acid anhydride	-	150-300	20-50
Methyl acrylate acid	-	7000-12000	6000-12000
Butadiene and styrene	4000-8000	2000-3200	50-100
Isocyanates	300-600	900-1600	200-500
Acrylates	1000-2000	800-1500	20-40
Ethylene and propylene	400-600	800-1200	40-75
Methyl and ethyl parathion	2000- 3500	4000-6000	50-100
Acrylic nitrile	200-500	600-1200	80-150
Raw materials for the pigment industry	200-400	1000-2000	80-200
Esters	5000-12000	10000-20000	20-100
Organic acids	300-600	40000-60000	150-300
Ketones	10000-20000	5000-15000	100- 200
Acetaldehyde	15000-25000	20000-40000	50-100
Organic phosphate compounds	500-1000	1500-3000	200-400

Usually, water in complex chemical industries is used for cooling, transportation of waste, raw material, and solvent. The following table represents typical characteristics of a chemical manufacturing wastewater. In 2011, Bianco et .al used Fenton process for treating complex wastewater. They consider COD removal as a criterion for the effectiveness of the process [27] and on average 80% of the COD has been removed from the complex wastewater. In another attempt that was intended to treat the mixture of different industrial wastewaters from foodstuff, dye house, refinery, electrochemical, and chemical industries, an RO system is used for separation of wide range of contaminants [28]. In a similar case a Nanofiltration integrated with forward osmosis was applied to reduce COD from mixture of different wastewaters and at the transmembrane pressure of 12 bar a chemical removal of 99% was obtained [29]. Moreover, Marko showed that NF90 could remove more than 70% of dissolved organic carbon from rendering plant wastewater [30].

1.3. Motivation and objective of the project

As mentioned in the introduction and background sections, some general reasons have been given for why industrial wastewater should be treated, and as this is an important ecological and economical issue, the governments of Canada and Ontario put a new strict standard on the effluent quality. The Wastewater Systems Effluent Regulations (WSER), which were established by the federal Fisheries Act in 2012 and came into force in 2015, are a new set of national effluent quality standards. The first compliance deadline for ‘high risk facilities’ to meet the WSER criteria is December 2020 and thus there is a pressing need for improved treatment technologies for industrial wastewater sources. One of these facilities is Aevitas that works on industrial wastewater treatment and the plant is situated at City of Brantford, Ontario. This plant is an off-site wastewater treatment plant and receives about 300 m³ (on average) of mixture of different industrial wastewaters from

several industries every day. To treat this volume of wastewater by meeting the standard criteria, Aevitas is applying several consecutive processes. According to Fig. 1, the mixture of industrial wastewater is shipped out from industrial plants to Aevitas for treatment and at the end of the treatment processes; it has been discharged into the municipal wastewater treatment plant. At the first stage, the received industrial wastewater is collected in an equalization tank for primary tests and if it is possible to be treated in the plant the wastewater then goes through the system, which is flocculation. After giving enough time for settling the formed floc, aeration and oxidation using Fenton-like process are the next processes for separation of supernatant.

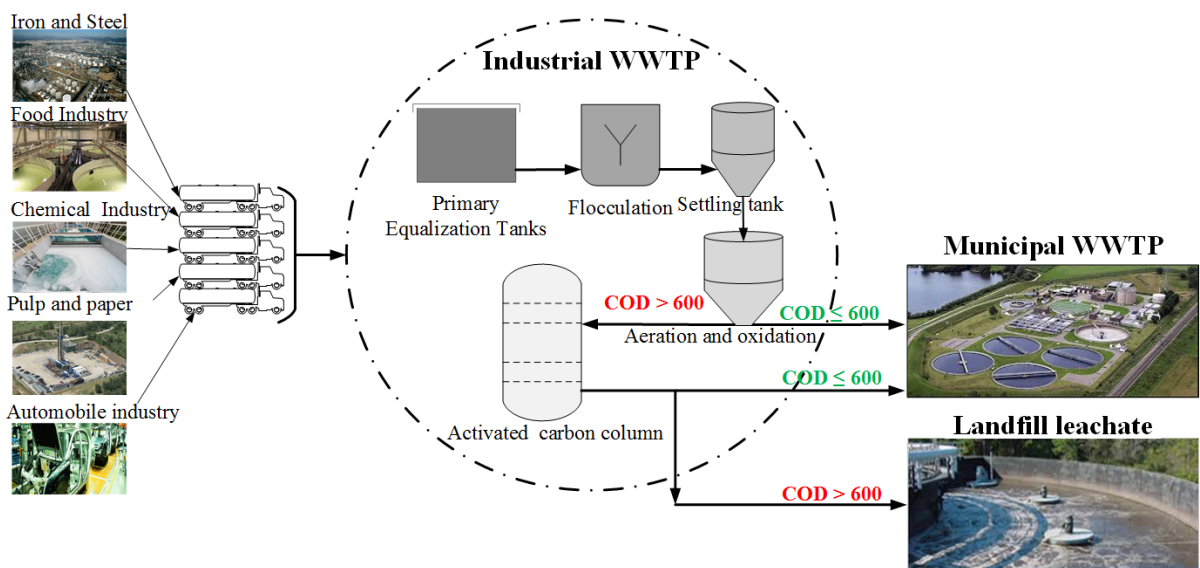


Figure 1. Schematic diagram of Aevitas industrial wastewater treatment plant.

The remained organic chemicals that are not being separated in the flocculation stage would be oxidize and volatilize in this stage of treatment. After these two main stages, the majority of COD is removed from the wastewater and then a sample is taken at the end of aeration/oxidation to see if the level of COD meets the environmental standards. Most of the times the effluent COD of this point of plant is higher than 600 (a concentration that City of Brantford enact for a safe discharging of the industrial effluent into the municipal

wastewater treatment plant) and thus needs further treatment to get the regulatory compliance requirements. Although the level of COD is one part of the problem for discharging the treated industrial wastewater into the municipal wastewater treatment plant, the presence of biocides even at low concentrations can be harmful for bacteria that are responsible for biodegradation.

Regarding these two aspects, at first step of work, a GC/MS-based characterisation technique was developed to capture the most organic chemicals that were the source of COD in the wastewater. Given the variety in composition of industrial wastewater from different sources, the conventional 'bulk measurements' of organic contaminants, such as chemical oxygen demand (COD) or total organic carbon (TOC) are not suitable. Thus, there was a strong need for advanced analytical techniques that can identify and quantify the specific compounds that were present in industrial wastewater sources. For this reason, a library of the identified chemicals was built to monitor the occurrence of each chemical in the wastewater treated by aeration/oxidation. As for the wastewater treatment technique, activated carbon in two modes of flow, batch and continuous (column), were used to overcome the two problems. The experimental results showed that the activated carbon is effective in both COD and biocide removal and, the cost of the removed COD per used activated carbon is high. This might be because of the limited capacity of activated carbon in adsorption process. To improve the polishing capacity, an alternative has been applied which was a membrane-based separation technique. A pressure-driven membrane filtration was used instead of activated carbon to reduce the spent cost as well as improving the effectiveness of the treatment process. The experimental results showed that membrane could be highly efficient in COD removal in most of the cases so that the environmental criteria is met.

2. Materials and Methods

2.1. *Sampling from Aevitas facility*

Taking sample from industrial wastewater treatment plant is a crucial step for obtaining a reliable and inclusive data. The type and the time of sampling highly depends upon the mode of the applied flow in the plant. Thus, the operators should be aware of the discharging procedure so that proper samples can be taken from which valuable information can be obtained [4]. The other things that operator must take into account is the standard criteria that the effluent should be discharged by low. This helps, as it tells us if the average concentration of a particular compound or bulk concentration of a wastewater (i.e. COD or BOD) at a particular time should be controlled. Moreover, the trend of the concentration should be monitored as well as the source of the wastewater that come into the plant. The concentration trend for a long time, which shows the fluctuation of COD, can be used where several times of sampling for decreasing the uncertainty is uneconomical.

Since the mode of flow in Aevitas plant is batch process, the samples are collected after each new batch to characterise the chemical composition of new wastewater sample. The samples were collected in 1L of bottle and then was received at McMaster University for further analytical tests. The collected samples in the bottle were stored in a 4 °C fridge to prevent changes in sample composition. The wastewater samples collected from Aevitas plant were based on two plans, A and B.

During plan A, about 75 samples in a 1L bottle were collected for characterisation. These samples were called ED01, ED02, ED03, ..., ED75, which the ED stands for effluent discharged and the following number is showing the order of samples that received at McMaster University. The same samples were used for treatment in the batch activated

carbon process and the sample after treatment were used for characterisation as well to observe the kind of organic chemicals that have been adsorbed on the activated carbon.

During plan B, 11 wastewaters which called BW1, BW2, ..., BW11 with volume of 20 L were received from Aevitas and 2 of these samples were used for the activated carbon column test and 9 of them were used for membrane filtration experiments. The chemical composition of each wastewater was different. Similarly, samples were taken from these experimental runs before and after treatment using activated carbon column and membrane filtration for analysing the variation in chemical composition.

2.2. Analytical procedures

2.2.1. Sample preparation and GC/MS analysis

A 100 mL aliquot of each industrial WW sample was pH-adjusted to 2.0 ± 0.2 via the addition of 1N HCl solution (LabChem), then combined with 100 mL of dichloromethane (DCM) (Caledon) in a separatory funnel and manually shaken for one minute. The resulting mixture was allowed to rest for five minutes in order to partition into two separate phases. Approximately 100 mL of the bottom DCM rich phase was extracted from the separatory funnel and then dehydrated by pouring it through approximately 5g of anhydrous sodium sulfate (Anachemia) contained on top of a 30 μm Whatman filter paper in a simple glass funnel. The dehydrated and filtered sample was then concentrated to 2 mL using a rotary vacuum evaporator operated at 37 °C. A 25 μL aliquot from the concentrated 2 mL sample was combined with 25 μL of N-methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA) (Sigma-Aldrich) containing 1% trimethylchlorosilane (Fluka) and 5 μL of 9-Anthracenemethanol (Sigma-Aldrich) in a 2 mL Clear Robo vial and then placed in a 60 °C oven for one hour; 9-Anthracenemethanol was included as an 'internal standard' for the GC-

MS analysis. The GC-MS analysis was performed using a 6890N gas chromatograph (Agilent), equipped with a DB-17ht column (30 m × 0.25 mm ID × 0.15 μm film, J & W Scientific) with a retention gap (deactivated fused silica, 5 m × 0.53 mm ID), and a 5973 MSD single quadrupole mass spectrometer (Agilent). A 1 μL aliquot of the sample was injected into the chromatograph using a 7683 auto-sampler (Agilent) in splitless mode. The injector temperature was 250 °C and the carrier gas (helium) flow rate was 1.1 mL/min. The transfer line temperature was 280 °C and the MS source temperature was 230 °C. The column temperature was initially at 50 °C, then was increased to 300 °C via an 8 °C/min ramp and held at 300 °C for 15 min for a total run time of 46.25 min. A full scan mass spectra between m/z (mass-to-charge ratios) of 50 and 800 were acquired; the multichannel ion detector of the mass spectrometer was turned off during the 0-2.5 and 2.8-3.9 minute due to rapid movement of toluene (solvent for the stationary phase when the injection mode is splitless) and MSTFA, respectively through the column. After analyzing the sample by GC/MS instrument a corresponded file was generated on the attached computer to the GC/MS instrument. This generated file is readable by a software named AMDIS from Agilent Company, and the software was connected to the National Institute of Standards and Technology (NIST) library so that the software can call different chemical (candidate) with different probability for the peaks in the spectrum. The selected peaks in the generated spectrum had two properties; first is that the peaks were sharps (the term 'sharp peaks' in this work refers to those peaks that their area under the peak is within the top 10% of all peaks) and the second is that the probability of selected putative compound corresponded to the peak was higher than 80%. Lack of the name of the compounds in the NIST Library might be a reason for not identifying the rest of the sharp peaks with probability of higher than 80%, as the last update of the used library in this analysis dates back to 2005.

2.2.2. LC/MS/MS analysis

2 mL of the wastewater was filtrated using 0.2 µm filter and then the 2 µL of the sample were separated on a Luna C18 (2) column (150 x 2.1 mm) with 0.1% formic acid and 0.1% formic acid in acetonitrile. After separation, the samples were analysed directly with Agilent 1200/1260-6550 LC-QTOF system.

2.2.3. COD measurement

The COD measurement was carried out using HACH kit, which is meant for measuring COD with value between 20 and 1500 mg/L. If the COD was out of the measurement range, the sample then has been diluted so that it falls within the measurement range. First, 2 mL of wastewater sample was added into the vial, then it has been fully shaken (for mixing the reagent and the sample), afterwards the vial containing mixed reagent and sample was placed in the Thermoreactor. Since the oxidation reaction happens at the high temperature, a Thermoreactor (DRB200: Digital Reactor, HACH) is provided to heat up the vial to 150 °C. After 2 hours of heating, the vial was taken out of Thermoreactor and placed in a vial rack to cool it down to the ambient temperature (for about 20 min). As mentioned, measuring the concentration of COD is a colourimetry test and thus a spectrophotometer (DR 3900 HACH) was used to quantify the COD amount of the added sample. The used spectrophotometer was programmed already and has a built-in calibration curve. To monitor the processes in terms of COD removal, the following equation is used where the COD_{in} and COD_{out} are the value of the COD in the feed or input stream and the output stream.

$$\frac{COD_{in} - COD_{out}}{COD_{in}} \times 100 \quad (1)$$

2.2.4. TOC measurement

To measure the TOC of the industrial wastewater using TOC-L (Shimadzu TOC-L Series of laboratory total organic carbon analysers), minimum volume of 5 mL was poured into the vial with total volume of 9 mL. Then the sample were put in the sample rack, which is connected to the main instrument so that the auto-sampler can draw the sample from each vial. To make the sample path cleaned (before drawing the sample from the vials) the path line should be rinsed by MiliQ water. In order to measure the amount of organic compound in the aqueous sample, first, it should be converted into the detectable form and this conversion reaction undergoes three main steps named acidification, oxidation, and detection. The purpose of acidification is to remove the inorganic carbon and purgeable organic carbon. When air along with acid is injected into the sample within the instrument, all carbonates and bicarbonate will be volatilized from the medium in form of CO₂ so that the infrared sensor in the apparatus can detect the inorganic carbon (IC) and volatile organic carbon (VOC). In the next stage, the rest of the sample is oxidized to CO₂ by high temperature catalytic oxidation. One of the requirements for running the TOC-L is the temperature of the furnace which should be about 680 °C. The platinum catalyst is placed into the furnace and its function is oxidation of the sample to CO₂ in the presence of high concentrations of oxygen. Therefore, this method could be an effective method for measuring organic compound with high molecular weight (Mw). The produced CO₂ is carried through a moisture trap via a non-contained CO₂ carrier gas to eliminate any water of vapour from the streams due to the interference of water in detection of CO₂ gas. Consequently, the produced CO₂ will be detected by a non-dispersive infrared (NDIR) detector. NDIR is an appropriate sensor for directly measurement of carbon dioxide right after oxidation of organic compound in the reactor. The main problem associated with this

method is the possible changes in the calibration baseline. The other drawback is the high concentration of salt in the samples which results in deposition of salt on the catalyst and thus a poor performance of the catalyst over time as well as showing a peak smaller than the actual peak. To calculate the percentage removal of the TOC in a process the following equation is used where the TOC_{in} and TOC_{out} are the values of the TOC in the feed or input stream and the output stream, respectively.

$$\frac{TOC_{in} - TOC_{out}}{TOC_{in}} \times 100 \quad (2)$$

2.2.5. pH and conductivity measurement

The pH meter (Hanna HI5522) is used to measure the pH of the samples before and after treatment. The pH meter firstly has been calibrated using three points standard buffers 4, 7, and 10. Then the electrode was rinsed using Milli-Q water wiped smoothly and immersed in the falcon tube that contains sample.

Different electrode was used to measure the conductivity of the wastewater; however, the instrument and the procedure were same. This analysis was used in membrane filtration to observe if any changes have been happened to the membrane during filtration process.

2.2.6. Turbidity measurement

A portable instrument called Hach® 2100Q Turbidimeter was used to measure the degree of transparency of wastewater. This analysis provides an idea about the contribution of suspended solid that can be a source of COD. The unit of turbidity is defined as Nephelometric Turbidity Units (NTU), which shows the amount of suspended particles. To measure the turbidity of the samples, at first, the instrument was calibrated using standard

solution, and then 10 mL of the wastewater sample was poured into the vial (which was meant for turbidity) and placed into the instrument for measuring the turbidity.

2.3. Experimental Set up

Three set ups have been used in conducting the entire experiments in this project. Two of them were for activated carbon and two of them were applied for membrane filtration. As for the activated carbon, batch and continuous modes were used using a beaker and rapid small-scale column, respectively. One set up for the pressure driven membrane filtration with two modules including SEPA cell (a module for sealing a piece of flat sheet membrane) and spiral wound were used.

2.3.1. Batch and Rapid Small Scale Column Test

Batch process was used for adsorption of contaminants from wastewater on the surface of the activated carbon. 150 mL beakers were filled with the wastewater sample. After adding the wastewater (with known concentration of COD) into the beakers, activated carbon was weighted and added into the beaker. The applied ratio of the amount of activated carbon to the mass of TOC in the medium for all the experiments was kept constant and was equal 100. A stirrer magnet bar was placed in the beaker, and then the beaker was placed on the multi-spot mixer to provide steady mixing in the medium. The experiments were run for about 24 h to ensure the system reached to a steady state in terms of pollutants adsorption. Next, the mixer has been off for about 3 h for settling down the activated carbon at the bottom of the beakers. A syringe with volume of 10 mL was used to draw sample from the supernatant. The samples were filtrated by 45 μm , and then this sample was used for COD and TOC measurement.

Although Aevitas installed a full-scale activated carbon column adsorption in its plant, it has not been used regularly as the cost of the replacing and regeneration of the adsorbent is not economical. Thus, a small-scale column (Rapid Small Scale Column Test) was built to analyse the COD removal. This system was designed by Crittenden et.al because of saving time as establishing pilot scale is a time consuming process to obtain result [31]. In another work by Zietzschmann this system has been used to adsorb organic micro-pollutants from domestic wastewater [32].

In our experimental work, a clay column was placed prior to the activated carbon column and the logic behind that was capturing suspended solid or nitrogen, and phosphorous. The height and diameter of the activated carbon column were 40.4 and 1.25 cm, respectively. With an 11.5 mL/min flowrate, the Empty Bed Contact Time of 4.3 min was obtained for the column. These design values were chosen according to the full-scale system properties at Aevitas, and to maintain enough contact time between activate carbon and wastewater. The granular activated carbon was provided from Continental Carbon Group. About 2 L of the industrial mixed wastewater was placed in the wastewater tank where the wastewater is kept for inserting in to the clay column first via a diaphragm pump and the entering into the followed carbon column. At different time scales, samples were collected from the bottom of the column for measuring the COD, TOC, and GC/MS analysis. After finishing the experiment, the saturated carbon was evacuated from the column and the column was washed and dried for next experiment.

2.3.2. Pressure driven membrane filtration and the types of used membranes

The membrane setup that has been used for industrial wastewater filtration consisted of several parts including wastewater tank with a chiller, pump, pressure gauges, membrane housing, rotameters, and a number of valves in the lines for adjusting pressure and flowrates

(Fig. 2). Two modules were used for membrane filtration, SEPA cell for flat sheet piece with membrane active area of 140 cm^2 and the spiral wound module. The picture of SEPA cell is shown in Fig. 3A and several reasons were involved for choosing this set-up for carrying out the experiments such as being cross flow, obtaining a precise data at a short time, and more importantly requiring small piece of membrane for conducting the experiments. Spiral wound housing is more preferable for industrial application as it is packed and can provide larger area at a small volume. The applied housing was 1812 (Fig. 3B), which can tolerate maximum pressure of 600 psi. Two ports were created at the ends of the membrane housing for retentate, permeate, and feeding of the wastewater in to the membrane. The length time for each experiment was ~ 2 h and every 20 min two samples were taken from the feed tank, and the permeate line for measuring the COD and TOC. During all the regular experiments, the pressure of the influent flow was kept constant at ~ 100 psi. Flux was another parameter that has been measured during this time. For this purpose the flow rate of the permeate was recorded and divided into the active surface area of the membrane. 11 different industrial wastewaters have been used for membrane filtration over 84 experimental runs. A salt test experiment was performed before and after using the membrane for wastewater treatment to check if the performance of the membrane changes due to the treatment.

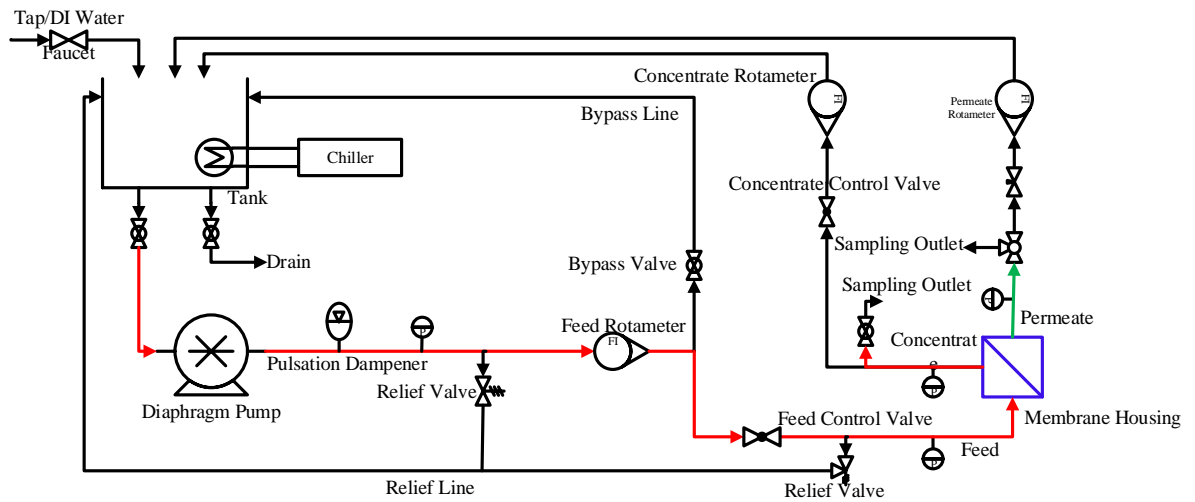
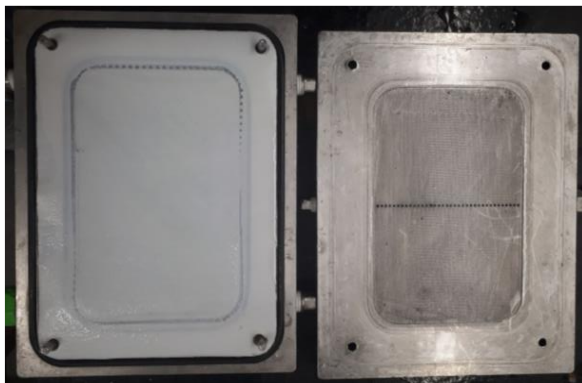


Figure 2. The pressure driven NF and RO membrane set up applied for wastewater treatment in two flat sheet and spiral wound modules.

A



B



Figure 3. SEPA cell pictures for testing flat sheet membranes (A) and the spiral wound 1812 module (B) that were used for industrial wastewater treatment.

NaCl was used for this post-experiment test with a concentration of 1 g/L and the quantity of salt in the solution was measured through conductivity test using the same pH meter instrument but different electrode.

Table 4. Properties of RO and NF membrane used in the experiment.

Manufacturer	Type	Module	MWCO*	pH	permeability (GFD/psi)	Rejection
Dow Filmtec™	NF270	Flat sheet	~200-400 Da	2-11	72-98/130	99.2% MgSO4
Dow Filmtec™	NF90	Flat sheet	~200-400 Da	2-11	46-60/130	99.0% MgSO4
Synder™	NFX	Flat sheet & Spiral wound	~150-300 Da	3-10.5	20-25/110	99.0% MgSO4 (40% NaCl)
Synder™	NFW	Flat sheet	~300-500 Da	4-10	45-50/110	97.0% MgSO4 (20% NaCl)
Synder™	NFS	Flat sheet & Spiral wound	~100-250 Da	3-10.5	30-40/110	99.5% MgSO4 (50% NaCl)
TriSep™	TS80	Flat sheet	~150 Da	2-11	20/110	99.0% MgSO4 (80-90% NaCl)
TriSep™	XN45	Flat sheet	~500 Da	2-11	35/110	95.0% MgSO4 (10-30% NaCl)
ExcellNano™	SXN2_L	Spiral wound	200-450 Da	4-9	30/50	94.0% MgSO4 (10-50% NaCl)
Dow Filmtec™	BW60	Spiral wound	-	2-11	50/50	98% NaCl
Dow Filmtec™	TW30	Spiral wound	-	2-11	75/50	98% NaCl

* Molecular weight cut-off (MWCO) is a molecular weight of a typical molecule that 90% of it can be retained by the membrane

10 types of membrane at two different formats of flat sheet and spiral wound and two categories of RO and NF were used. The operational parameters as well as their specifications are presented in Table 4. All of the membranes were polyamide polymeric membranes excluding XN45, which was made of Polypiperazine-amide. Three membranes, BW60, TW30, and SXN2_L were only used in spiral wound format whereas NFS and NFX

were available in both flat sheet and spiral wound formats. The reported pH in the table represents for the operational pH range reported by the manufacturer of each membrane.

3. Results and Discussion

The results and discussion is divided into three parts, the first part focuses on the results obtained from characterisation of wastewater, and the second part discusses the results related to the activated carbon and membrane filtration treatment processes and the third part is allocated on process modelling.

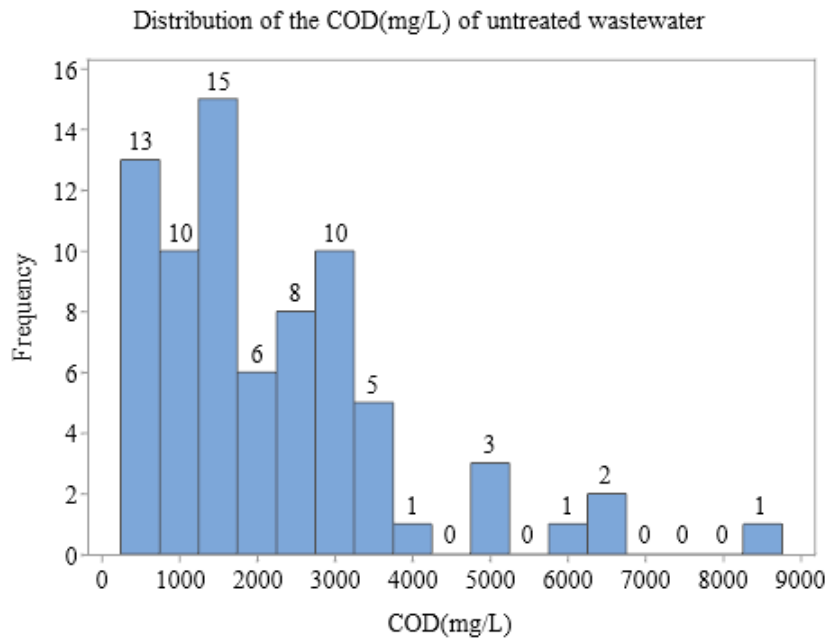


Figure 4. The frequency value of COD of 75 sample of raw wastewaters that were collected from Aevitas over 10 months; the COD of 13% of the samples were below 600 while 77% of the samples had a COD between 600 and 4000.

As already mentioned, the main problem of Aevitas (the major focus on this project) was the COD values of higher than 600 in the effluent. To this ends, all collected samples were measured for their COD and TOC, and pH. The results of the COD measurements are presented in Fig. 4. This figure shows how many untreated samples in 75 samples had the COD value more than 600. According to the Fig. 4, the vast majority of samples had the

COD values between 600 and 4000, which means the more effort should be performed in this range of COD.

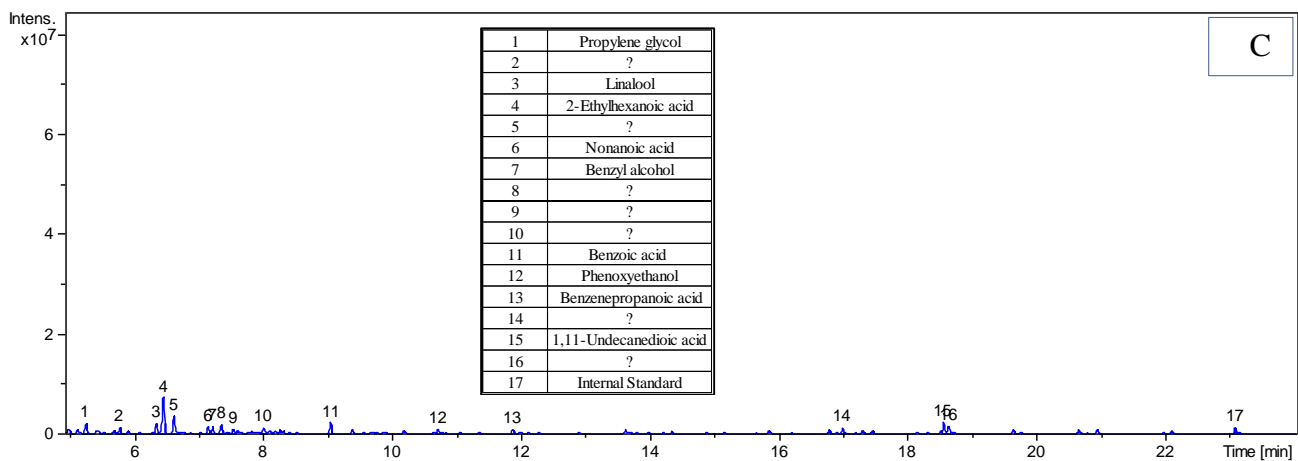
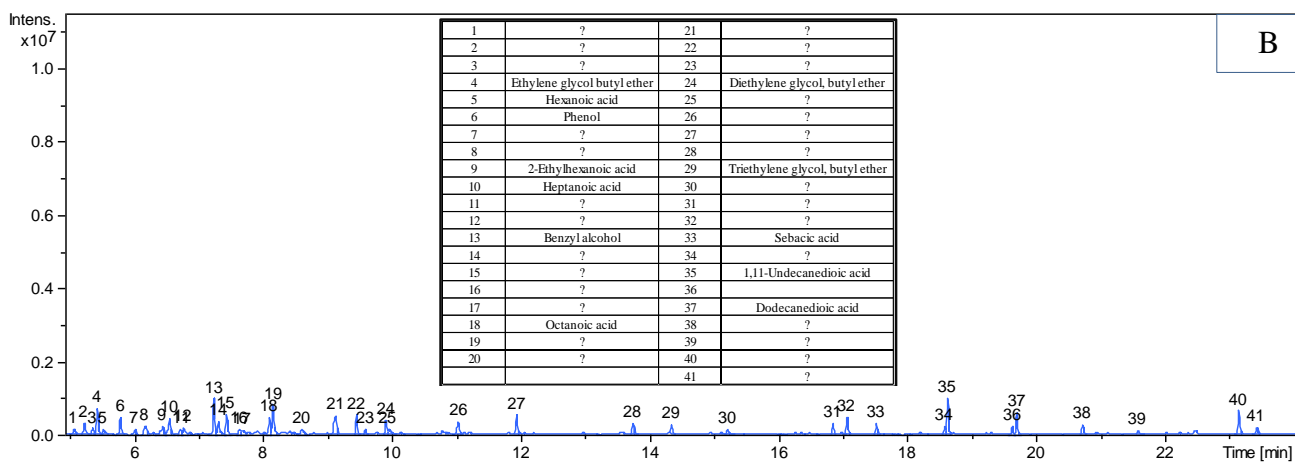
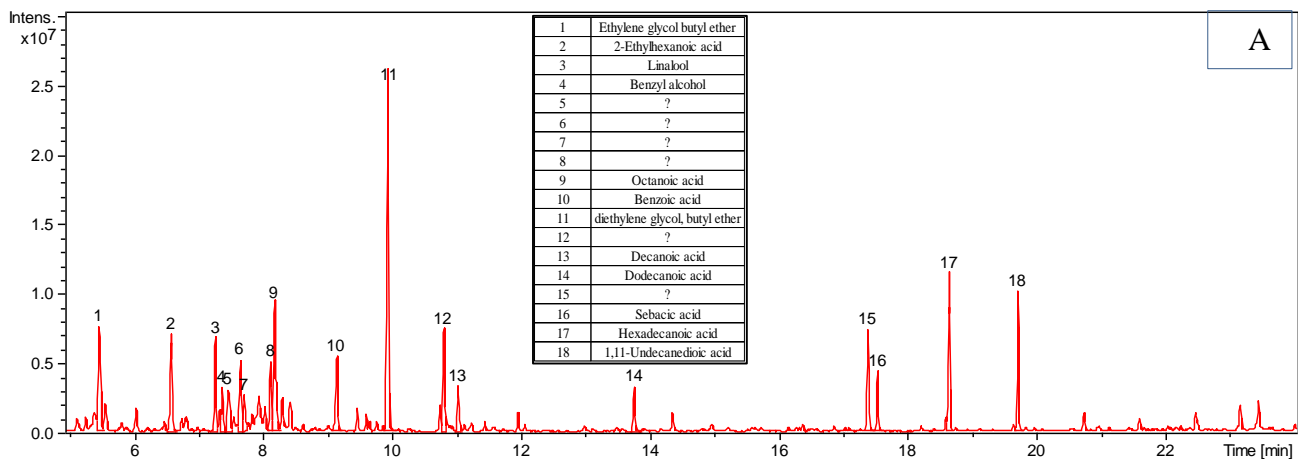
3.1. *Identifications and occurrences of organic chemicals in industrial wastewater*

After analyzing the wastewater provided from the Aevitas, their chemical composition was identified using GC/MS. As mentioned, 150 industrial wastewater samples were characterized before treatment (75 samples) and after treatment (75 samples) using activated carbon. The results of GC/MS spectrum could identify 1250 chemicals from different categories (e.g. organic acid, alcohols).

Table 5. The chemicals with high occurrences in Aevitas wastewater. These chemical are the results of 150 samples, which 75 of them were before treatment and 75 were after treatment.

Chemicals	Occurrences	RT (min)	Mw (g/mol)	Log Kow
Ethylene glycol butyl ether	73	5.6	118	0.83
Benzyl alcohol	60	7.3	108	1.1
Dodecanedioic acid	55	19.7	230	3.2
Benzoic acid	53	9.1	122	1.87
Diethylene glycol butyl ether	53	9.9	162	0.56
2-Ethylhexanoic acid	51	6.6	144	2.64
Sebacic acid	50	17.5	202	1.5
Octanoic acid	46	8.2	144	3.05
Hexanoic acid	38	5.6	116	1.92
1,11-Undecanedioic acid	38	18.6	216	NA
Phenol	31	5.8	94	1.46
Triethylene glycol butyl ether	31	14.3	206	0.02
Dicyclohexylamine	31	11.4	181	4.37
Nonanoic acid	30	9.6	158	3.42
Phenoxyethanol	25	11	138	1.16
Hexadecanoic acid	23	18.5	256	7.17
Heptanoic acid	22	6.8	130	2.42
2-Phenylethanol	13	8.4	122	1.36
Isoeugenol	12	12.7	164	3.04
Ricinoleic acid	9	22.4	298	6.19

Table 5 shows the chemicals with high occurrences in Aevitas industrial wastewater. According to the Table 5, chemicals with high occurrence in the industrial wastewater are used widely in many industries such as solvent-based coatings, water-based printing inks, pesticides synthesizing, and so on [33]. While the Mw of the all the identified chemicals are more than 100 g/mole, phenol is the one which has Mw of 94. The major concern in this table is Hexadecanoic acid due to the value of $\log K_{ow}$ (the ratio of the concentration of a chemical in n-octanol and water at equilibrium at a specified temperature) which is higher than 4. The K_{ow} of the most of the xenobiotic compounds is higher than 4 which means these compounds are more likely to bio-accumulate in living organisms and compounds [34]. Fig. 5 are provided to indicate the variation in the spectrum where different wastewaters were used to identify the chemicals in the medium. The spectrum of four wastewaters ED42, ED52, ED65, and ED68 are shown in Fig. 5, while their COD were different as well. It seems that there is no correlation between the number of sharp peaks and the value of COD; however, there is a strong correlation between the intensity of the peaks and their COD. For example, in wastewater ED42 (Fig.5A) and ED68 (Fig.5D) the amount of COD is about 5000 and higher than ED52 (Fig.5B) and ED65 (Fig. 5C) (where their COD is below 1000) and so, their related sharp peaks in the spectrum are more intense than the peaks in ED52 and ED65.



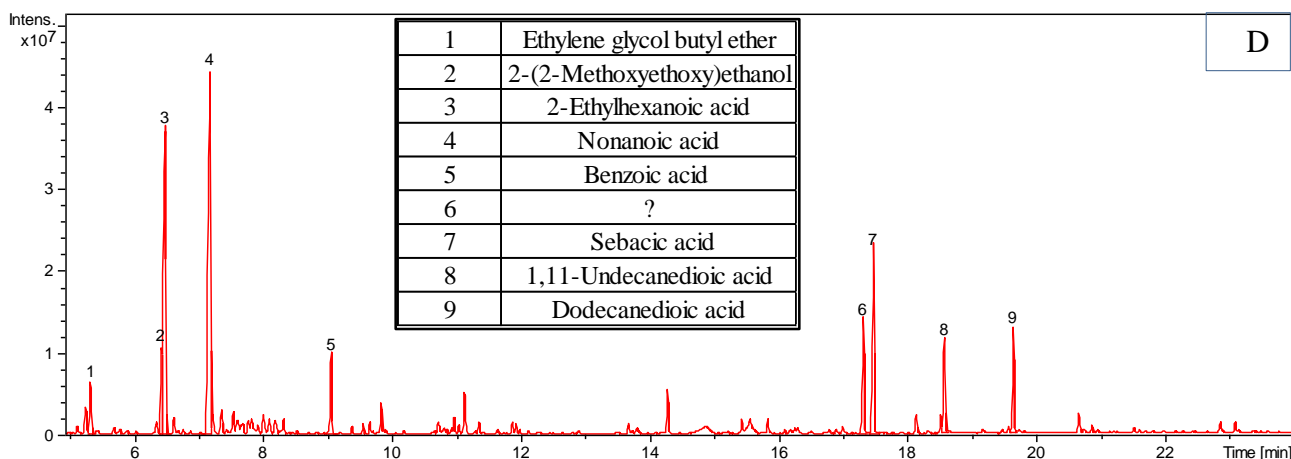


Figure 5. GC/MS spectrum of four industrial samples received from Aevitas; **A)** ED42, COD=4970 with 18 sharp peaks (67% known + 33% unknown); **B)** ED52, COD=720 with 41 sharp peaks (29% known + 71% unknown) **C)** ED65, COD=974 with 17 sharp peaks (59% known + 41% unknown); **D)** ED68, COD=6172 with 9 sharp peaks (89% known + 11% unknown). There is a positive correlation between the COD values and maximum intensity of the peaks (for spectrum (D) is 4.5×10^{-7} while for spectrum (B) is below 0.1×10^{-7}).

3.2. Adsorption of organic chemicals during Activated Carbon Process

The adsorption process were conducted through two formats. One in batch process and the other one was in column test.

3.2.1. Batch Process Activated Carbon Adsorption

Fig. 6 shows the COD of the samples that have been used for characterisation (with ED code) and then activated carbon was added into these wastewaters for COD removal of the wastewater. After treatment, only 28% of the wastewater had a COD higher than 600 and the rest of them could be discharged into the municipal wastewater treatment plant by meeting the standard requirement (while this value already was about 87%). According to the Fig. 6, despite applying the same ratio of activated carbon to TOC, the COD removal was different from one sample to another. This means that the COD removal is highly affected by chemical composition of the used wastewater.

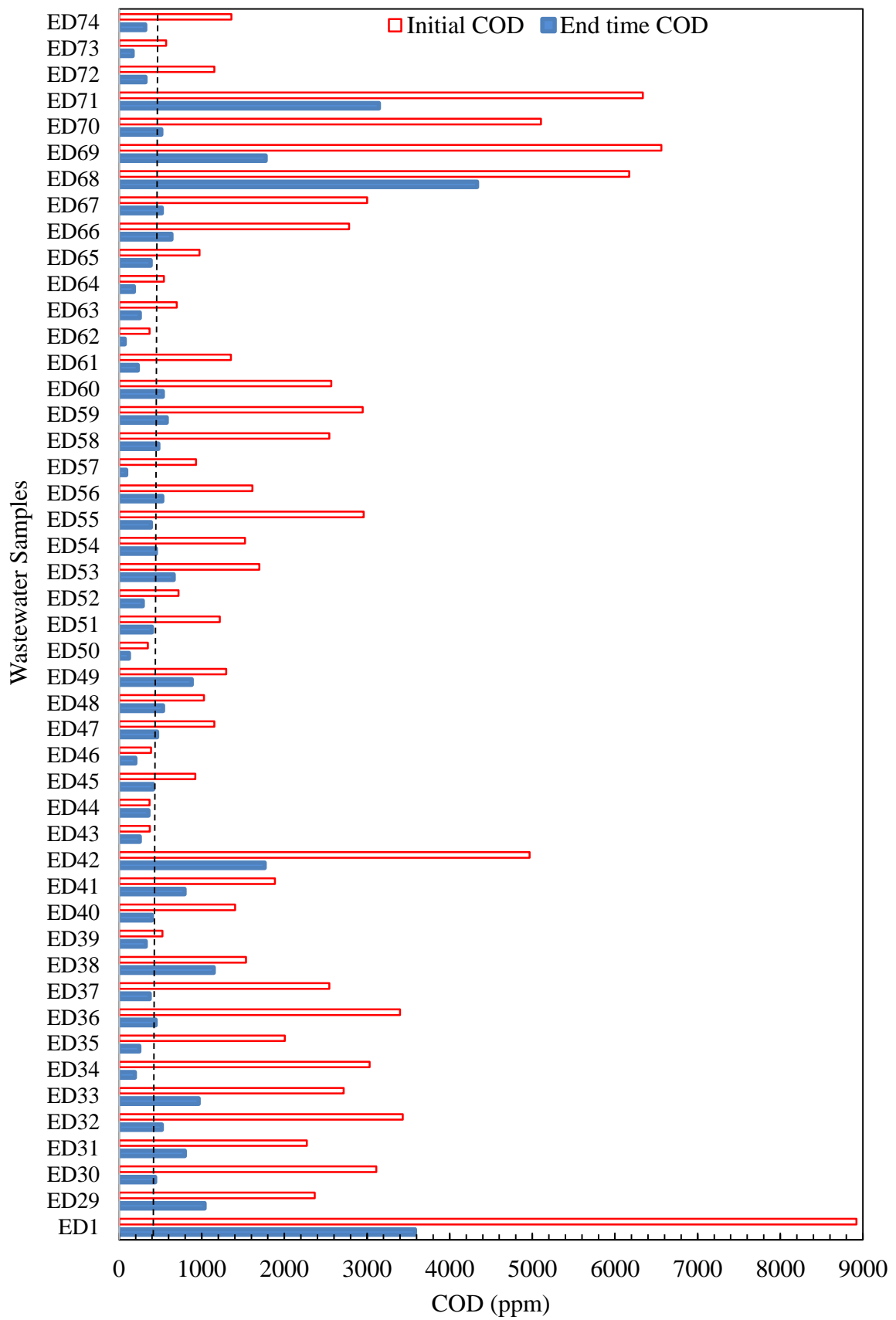


Figure 6. Treatment of the collected samples from Aevitas using activated carbon adsorption; the empty redline and the full blue bars are the amount of COD at the time before adding activated carbon and at the end of experiment, respectively. The applied amount of applied activated carbon for each experiment depends on the amount of their TOC were kept constant (1-gram activated carbon per 10 mg of TOC).

Fig. 7 A and B are provided to indicate how activated carbon can remove the vast majority of the organic chemicals. According to Fig. 7 A and B, the red line corresponds to the untreated wastewater and the blue line is the spectrum of the same sample after 24 h being treated using activated carbon. Several sharp peaks have appeared in the spectrum before treatment, whereas these peaks have been eliminated after treatment, which means that activated carbon successfully adsorbed the chemicals. Although the COD of the both ED42 and ED68 were about 5000 and higher, their COD removal percentage were 64 and 30%, respectively. In the both spectrum, it is difficult to observe the blue line, because of the low concentration of the detectable chemicals by GC/MS.

The other important results from batch experimentation showed that 1 gram of activated carbon adsorbs 7 mg of TOC or 25 mg of COD from industrial wastewater. These values are average number and clearly depending on the composition of the wastewater, (the values can be more or less).

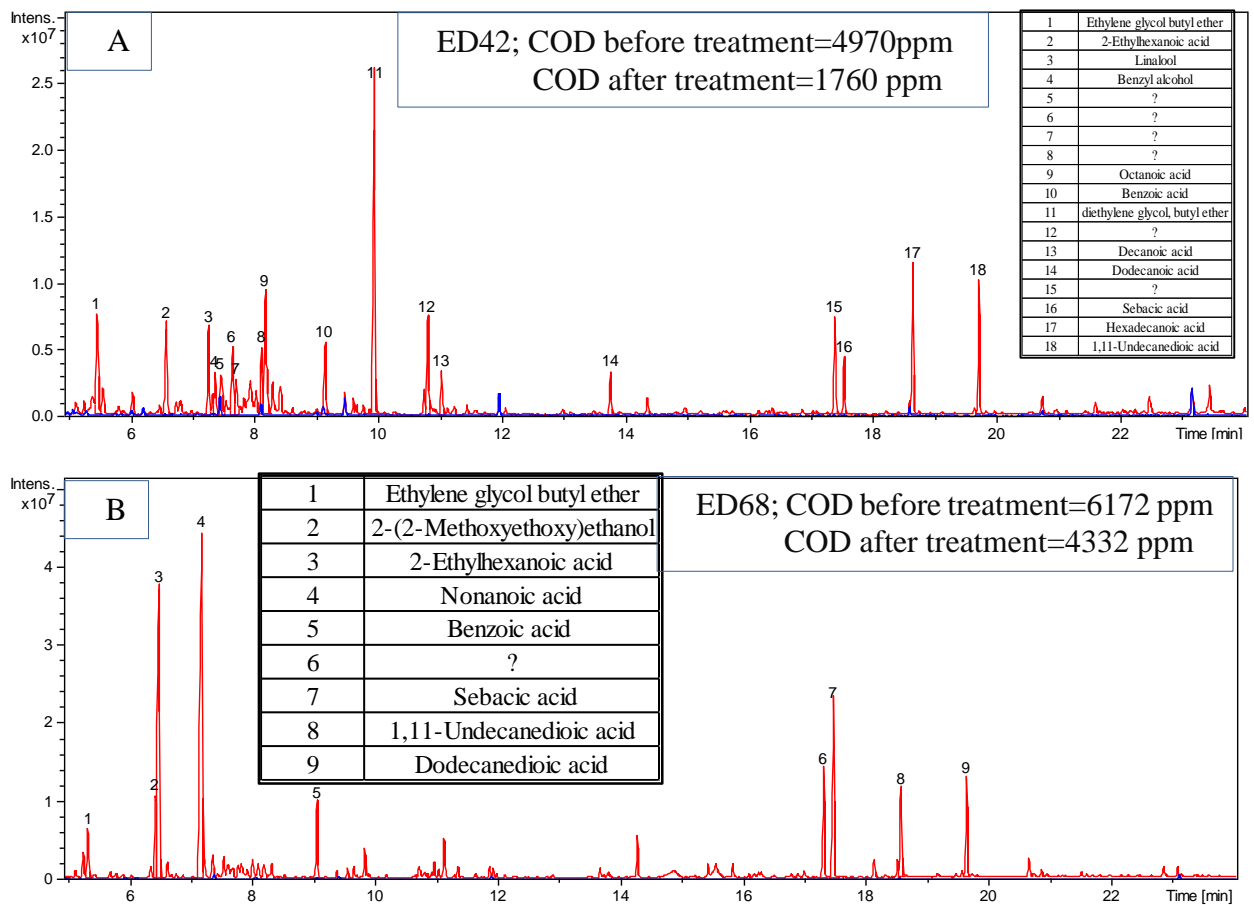


Figure 7. The full GC/MS spectrum of two samples (ED42 (A) and ED68 (B)) before treatment (redline) and after treatment (blue line) using activated carbon. Activated carbon successfully adsorbed all the detectable chemicals by GC/MS from wastewater and thus the COD values decreased.

3.2.2. Sequential Activated Carbon Adsorption

Sequential adsorption process using activated carbon was applied for wastewater treatment to observe if the remained chemicals can be adsorbed on the surface of new activated carbon. According to the Fig. 8, two different kind of industrial wastewaters BW7 (diluted) and BW8 were used for treatment using activated carbon (Continental Carbon Group). Experiments related to both first and second batches were carried out three times. The initial COD for the wastewater BW7 (diluted) and BW8 were 2016 and 748, respectively, while the original COD of the BW7 was 8400. The COD removal for BW8 in the first batch was measured as 76% whereas in the ED42 batch using the new activated carbon (unused) the

removal percentage dropped by 40%. Although there was the same percentage drop of the COD for BW7 was observed in the second batch, the COD removal at the first stage was around 57%. This means that the organic chemicals in BW8 have more tendency to be adsorbed on the surface of the activated carbon. The applied ratio of the amount of activated carbon to the mass of TOC in the wastewater was kept constant at 100 mg AC/mg TOC. Furthermore, the remained chemicals after the first batch were not able to be adsorbed on the surface of the new activated carbon. These chemicals might be polar and have a very low Mw (under 100 g/mole) as they have a very low affinity with activated carbon. In this regards, a surrogate wastewater has been prepared and then activated carbon was used for treatment of this wastewater. Methanol was the main source of COD in the surrogate wastewater with value of 2000 (Similarly, the same amount of surrogate was applied).

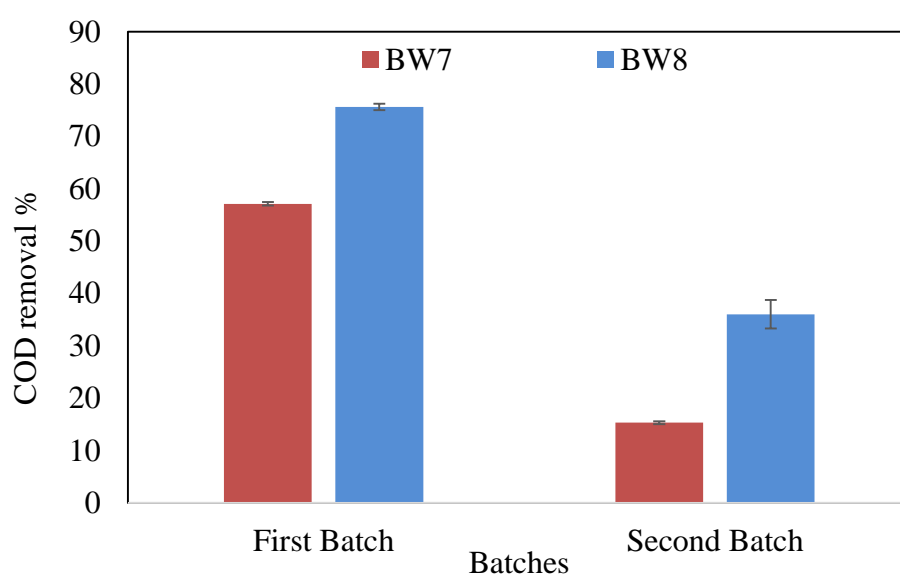


Figure 8. Sequential adsorption of organic chemicals from BW7 (diluted) and BW8 on the surface of activated carbon (continental carbon group); initial COD of BW7 (diluted) and BW8 were 2016 and 748, respectively; initial activate carbon in BW7 and 8 were 5.33 and 1.8 gram, respectively. The COD removal at the second stage was significantly lower than the first stage of adsorption.

The results of three times replication of batches showed the COD removal from surrogate wastewater were 37, 45, and 42%. A control experiment was run for tracking the COD removal due to the mixing over 24 h. Although the beakers were covered by Parafilm tape, the COD decreased by 7%. The results of activated carbon column test is presented in Fig. 9 with using two wastewaters namely BW2 and BW3.

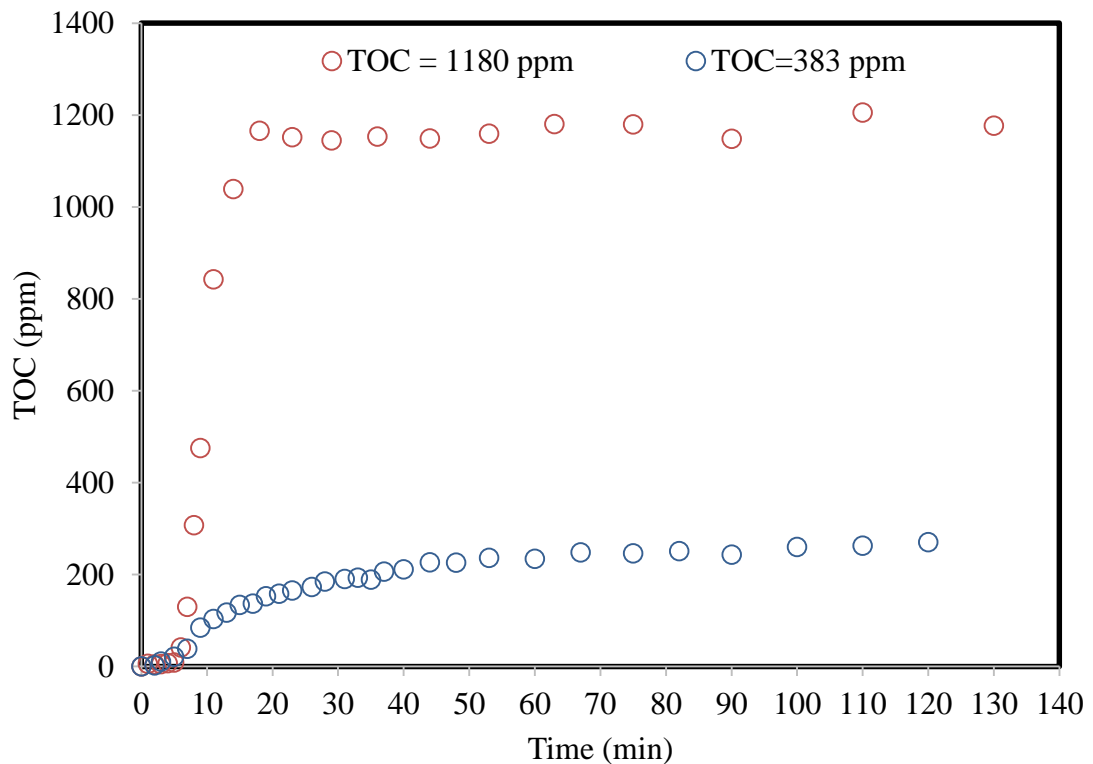


Figure 9. The result of Rapid Small-Scale Column Tests using BW2, and BW3 with influent TOC of 383 (COD of 1264) and 1180 (COD of 4400), respectively. The breakthrough curve is observed around 10 minutes in both conditions which means activated carbon column cannot tolerate even at TOC of 383 ppm (or COD of ~1264)

TOC in vertical axis is TOC concentration of influent of and as time goes on the output concentration of TOC increases. A very short breakthrough time of the column is due to the limited capacity of the activated carbon column in adsorption of organic chemicals. Also, at the steady state period of the run the output TOC sometimes cannot be the same as influent TOC, because of the pre-treatment with clay column and capturing the suspended materials.

The column itself was saturated between 10 and 20 min after running the experiment. Here, the concentration of TOC is reported instead of the COD because the strong correlation was found between COD and TOC with high coefficient of determination.

3.3. Pressure-driven membrane filtration for separation of organic chemicals from wastewater

The main purpose of using membrane filtration was COD reduction, the same as the activated carbon process. As mentioned, 12 wastewaters (named BW1, BW2, ..., BW12) with different chemical compositions were used for membrane filtration process. At the first step of filtration, the results obtained from wastewater characterisation were analysed statistically (in the out of the confidence interval of 95%) and the results confirmed that BW9 and BW12 were two wastewaters with abnormal properties in comparison with the other wastewater samples. According to the Fig. 10, one of the reasons that makes BW12 abnormal is related to the high amount of suspended solid in the wastewater, which for BW12 is measured about 504 NTU before treatment and this value was 10 times higher than normal wastewater. This picture compares between two wastewater samples, one normal (BW11) and the other one, which is outlier (BW12). The high amount of suspended solid in BW12 can be a source of COD and as this particles were not well dissolved in water and the size of particles are large, thus, they can easily be removed by membrane filtration. In this occasion, the COD of the influent is very high, while the rejection percentage is very high as well, which means the composition of the wastewater is abnormal. Since in most cases there were some portion of organic chemicals that could pass through the membrane, the composition of the COD in permeate samples are significant.

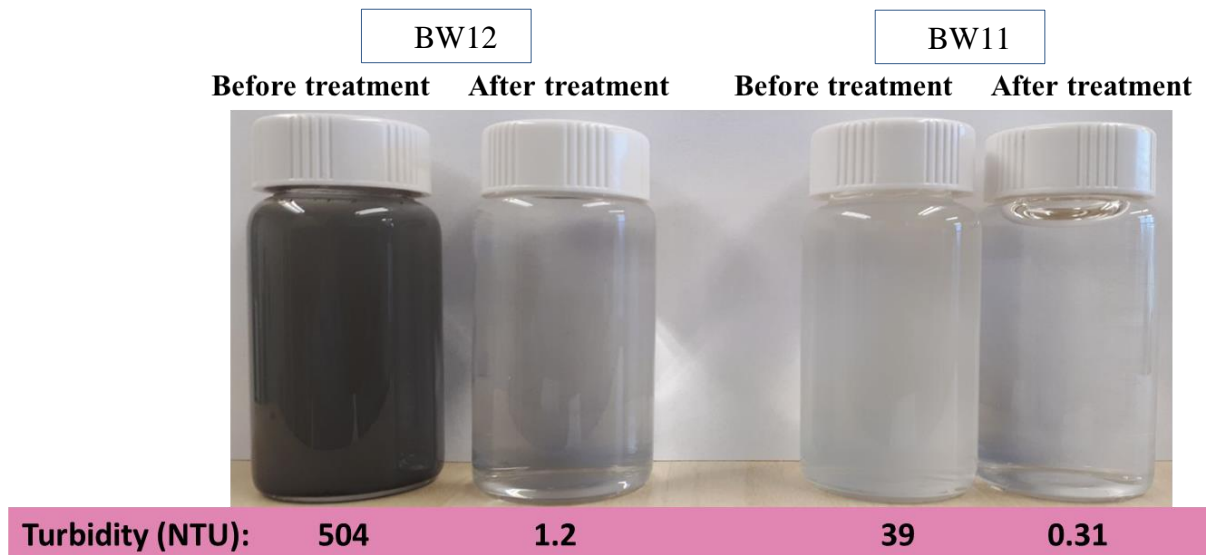


Figure 10. A comparison between two typical industrial wastewater (BW11 and 12) in terms of the amount of the suspended solid and their permeate after filtration by NF90.

Thus, the abnormality of the chemical composition of wastewater, or in other words a change in the ratio of separable COD and non-separable COD can highly affect the rejection percentage. Moreover, the results of COD measurements showed that a sample with high amount of suspended solid have a greater error between sampling and analysis in terms of COD values.

Although the other outlier is the wastewater BW9, the composition of COD is not similar to BW12's composition, and the source of COD in BW9 is different from BW12. The chemical analysis of the composition of the BW9 before and after treatment by membrane filtration showed that a considerable amount of chemical passed through the membrane and cannot be separated using NFs. Interestingly, even RO membrane cannot remove those chemicals that are the source of COD in some samples (30%). For example, an experiment have was carried out two times using spiral wound RO membrane (BW60) for COD removal from wastewater BW4. Unfortunately, GC/MS analysis was not able to identify the kind of the compounds which was the source of COD and can pass through the membrane thus Liquid chromatography/ Mass spectroscopy (LC/MS) was used as an alternative analysis method that can capture the chemicals in the permeate sample.

A t-statistic was performed on the two groups of RO and NF membranes that treating random wastewater samples provided from Aevitas. The t-test indicated RO had a better performance than NF in terms of COD removal. However, one of the main drawbacks of the RO is related to the low flux and the short length time that takes for the membrane, which causes rapid fouling of the membrane. To overcome this problem NF membrane can be used to obtain a higher flux as well as keeping the acceptable COD removal percentage. However, the experimental results showed that different NF membranes, which have been manufactured by same company with the same MWCO had different permeate flux. For example, the NF270 and NF90 are manufactured by Dow (Filmtech) and according to the company the MWCO of these two membranes falls within the same range of 200-400Da. While according to a study, the values of NF270 and NF90 have been estimated as 340Da and 180Da, respectively [35] (which there is close consistency between that study and the obtained results in our experiments)

3.3.1. COD removal from wastewater using different membranes

Since the wastewater BW9 has shown an abnormal characteristic, experiments were designed to observe the performances between different NF membranes in terms of COD removal. The original COD and TOC of this wastewater was about 9400 and 4220, respectively. As mentioned in Fig. 4, the COD of the most of the samples falls within the 1000 and 4000. Thus, to keep the concentration of COD at the same range the wastewater was diluted into two levels of COD ~2000 and ~4000. To design an effective experiment two levels of COD including 2000 and 4000 plus using 6 types of different flat sheet NF membranes including NFX (Synder), NF90 (Dow Filmtec), TS80 (TriSep™), NFW (Synder), NF270 (Dow Filmtec), and XN45 (TriSep™). The number of experiments with replication were 24 and randomized runs. Although there was a difference between

hypothetical influent COD and the real diluted COD of industrial wastewater to run the experiments, in most of cases, the deviation was less than 10%. Despite working in two levels of COD in the experiments, the statistical analysis evidently showed that the concentration of COD is not a key factor in COD removal, whereas the type of membrane significantly affects the COD removal (see Table 6).

Table 6. ANOVA table for the experiments using BW9.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Regression	11	1980	180	13.88	0.000
COD	1	64.68	64.68	4.99	0.045
NF-Membrane types	5	425.25	85.05	6.56	0.004
COD*NF-Membrane types	5	149	29.92	2.31	0.109
Error	12	155.59	12.97		
Total	23	2135			
R^2 (adj)=86%					

Based on the ANOVA table there is no interaction between the influent concentrations of COD and the type of membrane. For example, if a membrane shows a lower performance in COD removal (for a specific wastewater), the rest of the membranes may show the same performance but with a different ratio of reduction of COD removal. To confirm the results, Fig. 11 indicates that the COD removal variation for both concentrations of COD, 2000 and 4000 ppm (BW9) is almost similar where a particular membrane was used. The other main point that can be learned from Fig. 11 is the great performance of the NF90 in COD removal of BW9 and the poor COD removal of NFW and NF270. The red dashed line in Fig. 11 marks for the maximum allowable COD level for discharging effluent into the municipal sewer where NF90 can reduce the COD to around 600.

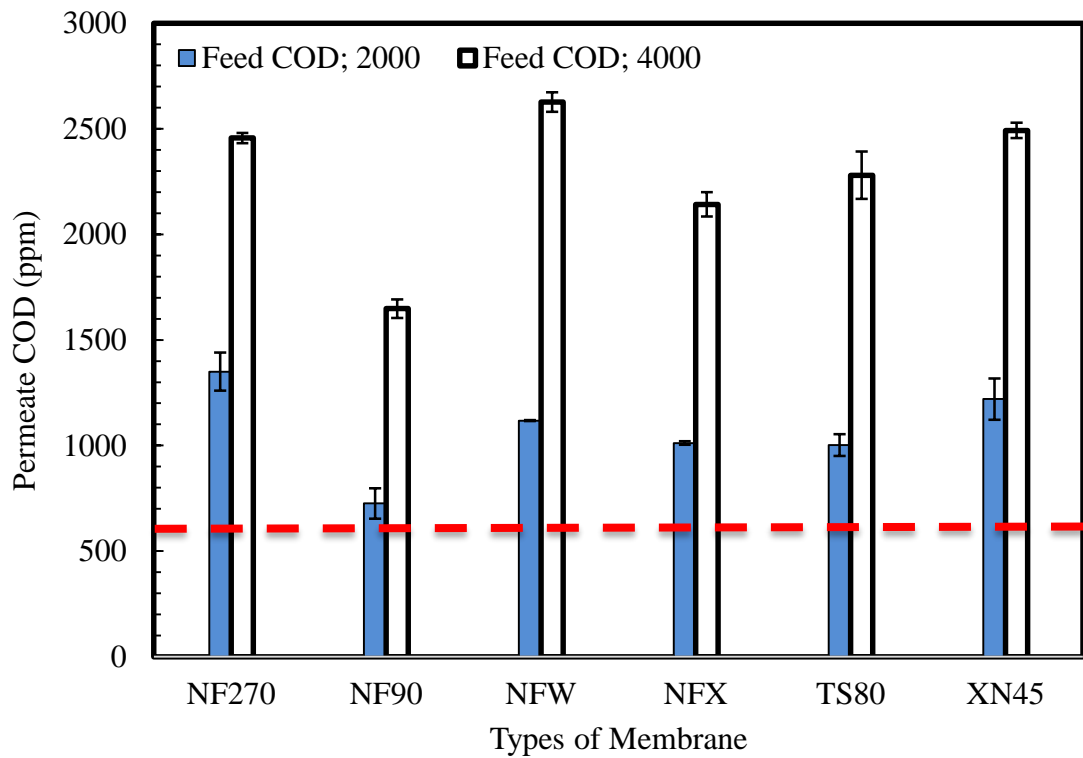


Figure 11. The concentration of COD in the permeate of BW9 (diluted) after using different NF membranes filtration; the input feed corresponds to the blue bar has been diluted 4 times (75% tap water + 25% wastewater) whereas the empty bars was the result of one time dilution (50% tap water + 50% wastewater) from the original wastewater. NF90 had a highest COD removal of 64%, but none of them reduced the COD below 600.

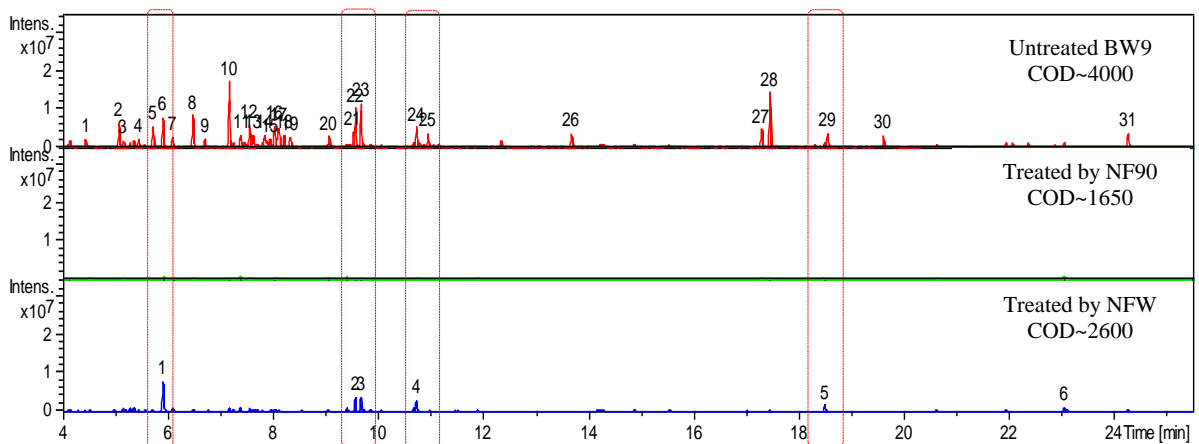


Figure 12. Comparison of GC spectrum of untreated BW9 (at the top), treated using NF90 (the middle) and NFW (at the bottom). While NF90 successfully removed all the peaks in the untreated sample, there was some chemicals remained in the NFW permeate.

In order to observe the differences between the performance of the membranes in terms of chemicals removal, a GC/MS spectrum of the untreated wastewater (BW9) and the treated wastewater using NF90 (as the best candidate of COD removal) and NFW (as the poor membrane) were shown in Fig. 12. According to the spectrum, there are at least 31 chemicals in the untreated wastewater that have significant peaks appeared by GC/MS analysis, whereas all of these chemicals have been eliminated by NF90 (the middle spectrum) so that no peaks appear in the spectrum. While there are still some peaks which shows the presence of some of the organic chemicals in the permeate sample of the NFW membrane. The removal efficiency percentage (shown in Table 7) was calculated by normalizing the area under the peaks (by dividing them by the area of internal standard). Accordingly, the removal of Butanoic acid using NFW is almost ignorable whereas NF90 can separate it by 91%. Although GC/MS cannot identify all the peaks appeared in the spectrum and some of them are introduced as unknown, their removal percentage can be calculated.

Table 7. Removal percentage of chemicals from BW9 using NF90 and NFW in according to Fig. 12.

Peak number	RT [min]	Compounds	Removal% using NF90 separation	Removal% using NFW separation
6	5.89	Butanoic acid	91	0
22	9.55	Unknown	98	70
23	9.66	Unknown	97	69
24	10.7	Unknown	97	51
29	18.52	1,11-Undecanedioic acid	95	55

The other interesting observation related to Fig. 12 is the amount of the COD in the permeate samples (1650 ppm) where NF90 was used, while there are no peaks in the spectrum marking for chemicals. Thus, there still are some organic chemicals in the permeate samples (as it is confirmed by TOC and COD analysis) that cannot be detected by GC/MS. In order to identify such chemicals, complementary sample preparations or using

other analytical instruments (Liquid chromatography) might requires for further insight. Although GC/MS is a high performance characterisation technique, it can only capture those chemicals that are volatile or can be separated at a higher temperature without any deformation of the molecular structure [36].

3.3.2. Membrane filtration COD removal versus flux

As already indicated in Fig. 11, three NF flat sheet membranes (NFX, TS80, and NF90) showed a better performances in terms of COD removal and thus, these three membranes were chosen for conducting further experiments. Three different wastewaters named BW11, BW12, and BW12 (at 3 different levels of COD, 1100, 1700, and 4200) were used to observe the COD removal percentage.

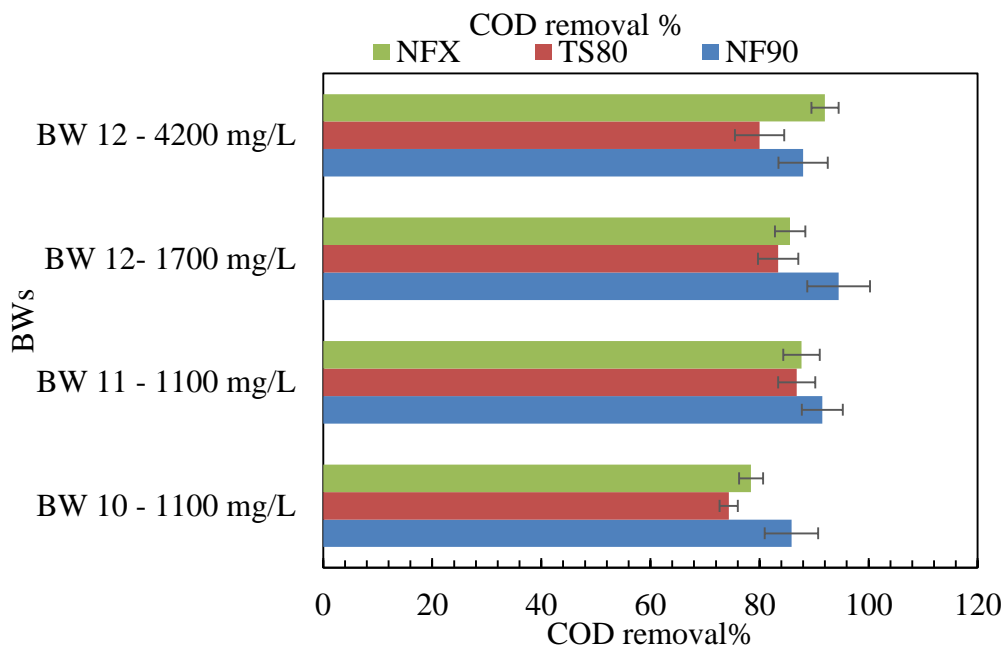


Figure 13. COD removal of three different wastewaters three wastewater BW10 (COD: 1100), BW11 (COD: 1100), and BW12 (diluted COD: 1700), BW12 (COD: 4200) using NFX, TS80, and NF90 flat sheet NF membranes. NF90 had a better performnce than others did.

The original COD of the BW12 was about 4200, and thus has been diluted by tap water to get the COD to the practical COD level (~1700). Based on Fig. 13, the overall COD removal of NF90 was still the highest while the difference between the performances of NF90, TS80, and NFX was not significant statistically. All three membranes can successfully remove almost more than 80 % of COD with no significant affecting from the type of wastewaters.

If a membrane is intended to be used for industrial wastewater treatment the other important parameter would be the permeate flux of membrane. Fig. 14 is provided to make a comparison between the permeate fluxes where different industrial wastewaters (BW10 (COD: 1100), BW11 (COD: 1100), and BW12 (diluted COD: 1700), BW12 (COD: 4200)) were used. Although the COD removal of NF90 and TS80 was relatively high, their permeate flux was not as high as that of NFX.

Therefore, there exists the trade-off between COD rejection and the permeate flux in industrial application. Due to the high amount of suspended solid in BW12 the permeate flux was affected by deposition of colloidal and solid particles on the surface of the membrane and blocking the pores of the NFs. In this occasion, to overcome the problem a microfiltration is needed to be installed before the NF so that the suspended solids and large colloidal particles can be separated from the wastewater earlier. This change can results in a higher permeate flux although it will take longer to complete the treatment. Designing a clarifier or a settling tank are the other options for solving this he mentioned issue. Without the pre-treatment steps, the membrane will be fouled and with a drop in flux.

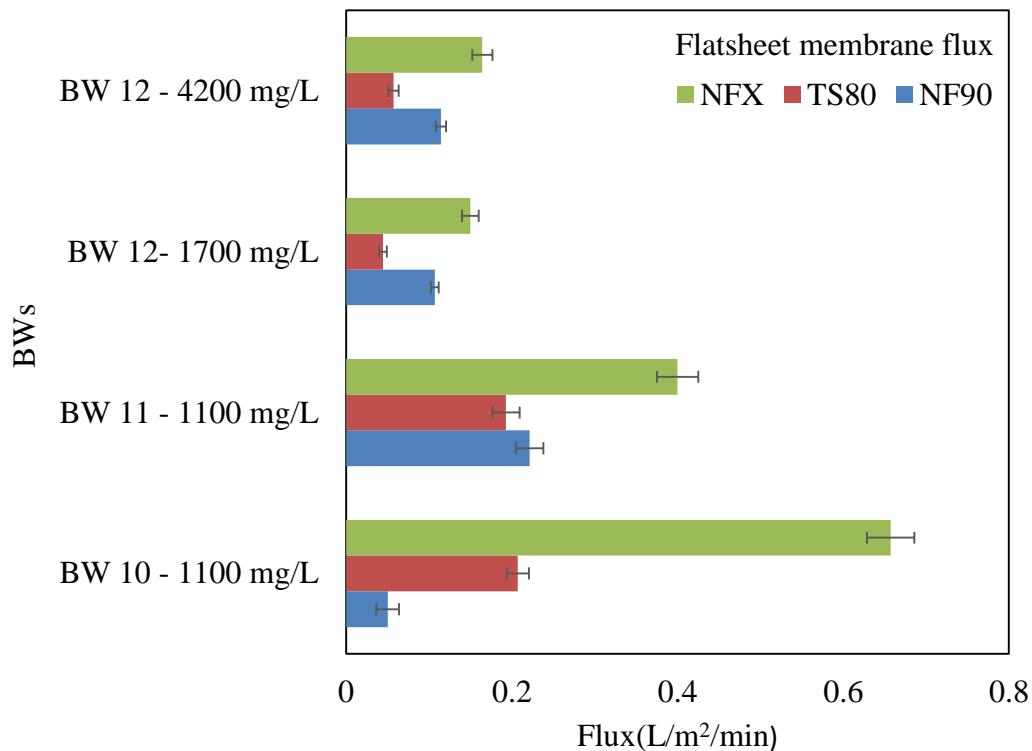


Figure 14. Flux of three different flat sheet NF membranes; NFX, TS80, and NF90, which were used for treating three wastewater BW10 (COD: 1100), BW11 (COD: 1100), and BW12 (diluted COD: 1700), BW12 (COD: 4200), NFX had a better flux than others did.

3.4. Sequential membrane filtration followed by activated carbon process

An attempt was made to observe the effectiveness of integrated wastewater treatment using membrane filtration followed by activated carbon. Activated carbon was used for further treatment of permeate sample of both RO and NF. The experimental results showed that activated carbon can adsorb about ~20% of the COD from the RO's (BW60 and TW30) permeate (BW7). This means the organic chemicals that can pass through the RO have a low tendency for being adsorbed on the activated carbon. The original COD of the BW7 was about ~8400 and so was diluted for being prepared for the experiment. The feed COD into the RO (BW60 and TW30) was ~1000 and the output permeate COD was measured ~365, which indicates a 63% of COD removal only by using the membrane. Treating the permeate sample (from RO) with the activated carbon could further reduce the COD by

20%. Applying NF membrane also showed similar results as RO did, for example, both flat sheet and spiral wound NFX reduced the COD by 60% (BW7) whereas the activated carbon could only adsorb 16% of the COD from the permeate samples. According to Fig. 15, as long as membrane has a good performances in COD removal (i.e. 60%) (i.e. XN45), the activated carbon adsorption process only remove 20% of the remaining COD, while the permeate from a poor membrane rejection (i.e. XN45) can be treated efficiently by activated carbon. It seems the chemicals that pass through XN45 have a great tendency for being adsorbed on the surface of the activated carbon. For example, the COD removal from XN45 permeate was about 28% in the post treatment step using activated carbon. The poor separation efficiency of the XN45 might be attributed to the high MWCO of this membrane which is ~500Da (similar to NFW) and the probably due to the used polymeric material (polypiperazine). A GC/MS spectrum is provided to monitor the performances of the integrated membrane – activated carbon process. This spectrum strongly confirmed the bulk measurement results of COD in feed, permeate, and after treating by the activated carbon. Since many of the peaks (each peak is candidate for a chemical) in the feed wastewater were eliminated after the treatment by membrane filtration, while in the next stage, activated carbon was not significantly influence the magnitude of the peaks . As indicated in Fig. 16, NFX spiral wound membrane separates two chemicals (Nonanoic acid and 2-Ethylhexanoic acid) which are the main source of COD in the BW7. Since the COD value of 1315 in the feed reduced to 511 in the permeate flow, it can be inferred that the cumulative COD of these eliminated peaks were about ~805.

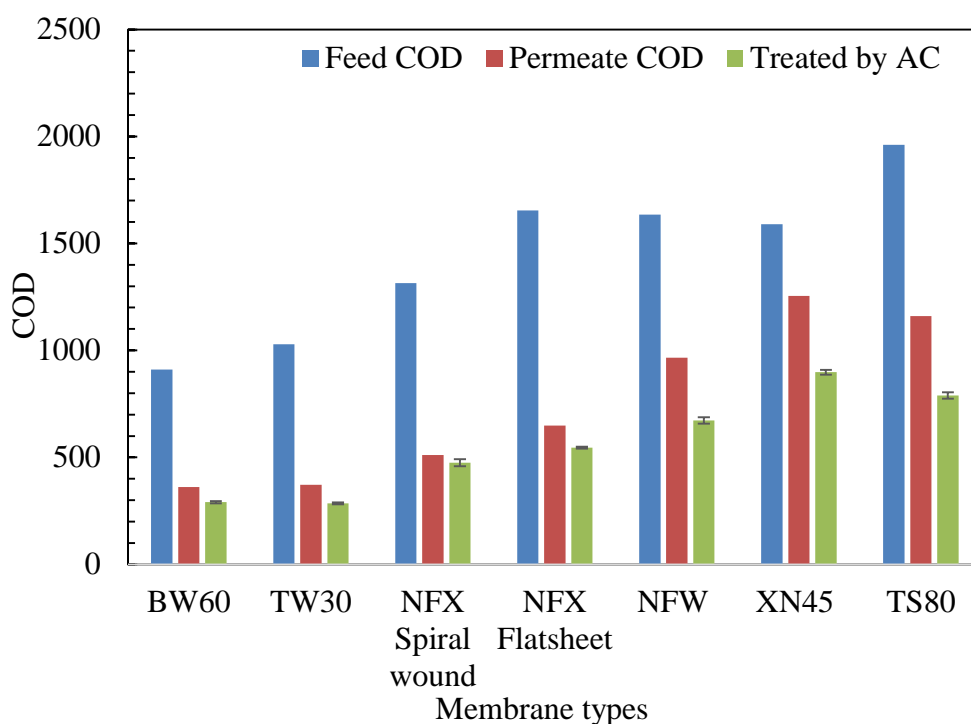


Figure 15. Sequential membrane (RO and NFs)-activated carbon treatment of wastewater (BW7) containing organic chemicals using. BW7 with original COD of 8400 was diluted for being used as an actual feed with a normal COD. Membrane filtration as first step had a great contribution in COD removal.

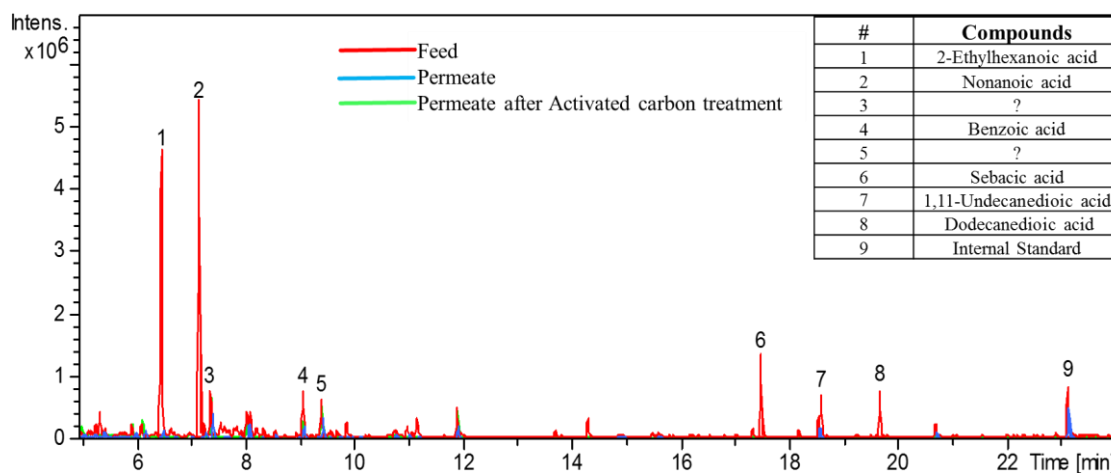


Figure 16. GC/MS spectrum of diluted BW7 when being treated by sequential membrane (NFX spiral wound)-activated carbon process. The COD of the feed, permeate, and treated permeate by activated carbon were, 1315, 511, and 475, respectively. Membrane filtration reduced the peaks considerably, while, the influence of activate carbon was not significant.

3.5. *Process modelling*

An integrated PCA-ANN modeling was used to predict the quality of the wastewater (with code EDxx) before and after treatment using activated carbon process. The source of the data for develop the model was from analyzing the collected industrial wastewater treatment plant during 10 months. After receiving the wastewater from the plant several parameters associated with the wastewater were measured using different tests. All the variables that are reported in this study called;

- Case (as categorical factor which was 2 forms of wastewater quality before and after treatment),
- Amount of applied activated carbon (gram),
- TOC (mg/L),
- Capacity of adsorption,
- COD (mg/L),
- pH,
- Number of sharp peaks (that has been appeared in the GC/MS spectrum),
- RT 4-6 (number of peaks that have been shown after retention time of 4 till 6 min), RT 6-8, RT 8-10, RT 10-12, RT 12-14, RT 14-16, RT 16-18, RT 18-20, and RT 20-24.

Only GC/MS analysis was the source of 9 variables. The retention time (RT) of the spectrum resulted of GC/MS is from 4 min till 24 min and the number of sharp peaks, which have been appeared every 2 min were considered one variable. The retention time from 4 to 20 min would be 8 variables plus two variables; one is the number of intense peaks after 20 min and the other one is the number of total peaks appeared in the spectrum. The other parameters were the capacity and the amount of the applied activated carbon, the order of

the intensity of the peaks, and ultimately a categorical factor before and after treatment. Therefore, sum of the all variables was 16.

3.5.1. Principal Component Analysis

PCA was the first model that has been built to analysis the quality of the industrial wastewater during treatment process using activated carbon. The software named Aspen ProMv was used to implement the model. PCA, as a method from big data, was used to express the trend and correlation among the variables and observations (the observation here means the characteristic of each sample before and after treatment using activated carbon) due to the size of the data obtained in this work. PCA is a suitable technique for compacting many data into something that comprises for the significant original data and the dataset with many variables will be flattened in to 2 or 3 dimensions so that we can observe the correlation among them [37]. The first principal component (PC1) is the line that can pass through all the data and can explain the most variance. The PC2 with the similar procedure is going to explain the most remaining variance of variables. As the number of component is added in to the model the goodness of a fit (R^2) increases where R^2 is between 0 and 1 ($R^2 = 1$ means best fit). The R^2 it-self is the amount of variability at the training stage and there is a similar value called Q^2 which is an indicator of how much variation is related to the test dataset. R^2 and Q^2 will be improved by adding components [38]. The outlier data are determined based on the three statistic named T2 Hoteling (distance of every point from center, taking (co)variance into account) and Squared prediction error (SPE (Distance off the model plane)). These two extensions are more effective statistic in big data analysis. The Hoteling's T2 value is a useful measure for monitoring the overall performance of the key factors of a system. The advantages of T2 Hoteling is its flexibility, being easy to use, presenting small changes in performances, and suggesting adequate marks to elucidate the

process. It is very similar to t-statistic, distance between the experimental data mean and their related population mean. However, using the T2 Hotelling alone does not show all the variances, a small amount of variance that has not been considered in the model and the residuals, usually known as SPE. Thus, SPE and T2 Hotelling are complementary for representing the residual [39]. Score plot is a helpful illustration that can be shown in PCA and each observation in the plot is a representative of one score. The score plot containing score values for each observation is a distance from the origin along the loading vector of the first component [40]. Loading vector in the loading plot defines direction and the loading itself is the correlation between components and the original variables. This helps us to interpret the effectiveness of the factors and the relationship between variable and group them in different categories based on their weights [41]. Moreover, along with this plot, contribution plot can help observing which variable is effective which provides more insight for making a decision to remove or keep the variables for the next step [41, 42]. Overall, 150 observations with 16 variables were used to build the PCA model.

3.5.2. Variation in Sampling, and outliers

Two analyses, SPE and T2 Hotelling have been used for showing the variation and the samples with the unusual characteristics. Fig. 17 presents the SPE statistic that was obtained from analysing the experimental data. This analysis showed that three wastewater samples (observations) were out of the normal range (0.99 confidence interval) and for further analysis, these three points were ignored. The abnormality of the observation have several reasons, for example for this case, the value of COD and TOC was significantly lower than expected level, and thus the analysis introduced these points as outliers.

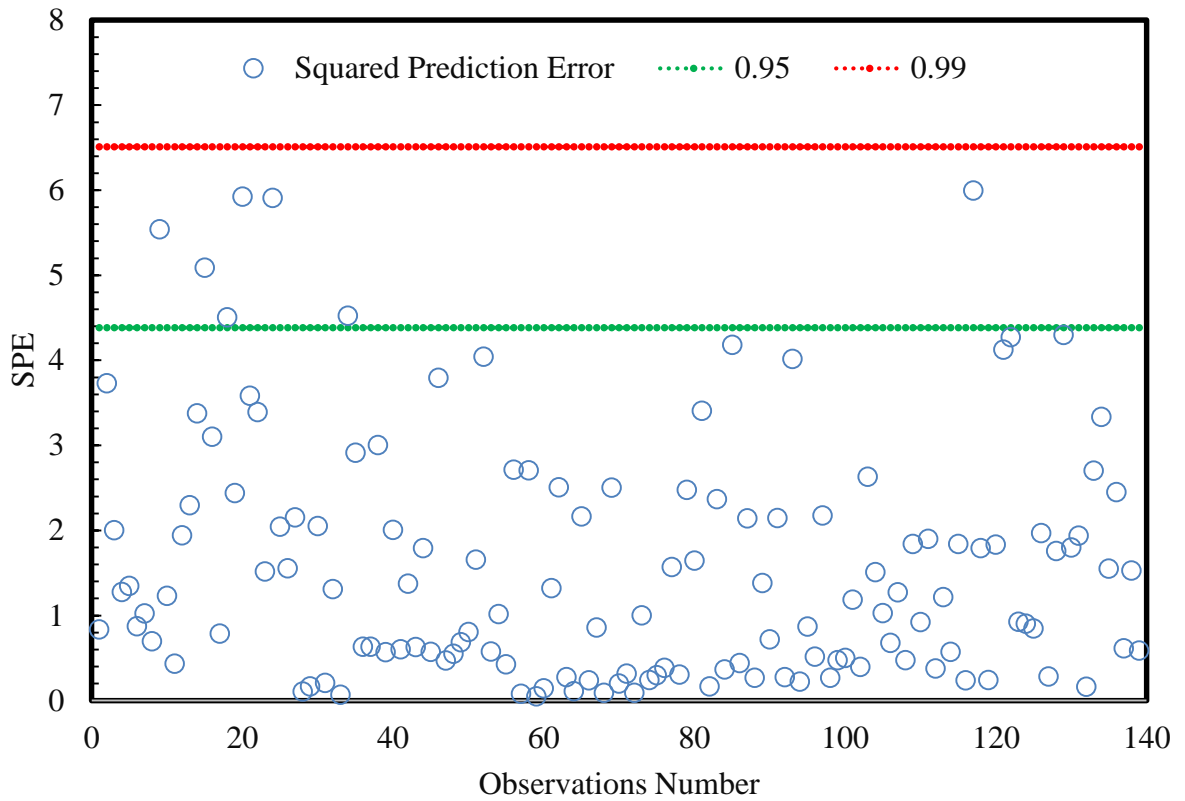


Figure 17. Squared Prediction Error to show and eliminate the wastewater (with code EDxx) that indicates abnormal properties; according to SPE, three data were ignored as they were outliers.

The other analysis is T2 Hotelling the theoretical function of this method has already been introduced and Fig. 18 is a demonstration of this analysis. According to the T2 Hotelling, seven observations were in outside of the limit and have been eliminated from the model, and then a new analysis was carried out. The physical interpretation from the abnormality is attributed to the pH with out of normal range. Similar to the SPE the horizontal axis is the observations or the characteristic of wastewater samples and the vertical axis shows the remained residual in the model.

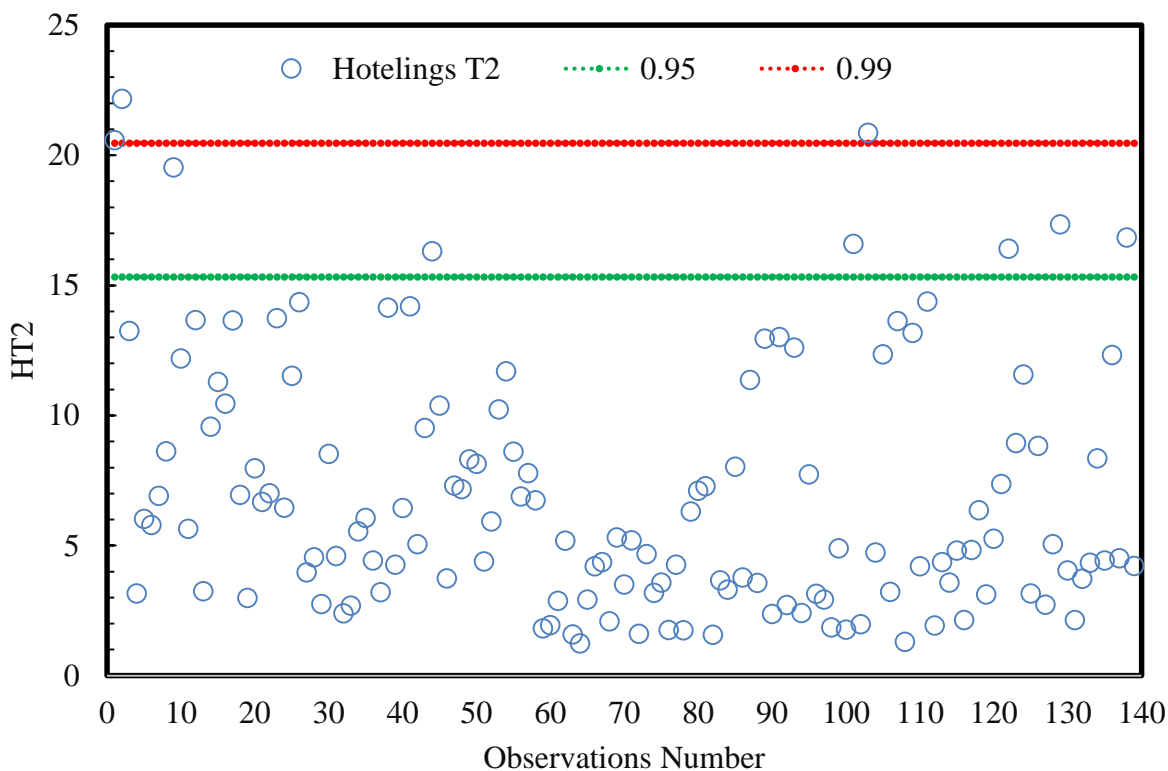


Figure 18. T2 Hoteling statistic for outliers to show and eliminate the wastewater (with code EDxx) that indicates abnormal properties; according to HT2, three data were ignored as they were outliers.

3.5.3. *Most Significant Process's Parameters and Chemicals in Wastewater before and after treatment using activated carbon*

Table 8 indicates after applying 4 components, the improvement of both Q^2 and R^2 were less than 10%, as a result, there was no point in using more components to build the model. As the number of components increase the amount of the residual decreases and the model would be more reliable. Since the numerical values of Q^2 and R^2 are very close, and the data in training stage was randomized, the built model works independently of the particular data that has been applied for training the PCA model.

Table 8. The R^2 and Q^2 of the PCA modelling when more seven components were used; as the number of components increases the model will be more accurate.

Training	Num.	R^2 Cumulative	Q^2 Cumulative
[1]	1	0.407401	0.391605
[2]	2	0.605222	0.586056
[3]	3	0.684606	0.641412
[4]	4	0.760122	0.732477
[5]	5	0.814914	0.789819
[6]	6	0.855303	0.819226
[7]	7	0.8932	0.868999

T Score plot of the model is shown in Fig. 19, and the samples before treatment were mostly distributed at the right hand side of the plot whereas after treatment all the data shift out to the left hand side of the plot. This graph shows if there is a sample of wastewater which has not been well-treated by activated carbon and there is still no changes in the characteristic of wastewater (no chemical adsorption). There might be some chemicals in the wastewater that do not tend to be adsorbed on the activated carbon. According to this plot, two observations are out of 0.95 confidence interval which belongs to the samples before treatment with the highest values of COD and TOC. The samples after treatment are more convergent than those before treatment. This means that the capacity of the applied activated carbon was proper and thus the quality of the output samples was similar. However, some of the samples after treatment were gathered at the top part of the T score plot which implies that these industrial wastewater samples might belong to an specific facility so that after treatment the quality of them were similar to each other but different from the rest of the data.

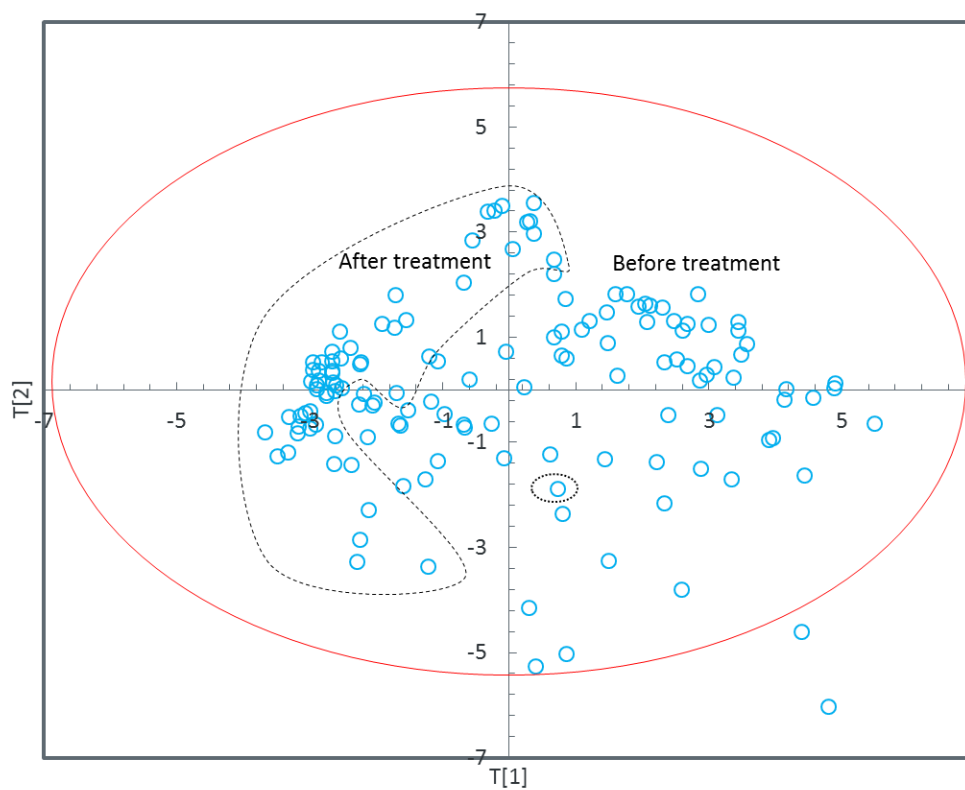


Figure 19. T Score plot for PCA model. Untreated sample were placed in the right hand side and after treatment by activated carbon they shifted into left hand side; this helps to see if a conducted experiment was abnormal or the characteristic of sample before/after treatment was abnormal.

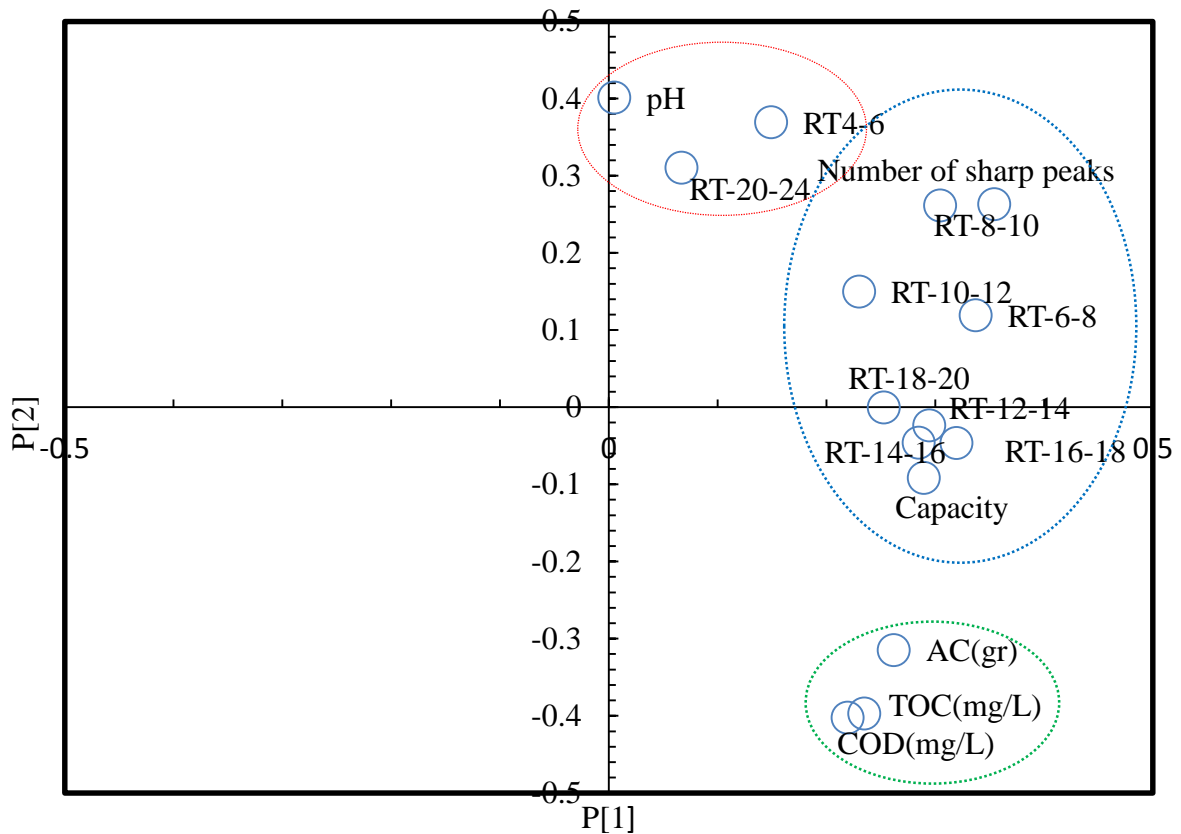


Figure 20. Loading plot: the relationship between all the variables used to build PCA model and shows which variable had the most similar influence in building the model.

Loading plot is one of the most useful plots from PCA model, which shows the group of variables that have a similar influence on the quality of wastewater. Accordingly, in Fig. 20, the retention time of the spectrum from 6 to 20 had almost the same effect on the quality of the industrial wastewater whereas pH, retention time between 4-6 min, and the retention time after 20 min are similar. As expected the adsorption process parameters including the initial value of COD and TOC as well as the amount of activated carbon play a similar role.

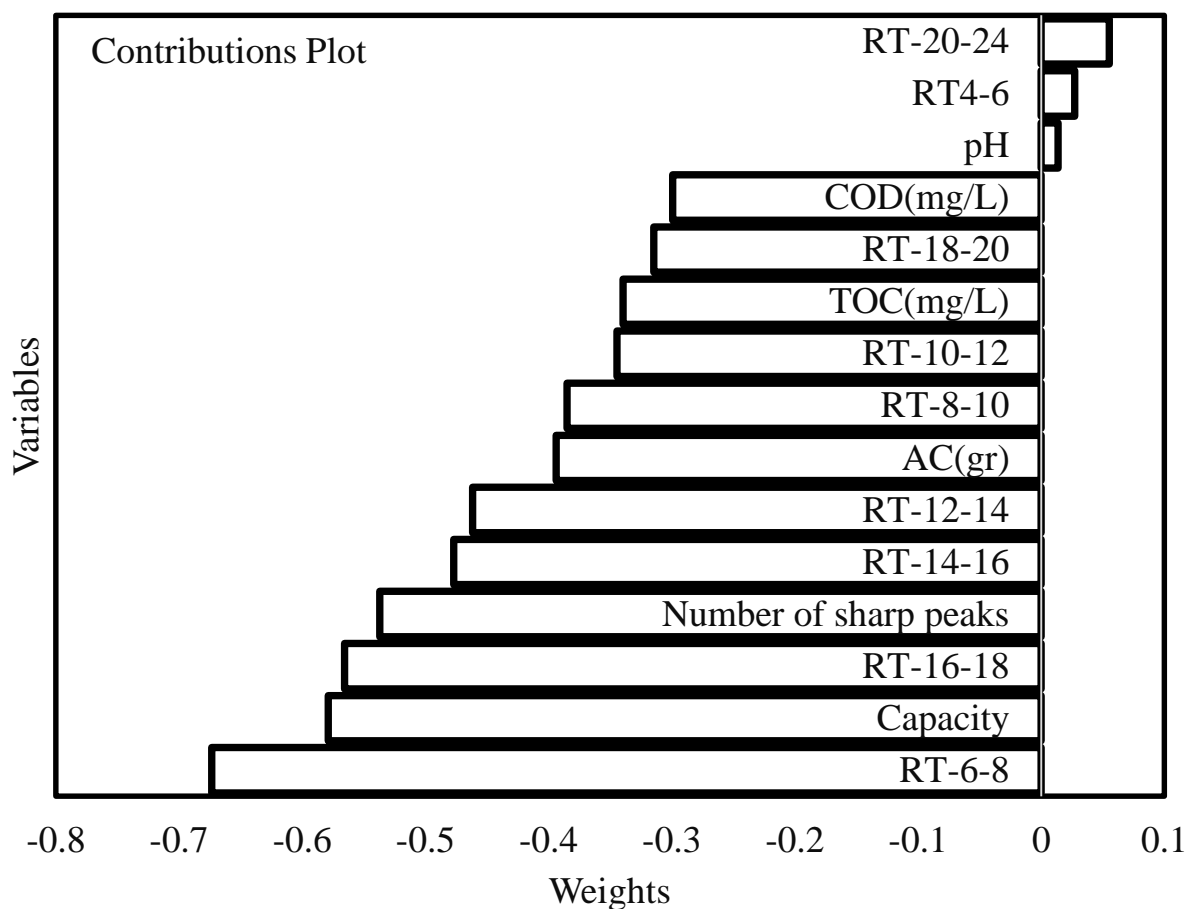


Figure 21. Contribution plot of the PCA model based on the applied variables. This shows the magnitude of the variation of each variable. The variation in RT-6-8 was the highest, which means using activated carbon can remove all the peaks appeared between 6 and 8 min in untreated sample.

Moreover, it is possible to observe the relative importance of each variable over the contribution plot. The variables with the lowest contribution can be excluded from the measurement item without any significant changes in the robustness of the built model. Based on Fig. 21, most of the chemicals that are adsorbed on the surface of the activated carbon have appeared in the retention time of 6-8 min and 16-18 min. While the number of sharp peaks which are the index of the majority of the chemicals have undergone a significant change. This means activated carbon is able to adsorb the vast majority of chemicals in the industrial wastewater.

3.5.4. Artificial Neural Network

After preprocessing the data using PCA, and determining the significant variables (based on Fig. 21), an effort was made to build a nonlinear model to predict the quality of the effluent after being treated by activated carbon. The PCA model indicated that some of the variables that have a minor contributions to the quality of water have been excluded for developing the ANN model due to the improving the prediction process. Totally 649 data over 11 variables (TOC, COD, Number of sharp peaks, RT 6-8, RT 8-10, RT 10-12, RT 12-14, RT 14-16, RT 16-18, RT 18-20, AC (for input)/Capacity (for output)) were considered as input and the same number of variables as the output. To determine the optimum number of neuron in the hidden layer, different number of neurons, from 3 to 20, in the hidden layer were evaluated, and then each topology was repeated 10 times. The topology with a minimum value of mean square error and high correlation coefficient was selected. The trial and error running the ANN showed that 2000 for the number of epoch would be enough for these datasets (obtained from measuring the properties of wastewater before and after treatment using activated carbon) and thus, the iterations for training was set on this number. As shown in Fig. 22, after about 1600 epoch the MSE reached to a steady state. The data randomly were introduced into the net and a function named Scaled Conjugate Gradient (trainscg) was employed for the training stage. The best training process for this case was Multi-Layer Feed Forward (MLF) according to the obtained results from trial and error strategy. After conducting computational processes, the bias and weights were obtained to define how much the input variable influence on outputs. The architecture of the built model is shown in Fig. 23.

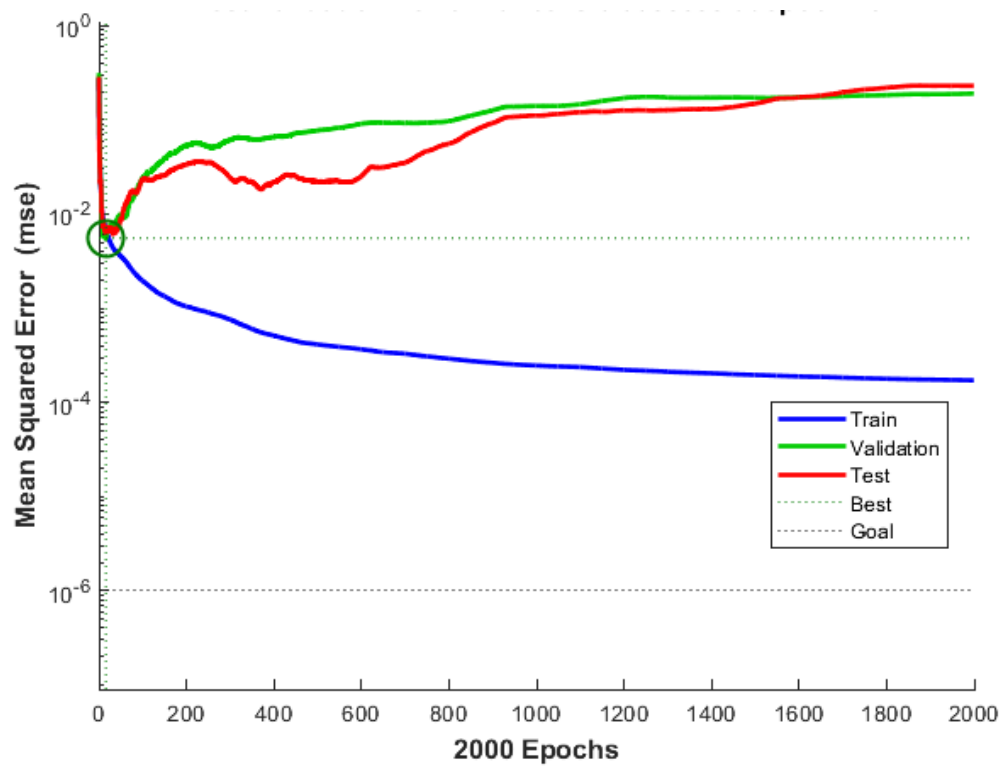


Figure 22. The calculated MSE for Train, Validation, and Test stages of the dataset (obtained from measuring the properties of wastewater before and after treatment using activated carbon).

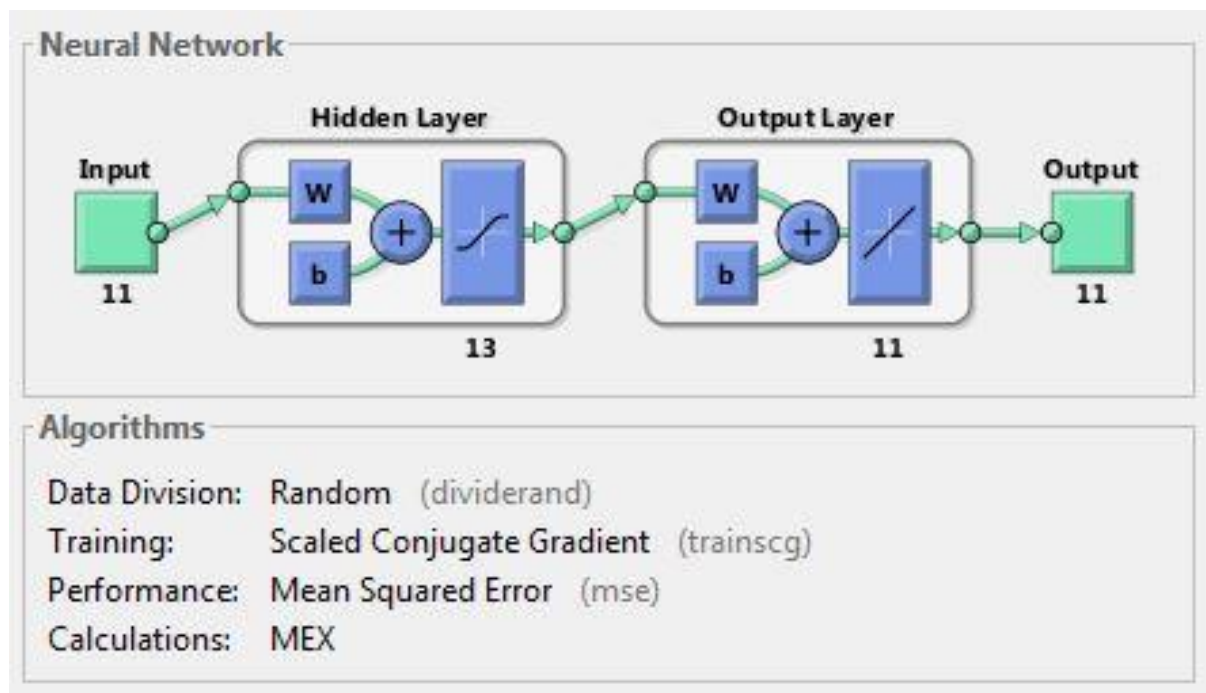


Figure 23. Architecture of the built ANN model; 11 variables were considered as input of 649 data and the same number of variables were predicted based on the input; hidden layer is non-linear and the output layer is linear.

3.5.5. Process performance prediction by definition of water quality using ANN

The built model was tested, then the best net in terms of the lowest MSE ($\sim 10^{-4}$) and the highest coefficient of determination (0.67) were selected (Fig. 24) for further prediction. According to Fig. 24, the model can explain the performance prediction of 68% of all the data. The coefficient of determination of the three stages, training, validation and testing was very close to each other, which means the built model is reliable. The number of the neuron in the hidden layer found to be 13 that can predict the values for the outputs optimally. The obtained weight and bias for the best net that will be used for further prediction process using ANN. The main role of weights is to indicate the influence of the input variables on the outputs. If the weights were near zero for a variable, then changing the input does not change the output significantly and also positive weights mean decreasing the input will increase the output.

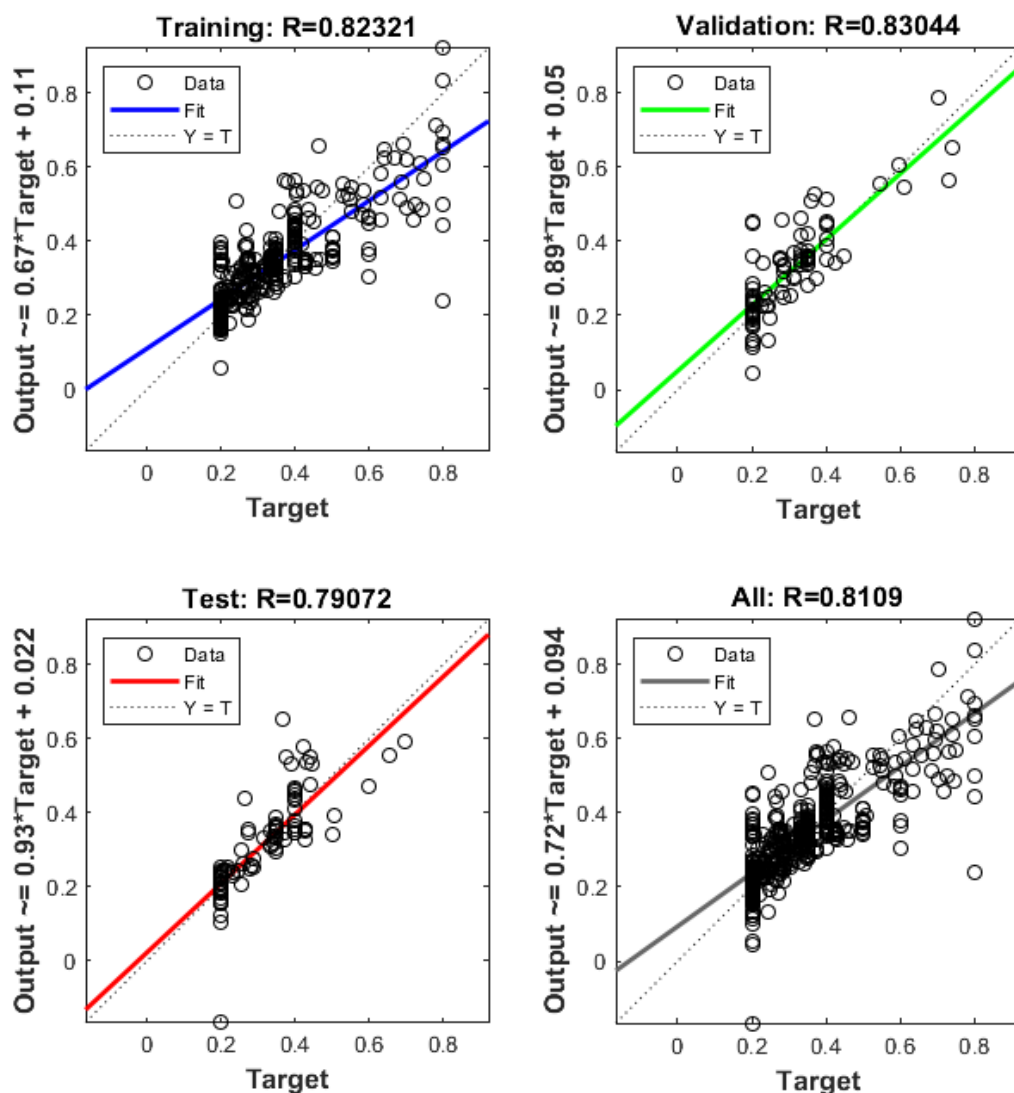


Figure 24. Performances of the ANN in prediction quality of industrial wastewater treated by activated carbon; the obtained MSE for building the model was $\sim 10^{-4}$ and the R^2 was 0.68. It means this model can predict the quality of 68% of wastewater with confidence interval of 0.95.

4. Conclusions

The conclusions of this project are categorized in three different parts as the whole process has been conducted in three stages including, characterisation, activated carbon, and membrane filtration processes. At the first stage, industrial wastewater was collected from Aevitas plant (before being drained into municipal wastewater treatment plant and after partially oxidation-aeration stage) have been characterised using both bulk measurements (COD, TOC, and pH) and species-based identification. The second stage is using activated carbon for adsorbing the chemicals species in the wastewater to reduce the COD. Furthermore, membrane filtration was considered and studied as an alternative treatment process instead of activated carbon for the industrial wastewater treatment. The outcomes are summarized below:

1) Conclusion from the first stage:

- The chemical composition and the COD of the wastewaters, which were collected from the Aevitas plant, are varying at different times of sampling as they receive mixture of wastewater from different industries.
- Characterisation of industrial wastewater using GC/MS is an effective way to identify the chemicals that are source of COD; however, it does not show all the organic chemicals. The results from GC/MS are helpful in designing an effective process for wastewater treatment.
- The results of bulk measurements have shown the COD of that most of the samples that have been taken from the plant falls between 1000 and 4000. Therefore, the population of the interested COD range is defined and an effective process is needed to overcome the problem.

- About 1250 chemicals were identified while the occurrence of some organic chemicals were between 22 and 73. Most of these chemicals were from alcohol and organic acid groups. The pH of these samples were between 5 and 8, which does not require particular adjustment for being discharged to environment.
- COD removal of a wastewater with COD of higher than 5000 and low amount of TSS/turbidity is very difficult, especially by activated carbon and membrane filtration. These kinds of wastewater usually contain very low Mw organic chemicals that are likely polar. Interestingly, the chemicals, which were not separated by activated carbon or membrane filtration, do not show significant peaks in the GC/MS spectrum while TOC indicates a value for presenting organic carbon in the wastewater.
- The chemical composition of wastewaters BW4, BW7, BW9, and BW13 was quite different. While the COD of all four samples were higher than 5000, the amount of TSS in BW13 was ~10 times higher than the rest of the wastewaters.

2) Activated carbon process

- The average amount of COD and TOC that can be adsorbed by 1 gram of activated carbon are 25 and 7 mg, respectively.
- The average COD removal from industrial wastewater using activated carbon is about 67% with standard deviation of 18.6. On average 33% of COD in the Aevitas industrial wastewaters cannot be adsorbed by activated carbon due to the several factors which are related to the chemical properties such as polarity, size and the molecular shape of chemicals, and hydrophobicity.
- The adsorption of chemicals from industrial wastewater samples using activated carbon can be modelled by multivariate big data (PCA) integrated by ANN so that

the quality of water before and after treatment can be predicted with an acceptable reliability.

3) Membrane Filtration

- Depending on the chemical composition of the wastewater, the COD removal in the membrane filtration process can vary from 30 to 90%. For a typical wastewater with high amounts of suspended solids (BW13) a pre-filtration using microfiltration can be helpful from two aspects, one is membrane fouling during longer time span and the other is effectiveness in COD removal.
- BW4 and BW9 were two types of wastewaters that their COD were not decrease under 600 using every types of NF and RO, however, NF90 can reduce the COD of diluted BW9 (~2000) to under 1000.
- The experimental results did not show any interactions between the types of wastewater and used membranes for filtration.
- Among the NF membranes, the COD removal of NF90, NFX, NFS, and TS80 was higher than the other membranes. Moreover, in terms of permeate flux, the NFS and NFX had a higher membrane permeate flux compared to the other membranes. Therefore, NFX and NFS are two proper candidates for wastewater filtration with a high rejection percentage and a high permeate flux.
- Although the efficiency of integrated membrane-activated carbon process totally was higher than either of the processes alone, the vast majority of COD removal from the wastewater happened at the first stage (~80%).

5. Recommendations for future works

- In order to better fractionate the chemical species related to COD, a parallel analysis of GC/MS along with LC/MS/MS can be used for the identification of the chemicals especially the ones that neither can be adsorbed on the surface of the activated carbon nor separated by membrane filtration. To this end, an accurate quantitative analysis of the concentration of the species is required. Then, a comparison is needed to be made between the measured COD, TOC, and the contribution of sum of the chemicals that have been identified by GC/MS and LC/MS/MS.
- In this work, a number of polymeric membranes have been used. Application of polymeric membranes for industrial wastewater treatment suffer from several drawbacks, especially if the TSS content of wastewater is high. Two major problems are membrane fouling and membrane compatibility with different solvents (i.e. methanol or ethanol) which can result in poor membrane filtration performance due to swelling of the membrane. The best alternative for the challenges is using ceramic membranes for filtration of wastewater containing variety of many different chemicals. Although ceramic membranes have higher packing densities and are heavier than polymeric membranes, they are more stable against the harsh operating conditions such as extreme pH, and chemicals. Moreover, the life span of ceramic membranes are longer than polymeric membranes [43].
- Since most of the chemicals that have a low tendency of adsorption on the surface of activated carbon are very small and polar, using other degradation-based treatment methods, (e.g. Electrochemical Oxidation) may be appropriate for

further COD reduction after aeration process. This would be extraordinary important as the Aevitas plant is using batch process, the same process, which is common in electro-oxidation, however, the following process must be in optimum working conditions. The introduced method carries several advantages; including maintaining high effectiveness at even lower temperatures with production of less amount of by-products. Two path of direct and indirect oxidation are common in this process which results in a considerable reduction of COD [44].

- One of the main problems associated with the Aevitas effluent is the high level of toxicity of the chemicals in the effluent. Although the concentration of the hazardous materials might be trace, it can have a negative effect on the performance of the municipal wastewater treatment as microorganisms run it. Therefore, an effective process in one system that can meet two requirements of high COD reduction and toxic chemicals removal could be a proper remedy for the challenge aroused. This system can be a combination of ozone process with activated carbon in one system. The function of activated carbon is adsorption of high toxic substances in the system and the role of ozonation process is simultaneous volatilization of VOCs and oxidation of recalcitrant chemicals for COD reduction.

6. References

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