Waste Based Separation Media for Environmental Applications

A Dissertation Report

submitted in partial fulfilment of the requirements

for the award of degree of

Master of Technology

in

Environmental Science and Technology

Submitted

By

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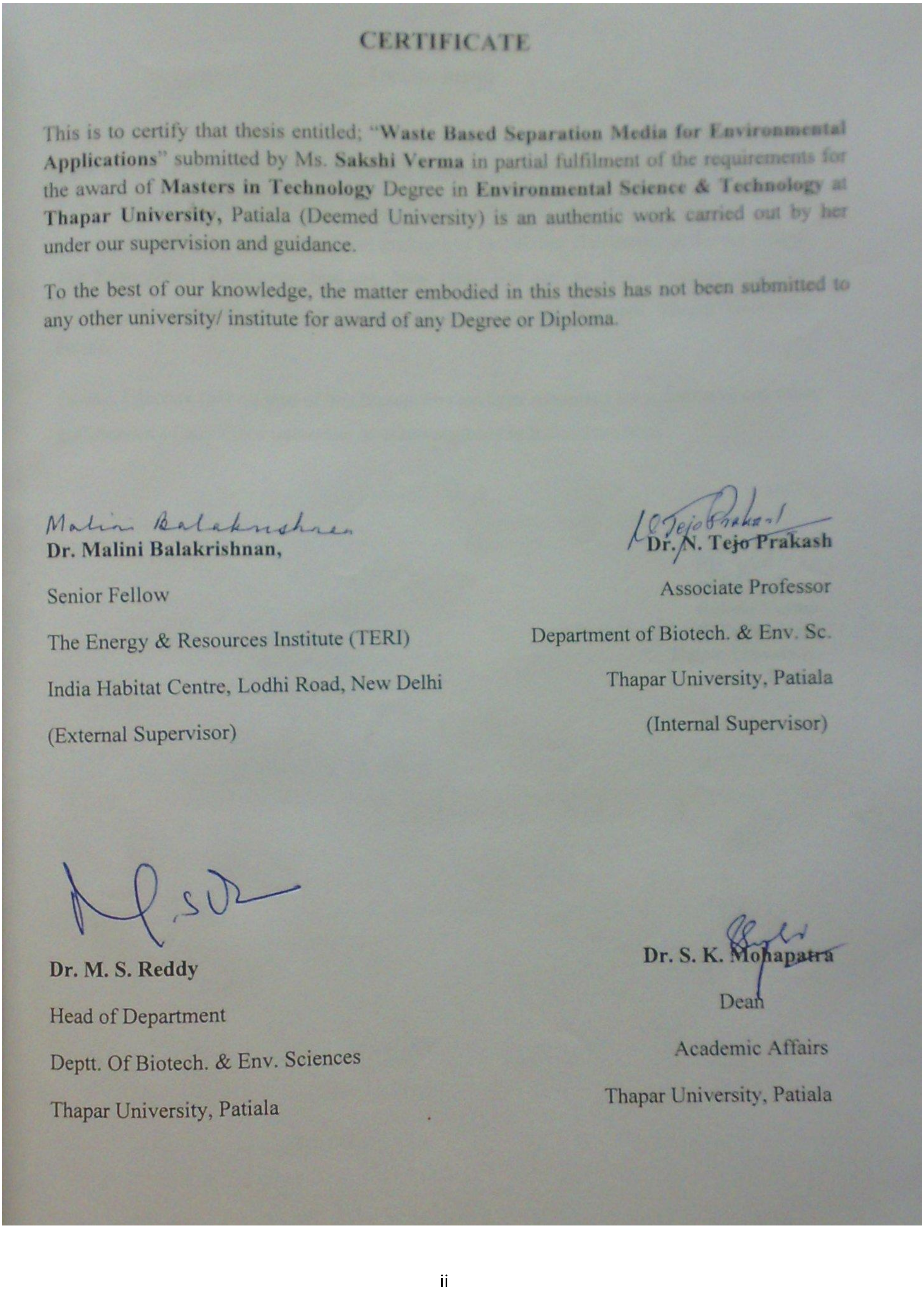
July 2011



CERTIFICATE

This is to certify that thesis entitled; "**Waste Based Separation Media for Environmental Applications**" submitted by Ms. **Sakshi Verma** in partial fulfilment of the requirements for the award of **Masters in Technology** Degree in **Environmental Science & Technology** at **Thapar University,** Patiala (Deemed University) is an authentic work carried out by her under our supervision and guidance.

To the best of our knowledge, the matter embodied in this thesis has not been submitted to any other university/ institute for award of any Degree or Diploma.

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Declaration

I, the undersigned, hereby declare that the research work presented in the M.Tech project entitled “Waste based Separation Media for Environmental Applications” has been carried out by me under the supervision and guidance of Dr. Malini Balakrishnan, Senior Fellow, The Energy and Resources Institute, New Delhi and Dr. N. Tejo Prakash, Associate Professor, Department of Biotechnology and Environmental Sciences, Thapar University, Patiala.

Further, I declare that no part of this Dissertation has been submitted for a degree or any other qualification of any other university or examining body in India/elsewhere.

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Acknowledgements

I would like to express my special gratitude to **Dr. Malini Balakrishnan** and D**r. Vidya S. Batra**, Senior Fellow, The Energy and Resources Institute, New Delhi, for giving me this opportunity to work in this project and their continuous support and guidance throughout the project. I thank them immensely for giving me excellent technical knowledge whenever required.

I would like to express my special thanks to **Dr. N. Tejo Prakash**, Associate Professor, Department of Biotechnology & Environmental Sciences, Thapar University, and also the rest of my professors for their encouragement and guidance.

I also express gratitude to **Mr. Ravi Karan Singh**, **Mr. Prahlad Kumar Tewari** and **Mr. Rajeev Pillai** for providing me immense help and support in handling and working on the instruments without which this project could not be completed and for providing the relevant data whenever required.

I would also like to give a special thanks to **Mr. Ajit** for the help and cooperation he has provided me.

I would like to thank **Ms. Snehlata**, **Ms. Kruthi**, **Ms. Nidhi**, **Ms. Aditi**, **Mr. Uday**, **Mr. Gaurav**, and **Ms. Swati** for providing excellent working conditions in the lab and their constant support and help.

Finally and most importantly, I would like to thank all my classmates for providing excellent working conditions in the class and supporting me.

Sakshi Verma

Abstract

With an increased pace of industrialization especially in developing countries, environmental problems have also increased. More waste is being generated and thus there is an emerging interest in waste utilization. At the same time, with growing population and economic development, there is a rise in water consumption and wastewater generation. Due to the large variety of pollutants that are now entering our water resources, there is a need for improved technologies for removing different contaminants in water. In this context, hybrid membranes combining both adsorption and filtration present an interesting alternative for the treatment of contaminated waters.

This work reports the use of low cost carbon membranes prepared from fly ash (generated from burning of sugarcane bagasse) and different commercial activated carbons. The removal of two organic contaminants viz. low molecular weight phenol and high molecular weight humic acid was examined. Different filtration set-ups were used and the most suitable one identified. The filtration performance in terms of % contaminant removal, flux and transmembrane pressure was studied. The changes in membrane properties were examined by mercury porosimetry and surface area analysis. Select batch adsorption studies were also conducted to verify some of the findings.

This work proves that carbon membranes can be used for removal of low and high molecular compounds from aqueous streams. Membranes prepared with lower surface area activated carbons were more stable and suitable for treating aqueous streams. Compared to testing in a closed filtration cell, testing in an open reactor using a submerged membrane module is recommended for these membranes. The membrane configuration (straight or reverse placement) appears to have an effect on the removal of organic pollutants. Of the membranes tested, Innova coated membrane (CI) in straight configuration appears to be most suited for phenol removal. For humic acid removal, the carbon coating appears unnecessary and the uncoated membrane in reverse configuration is most suitable.

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1. Introduction

Increasing population combined with growing industrialization has led to increasing waste generation and environmental pollution. In addition, there is a growing demand for clean water for human consumption, agricultural application, or industrial use [Cicek N, 2003]. Rapid and continuous economic development and growth especially in developing countries around the world have led to significant pollution of freshwater resources along with a considerable increase in water demand. The worldwide demand for high quality water for various end-uses will thus be difficult to meet in the foreseeable future unless appropriate, cost-effective treatment options are readily available.

As water quality becomes increasingly inferior, successful alternative treatment measures are urgently required for removal of an increasing number of pollutants. Application of particulate filters as well as micro/ ultra filters followed by activated carbon based adsorbents is well established in the field of drinking water purification as well as wastewater treatment. Removal of organic pollutants has been done using membrane processes [e.g. Kujawski et al, 2004] as well as adsorption [e.g. Dutta et al., 2001]. The cost of adsorptive removal is high when pure sorbents (i.e. activated carbon) are used due to their high price [Rong et al., 2005; Figueiredo et al., 2005]. Consequently, sorbents obtained from industrial and agricultural waste such as bagasse fly ash [Mukherjee et al., 2007], corncob [El-Hendawy et al., 2001], activated sludge [Martin et al., 2004], red mud [Tor et al., 2006], lignin [Gonzalez-Serranoa et al., 2004], wood charcoal [Mukherjee et al., 2007], coconut shell [Radhika and Palanivelu, 2006] etc. have been explored. Alternatively, the cost can be reduced by reducing the amount of pure sorbent used.

The application of pressure driven membrane processes for the removal of low molecular weight organic compounds from wastewater has been analyzed [e.g. David et al., 2006]. Unfortunately, despite excellent rejection of salts, those processes often show low rejection levels for many small organic molecules. So hybrid processes combining pressure driven membrane process with adsorption have been suggested [Ipek, 2004].

Since membrane filters are also expensive, there is an effort towards use of waste materials like fly ash for their preparation (Jo et al., 1996).

Fly ash is the waste generated by the incineration of coal, municipal solid wastes and agricultural residues like sugar cane bagasse, rice husk etc. Fly ash from coal fired power stations finds use primarily in bulk applications like cementitious (concrete and cement) products [Al and McCarthy, 1994] as well as in construction sector, such as highway road bases [Takada et al., 1995], grout mixes [Akram et al., 1994] and stabilizing clay based building materials [Temimi et al., 1995].

This work examines adsorption combined with filtration for the removal of specific low and high molecular weight compounds from water. Waste based separation media viz. fly ash based filters coated with wood / coconut shell based activated carbon has been used for this purpose. The hybrid adsorption- filtration technique is expected to be useful for the advanced treatment of industrial wastewaters and in drinking water treatment applications.

2. Objectives

The objectives of this work are as follows:

- To evaluate the performance of fly ash membranes, with and without activated carbon coating, for phenol and humic acid removal.
- To characterize the fresh / used membranes using techniques such as pore size analysis, surface area.
- To examine removal of humic acid and phenol by the membrane components (fly ash, activated carbons) under batch adsorption conditions.

3. Literature Review

3.1. Water Pollution: Challenges and Opportunities

The consequences of pollution of all types of water resources are associated with an increase in the concentration of toxic compounds in drinking water, which is also responsible for the high cost of water potabilisation [Hestekin et al, 1998]. In addition, most of the pollutants (non degradable) accumulate in different trophic levels of the environment through the natural processes of bioaccumulation and biomagnification. This results in various costs to the environment, principally the loss of biodiversity that leads to the present global concern – loss of ecosystem stability. Very little attention had been given to this problem until shortly before the 19th century. Nowadays, the conservation of water resources by preventing their pollution by hazardous and toxic elements is one of the most important challenges to the human race.

3.2. Organic Compound Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (adsorbate). The concept of an organic compound adsorption on activated carbon is not new, and since the beginning of the century, filters have been used to remedy the objectionable taste and odour of the water. Activated carbons are among adsorbents having a high specific surface area; they exhibit a strong adsorption capacity for phenolic compounds. Their systematic use in water treatment is the result of several factors: (a) creation of an efficient technology of carbon activation, (b) decrease in prices of water treatment by reusing carbon after its regeneration and (c) the use of carbonaceous wastes material for the manufacture of activated carbon.

As such, various waste biomass such as, apricot stones, rubber seed coat, coconut shells, rice husks etc. has also been used as precursors for activated carbon preparation; waste tire rubber, etc. have been utilized for this purpose [Girgis et al, 2002; Laine, Calafat, 1991; Youssef, Mostafa, 1992].

The adsorption by activated carbon has emerged as the most efficient and the most economical process for removing undesirable organic materials from aqueous solution [Gupta et al, 2004; Tay et al., 2001]. Feasibility of less expensive activated carbons prepared from spent oil shake [Darwish et al., 1996], bagasse fly ash [Gupta et al., 1998], tamarind nut

[Srinivasan et al., 1998], soyabean hulls [Flock et al., 1999] and coconut husk [Vinod, Anirudhan, 2002] for the removal of organic compounds has also been studied.

Adsorption of phenolic compounds on activated carbon is relatively simple; the process of regenerating the adsorbent by desorption of the organic compounds is important since it has high affinity for the compounds to the sorbent surface. Currently, techniques, such as thermal regeneration [Torrents et al., 1997], chemical regeneration [Qadeer et al., 2002], bio regeneration [Hutchinson et al., 1990] and ultrasound [Rege et al., 1998] are used for the desorption of phenols from activated carbon.

3.3. Utilization of waste materials as a resource

Some of the common agricultural wastes include bagasse, rice husk, cashew nut shell, areca nut shell and groundnut shell. Bagasse is the fibrous residue from sugarcane juice extraction and is one of the most valuable by-products in sugar mills. Bagasse has a calorific value of 8021 kJ/kg and is utilised as a fuel in boilers to generate steam and electricity through co-generation. Bagasse fly ash has been examined as an adsorbent as well as an additive in cement and concrete [Gupta et al., 2003; Srivastava et al., 2006]. However, its high carbon content can cause a hindrance in its application for concrete.

Carbonization of one tonne of coconut shells produces around 300 kg of charcoal, which can be converted into 120 kg of activated carbon [Bhatnagar et al., 2010]. Coconut shell is very suitable to be converted into activated carbon due to its hardness and abrasion resistance. Further, coconut shell chemical composition is akin to hard wood which mainly composed by lignin and cellulose [Rodrigue, Pinto, 2007]. The production of activated carbon involves two major steps viz. - carbonization and activation step. Carbonization is an inert thermal process to convert raw material into solid char generating liquid and gaseous by- products [Chattopadhyaya et al., 2006]. Whilst, activation is a subsequent process to enhance the char porosity and to clean out the tar-clogging pores; thus increasing the total surface area of the produced activated carbon [Turmuzi et al., 2004].

The true fruit of cashew is the nut, a kidney-shaped structure of approximately 2-3 cm in length, which is attached to the end of a fleshy bulb, generally called the cashew apple. The shell comprises some 50% of the weight of the raw nut, the kernel represents 25% and the remaining 25% consists of the natural cashew nut shell liquid (CNSL), a viscous, reddish brown liquid. CNSL has a variety of industrial uses, which were first developed in the 1930s. CNSL exhibits some outstanding properties such as excellent corrosion and water resistance, satisfactory chemical resistance, better flexibility and drying than other oils and can be used as a binding material. CNSL also suffers from some drawbacks like dark colour, lack of hardness and lack of toughness.

3.4. Humic Substances

Humic substances represent a wide range of non-biodegradable organic matter that needs to be removed from drinking water supply. In rivers, lakes and ground waters, humics come from the leaching of soils, sediments, aquatic animal and vegetal life, as well as from the effluents of sewage treatment works. Humics consist of numerous organic functions, particularly the carboxylic and phenolic groups that have specific properties, such as the ability to ionise and to form complexes with metallic salts. Consequently, they can coagulate and be filtered through bio filters or membranes.

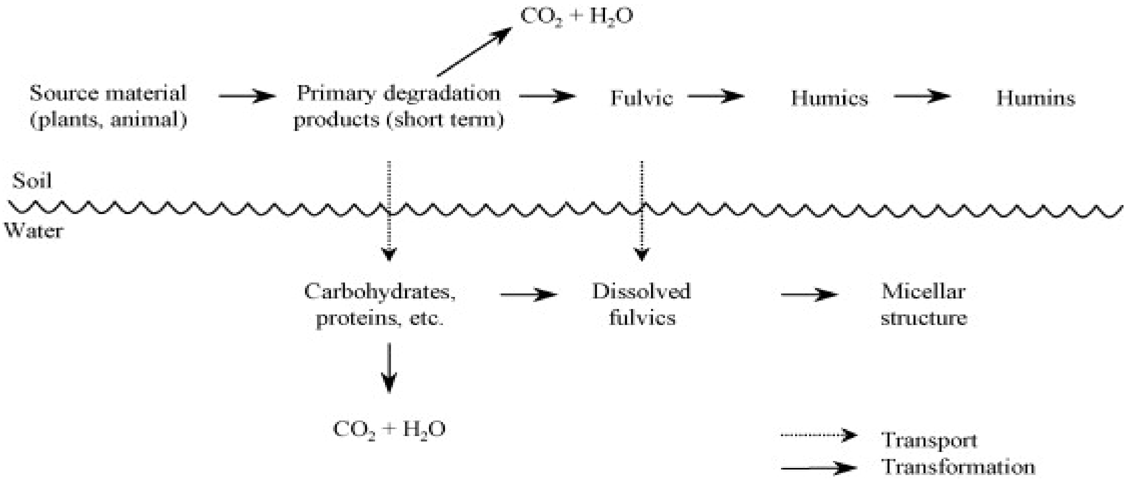


Fig. 1. The formation path way of humic substances [André and Khraisheh, 2009]

They cover such a large molecular mass range (from one to several thousands daltons) that a satisfactory removal mechanism has been difficult to determine, prompting an investigation into this particular problem [André and Khraisheh, 2009].

3.4.1. Formation of Humic Acid

Humic acids are primarily a result of the microbiological degradation of surrounding vegetation and animal decay and enter surface waters through rain water run-off from the surrounding land. This often gives rise to large seasonal variations, high concentrations in the wet season and lower concentrations in the dry season.

3.4.2. Structure of Humic Acid

Humic acids (HAs) consist of a skeleton of alkyl/aromatic units cross-linked by a variety of functional groups such as carboxylic, phenolic and alcoholic hydroxyls, ketone and quinone groups [Stevenson, 1994; Alvarez-Puebla et al., 2006]. The existence of carboxyl and phenolic groups causes humic acid to have negative charges in aqueous solutions. The solubility of humic acid in aqueous media also depends on the number of –COOH and –OH groups. Humic acids show spontaneous changes in their conformation and aggregation state as a function of solution conditions such as concentration, pH and ionic strength [Alvarez-Puebla et al., 2006; Senesi, 1999; Senesi et al., 1997].

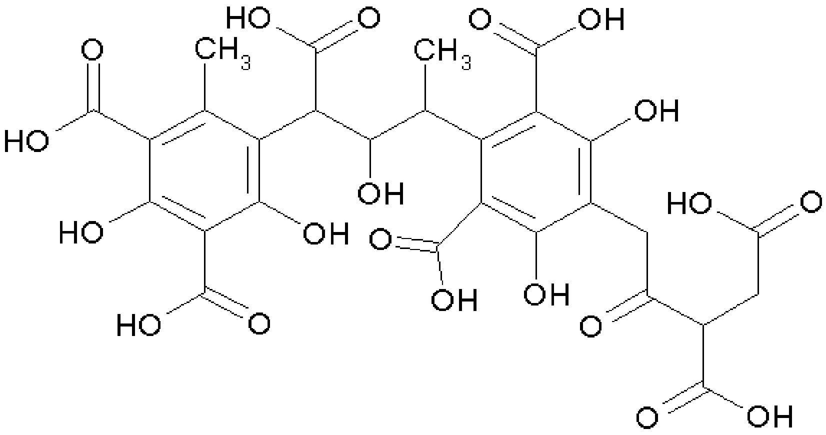


Fig. 2: Structure of Humic Acid [Stevenson, 1994]

3.4.3. Problems with Humic Acid

- Imparts yellow to brownish colour to water.
- When present in conventional treatment processes like chlorination, carcinogenic by-products like trihalomethane (THM) and haloacetic acid are formed.
- When both mineral particles and dissolved humic substance exist in the solution, the latter controls the coagulation process. [Rebhun and Lurie, 1993]
- The presence of humic substances yields bulky flocs, whose settleability is poor hence leading to high supernatant turbidity. [Tambo and Watanabe, 1979; Rebhun et al., 1984; Rebhun, 1990]
- Can cause fouling problems in filtration of surface waters.

3.5. Phenol

Phenol, also known as carbolic acid, is an organic compound with the chemical formula C_6H_5OH. It is a white, crystalline solid at room temperature. It consists of a phenyl ($-C_6H_5$) group, bonded to a hydroxyl (-OH) group. It is only mildly acidic but requires careful handling due to its toxicity and its propensity to cause severe burns.

Phenol is produced on a large scale (about 7 billion kg/year) as a precursor to many materials and useful compounds, some of which are listed below [Weber et al., 2004].

- Condensation with acetone gives bisphenol-A, a key building block for polycarbonates.
- Condensation with formaldehyde gives phenolic resins, the most famous of which is Bakelite.
- Hydrogenation of phenol gives cyclohexanone, an intermediate en route to nylon.
- Nonionic detergents are produced by alkylation of phenol to give the alkylphenols, which are then subjected to ethoxylation.
- Phenol is also a versatile precursor to a large collection of drugs, most notably aspirin but also many herbicides and pharmaceuticals. Phenol is also used as an oral anesthetic/analgesic, commonly used to temporarily treat pharyngitis.

Phenols (consiting of -OH group bound to an aromatic group) are considered as priority pollutants because of their potential harm to human health. They also have adverse effect on some useful bacteria (nitrification bacteria, bacteria in sediment, etc.). (Namane et al., 2006). Phenolic compounds impart objectionable taste and nauseous odor to water. As such, stringent US Environmental Protection Agency (EPA) regulations call for lowering phenol content in wastewater to less than 1 mg/l [US Environmental Protection Agency. Toxicological review: CAS phenol, 2000]. Various options for removal of phenolic compounds from aqueous streams include adsorption [Carmona et al., 2006], enzymatic treatments [Wabner et al., 2001], oxidation [Sobecka et al., 2005] and combined techniques [Hamad et al., 2005].

3.6. Membrane filtration for the removal of organic compounds

Various kinds of membranes have been tested to remove phenol from wastewaters [Bodalo et al., 2009] viz. - liquid membranes [Reis et al., 2007], anion exchange membranes [Kojima et al., 1995], nanofiltration/reverse osmosis membranes [Arsuaga et al., 2006], and pervaporation membranes [Gupta et al., 2003]. Powdered activated carbon has been combined with microfiltration (MF) membrane forming a hybrid system to remove organic compounds [Li, Chen, 2004; Tomaszewska, Mozia, 2002; Vigneswaran, 2003; Khana, 2011]. In order to enhance the removal of humic acid and some other contaminants, adsorbent particles such as powdered activated carbon (PAC) had been added to the ultrafiltration/ microfiltration system [Zhang et al, 2003; Tomaszewska, Mozia, 2002; Oh et al., 2007; Gai, Kim, 2008].

Low-pressure membrane systems are attractive in drinking water treatment and as pre-treatments prior to desalination by reverse osmosis (RO) because they efficiently remove colloids and particles from the source water. However, their performance is often limited by membrane fouling, much of which is attributable to natural organic matter (NOM) [Howe et al., 2006]. In an ongoing study of hybrid adsorbent/membrane processes [Kim et al., 2008], it was found that pre-deposition of the adsorbent on the membrane surface reduces fouling more than addition of an equivalent dose of the adsorbent to the feed.

3.6.1. Pressure driven membrane processes

Pressure driven membrane processes can be categorised as shown below. Broadly, microfiltration is used for removal of suspended solids etc. and requires the lowest applied pressure while reverse osmosis is used for removal of monovalent ions and requires the highest applied pressure.

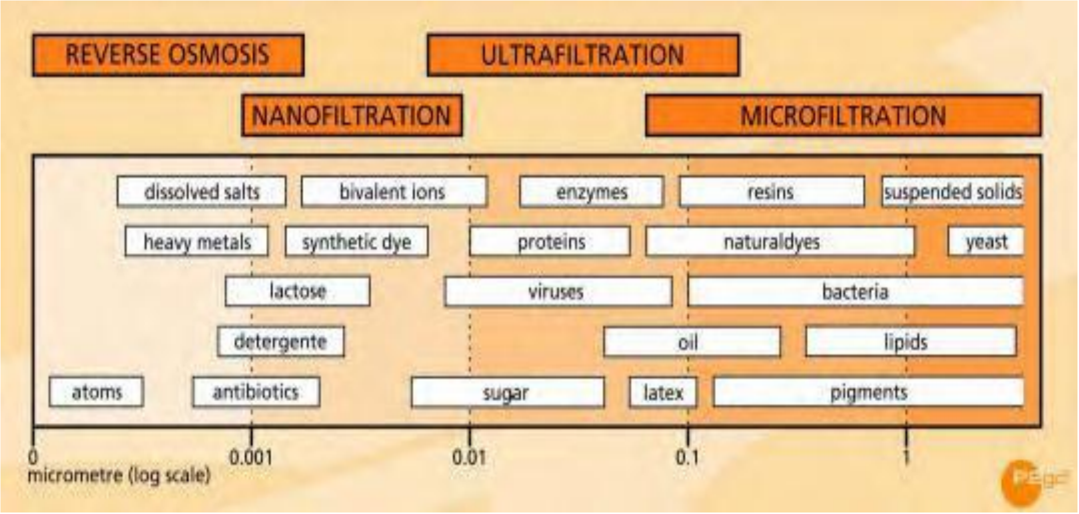


Fig. 3: Application size range of membrane filtration process (Scott, 1996)

3.6.2. Advantages and limitations of membrane filtration [Scott, 1996]

Advantages	Disadvantages
High pathogens removal rate	High capital cost
High natural organic mater removal rate (when enhanced by pre-treatment)	Complicated operation
Small area requirement (compact)	Skilled and trained human power requirement
Save chemical utilization	Pressure limitations
Low energy consumption (low membrane pressure)	Problems related to fouling

3.6.3. Advantages of ceramic membranes

Compared with polymer or organic membranes, ceramic membrane filters have many advantages (Doeke et al, 2006):

- Excellent resistance to acid/alkaline and oxidation chemicals
- Solvent stability
- High thermal stability
- Excellent mechanical and abrasive resistance
- Long life compared with polymeric membrane
- Easy to be cleaned and sanitized with short backwash interval (with air flush), chemical cleaning.

3.6.4. Filtration Configurations (http://www.yale.edu/env/elimelech/AWWA99/sld004.htm)

- Dead End & Cross Flow Filtration system

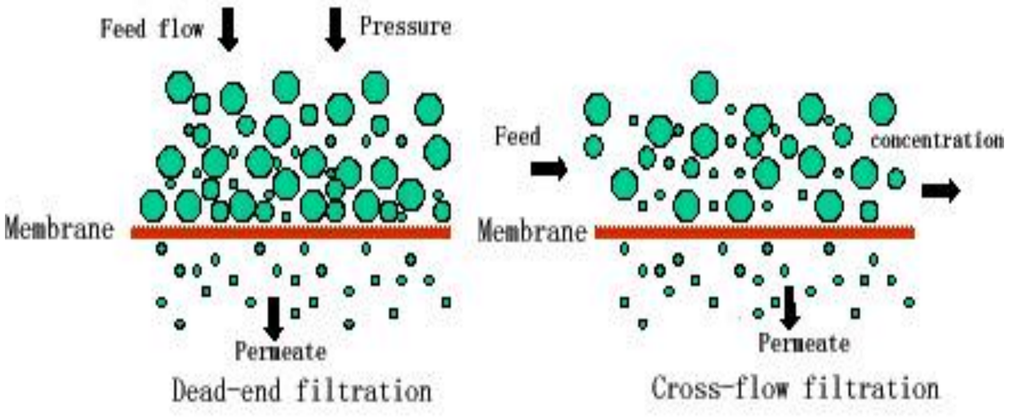
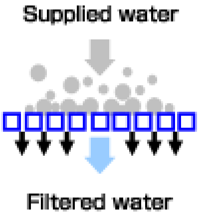
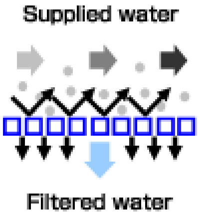


Fig. 4: Dead end and crossflow systems

Table 1: Advantages & Disadvantages of Dead-end and Cross flow systems (http://www.yale.edu/env/elimelech/AWWA 99/sld004.htm)

	Outline	Advantages	Disadvantages
Dead-end (Total) Filtration		• High collection rate (almost100%) • Miniaturization possible • Low cost • Backwashing and chemical cleaning not required.	• Filters must be replaced often • Cannot be used if large amounts of insoluble materials are present.
Crossflow Filtration		• Low filter maintenance frequency • Can be used even if large amounts of insoluble materials are included • Can be used for viscous liquids as well • Can be reused with backwashing and chemical cleaning	• Low collection rate. (Due to separation into filtered water and concentrated water) • Treatment of concentrated water required • Unit is large and complicated • Relatively high cost.

3.6.5. Membrane fouling

If membrane separations are to be economical, high fluxes (flow rate per unit membrane area) are required. Unfortunately, most membrane separations exhibit flux decline as a result of fouling. Fouling may be defined as the deposition of matter on or in the membrane such that the membrane performance is altered. During the flow of a clean liquid through a porous layer, the resistance is constant and the flow rate is constant for a given pressure difference. But when the liquid contains suspended particles, the resistance of the porous layer will progressively increase as the particles accumulate on it, resulting a corresponding drop in the permeate rate at a constant pressure drop. Although fouling is very complicated, it can be classified into two types (Davis, 1992):

(1) **Internal membrane fouling**: The attachment of material within the internal pore structure of the membrane or directly to the membrane surface due to adsorption, precipitation, pore plugging, particulate adhesion, etc.

(2) **External cake fouling**: The formation of a stagnant cake layer of the membrane surface due to concentration polarization as the material being filtered is carried to the membrane by permeate flow and is then rejected by the membrane.

Based on fouling materials, membrane fouling can be distinguished by four types:

(1) **Inorganic fouling/scaling:** This is caused by the accumulation of inorganic precipitates such as metal hydroxides, and “scales” on membrane surface or within pore structure. Precipitates are formed when the concentration of chemical species exceeding their saturation concentrations.

(2) **Particle/colloids fouling:** In most cases, particles and colloids do not really foul the membrane because the flux decline caused by their accumulation on the membrane surface is largely reversible by hydraulic cleaning measures such as backwash and air scrubbing. A rare case of irreversible fouling by particles and colloids is when they have smaller size relative to membrane pores. Therefore, those particles and colloids can enter and be trapped within the membrane structure matrix, and not easily be cleaned by hydraulic cleaning.

(3) **Microbial fouling**: This refers to the formation of biofilms on membrane surfaces. Once bacteria attach to the membrane, they start to multiple and produce extracellular polymeric substances (EPS) to form a viscous, slimy, hydrated gel. This gel structure protects bacterial cells from hydraulic shearing and from chemical attacks of biocides such as chlorine (Syed et al., 2000).

(4) **Organic fouling**: Organic fouling is profound in membrane filtration with source water containing relatively high natural organic matters (NOM). Surface water (lake, river) typically contains higher NOM than ground water, with exceptions. For source water high in NOM, organic fouling is believed to be the most significant factor contributed to flux decline (Mallevialle et al., 1996; Lahoussine et al, 1990).

3.6.6. Resistance to filtration

Membrane resistance to filtration is a good indicator of the extent of membrane fouling. As the resistance increases due to adsorption or clogging of pores, the permeate flux declines and the transmembrane pressure (TMP) increases. The total resistance to filtration can be evaluated from Darcy's law:

$$\mathbf{J=Q/A=\Delta P/\mu R_T} \qquad \mathbf{(1)}$$

Where, J is the flux through the membrane, A is the membrane filtration surface area, Q is the volumetric flow rate through the membrane, μ is the dynamic viscosity, R_T is the total resistance to filtration, and ΔP is the transmembrane pressure.

The total membrane resistance is modelled as the sum of the resistances to filtration through the membrane (R_m) and through the cake layer (R_c). Further, the resistance to filtration through the cake layer has two components: pore blocking (R_p), primarily due to particles of the same size range as the membrane pores, and adsorption (R_a), which alters the membrane pore size through micro/nano-scale interactions with the pore openings and walls. It has been observed that the cake layer could not be thoroughly removed, so that R_a and R_p cannot be separated accurately [Fang and Shi, 2005]. Based on the above, Eq. (1) can be modified as:

$$\mathbf{J=Q/A=(\Delta P/\mu).\ (1/\ (R_m+R_c))} \qquad \mathbf{(2)}$$

4. Materials & Methods

4.1. Materials

The **bagasse fly ash** for preparing the filters was obtained from Simbhaoli Sugar Mills, Ghaziabad District, Uttar Pradesh.

Merck Activated Carbon: is a commercially available carbon obtained from Merck Chemicals, Mumbai.

Innova Carbon: generated from waste coconut shells was obtained from Innova Corporation, New Delhi.

SR Carbon: generated from waste coconut shells was obtained from SR Carbons, Bellary, Karnataka

The **binder**: used for the preparation of carbon membranes was obtained from waste cashewnut shells and obtained from Satya Cashew Chemicals Pvt. Ltd., Nanganallur, Chennai.

Humic acid was supplied by Himedia Chemicals, Mumbai. **Phenol** was obtained from Qualigens, New Delhi. All chemicals used in sample analysis were analytical grade and were procured locally.

The carbon membranes used in this work (Figure 5) were prepared by coating the activated carbon on sintered fly ash supports as per the procedure developed at TERI [Batra, Tewari, 2009]. The fly ash supports consisted of two layers viz. support and intermediate layer with varying pore size.

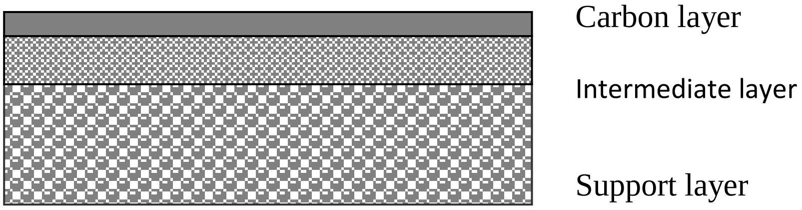


Fig. 5: Structure of carbon membrane

The following membranes were tested.

Table 2: Membranes tested

Membrane	Abbreviation
Carbon membrane prepared with Merck activated carbon	CM
Carbon membrane prepared with SR activated carbon	CSR
Carbon membrane prepared with Innova activated carbon	CI
Carbon membrane prepared with binder alone	PR
No carbon coating (uncoated flyash membranes)	UN

4. 2. Methods

4. 2. 1. Characterization of Filters

4. 2. 1. 1. Pore Size Analysis [https://www.micromeritics.com]

The term “porosimetry” is often used to include the measurements of pore size, volume, distribution, density, and other porosity-related characteristics of a material. Porosity is especially important in understanding the formation, structure, and potential use of many substances.

Mercury porosimetry analysis is the progressive intrusion of mercury into a porous structure under stringently controlled pressures. From the pressure versus intrusion data, the instrument generates volume and size distributions using the Washburn equation. If mercury is placed in contact with a pore opening, the surface tension of the mercury acts along the line of contact with the opening equal in length to the perimeter of the opening and creating a force-resisting entry. The magnitude of resisting force is proportional to the length of the line of contact, the surface tension (Υ) of mercury, and the cosine of the contact angle (θ). For a pore with a circular opening at the surface, the resisting force is expressed as

$$\mathbf{f_R = \pi D \Upsilon \cos\theta}$$

An externally applied pressure tending to force mercury into the opening acts over the surface of the interface bridging the opening. The externally applied force, therefore, is the product of the pressure (P) and area (A) over which the pressure is applied. For a pore of circular cross-section,

$$\mathbf{f_{Ext} = PA = P\pi D^2/4}$$

At equilibrium, just before the resistive force is overcome, the equation is,

$$-\pi D \Upsilon \cos\theta = \pi D^2 P/4$$

Therefore, at any pressure, the pores into which mercury has intruded have diameters greater than

$$D = -4\Upsilon \cos\theta /P$$

By measuring the volume of mercury that intrudes into the sample material with each pressure change, the volume of pores in the corresponding size class is known. The volume of mercury that enters pores is measured by a mercury penetrometer (an electrical capacitance dilatometer). These devices are very sensitive and can detect a change in mercury volume of under 0.1µL.

In this work, mercury porosimetry measurements were done for the fresh and used membranes using a Micromeritics pore sizer, U.S.A. For the testing, the membranes along with the separation layer were cut into small chunks with the help of a plier. Then the samples were kept for drying in oven at a temperature of 105^oC for about 1h.

The dried sample was then kept in the dessicator for about 10 min and then 1g of sample was introduced into the dried and weighed pentrometer. The pentrometer containing the sample was then fitted into the instrument for analysis.

4.2.1.2. Surface Area Analysis

Measurements of gas adsorption isotherms are widely used for determining surface area and pore size distribution of solids. Generally nitrogen gas is recommended when the values are above $5m^2/g$. The non-specific Brunauer-Emmett-Teller (BET) isotherm method is commonly used. The BET equation is applicable at low p/po range and is written in the linear form (Wachs 1992).

$$p/[na(p - po)] = (1/namC) + [(C - 1)/ namC]*(p/po)$$

Where:

p = Sample pressure

po = Saturation vapour pressure

nam = Monolayer capacity

na = Amount of gas adsorbed at the relative pressure

C = BET constant

Sample is first regenerated to remove the adsorbed gases & moisture from the surface.

Mixture of helium gas (70%) and nitrogen gas (30%) is passed over the sample in the tube.

Sample is then dipped in liquid nitrogen. Sample powder adsorbs nitrogen on the surface at liquid nitrogen temperature. After confirming that adsorption is over, sample tube is dipped in the water. This leads to desorption of adsorbed nitrogen from sample, which is quantitatively determined using a Thermal Conductivity Detector coupled with an in-built Electronic Integrator.

In this work, surface area was determined for the activated carbons and the carbon membranes using Smartsorb 92/ 93 surface area analyser procured from Smart Instruments Co. Pvt. Ltd.

4.2.2. Filtration experiments: The membranes were fitted in different modules, depending on their shapes and sizes.

The membranes were fitted in different modules and tested.

- **25mm. Stainless Steel Microfilter**: This set-up was used for a rapid preliminary screening. Each 25mm. diameter membrane disc was inserted in a stainless steel module as shown in Figure no. 6. 5ml. of humic acid (10mg/L) was injected slowly from the upper end and permeate was collected from below. About 200 mL was filtered through the module. Permeate through each 5mL. filtration was collected in test tubes and analyzed spectrophotometrically.

Fig. 6: 25mm module

- **6cm. Dead End (Pressurized Unit):** The membrane was fixed into the module as shown in Figure no. Humic acid (10 mg/L) was taken in 2L beaker and was pumped into the cylindrical module from the upper end through a peristaltic pump (Enertech, Mumbai, India). A constant liquid head was maintained over the membrane, in the module. The permeate was collected in a measuring cylinder from the bottom tubing at 5 min intervals over 2 h duration. The volume of permeate collected after each 5 min was noted for flux calculations and the samples were analyzed spectrophotometrically.

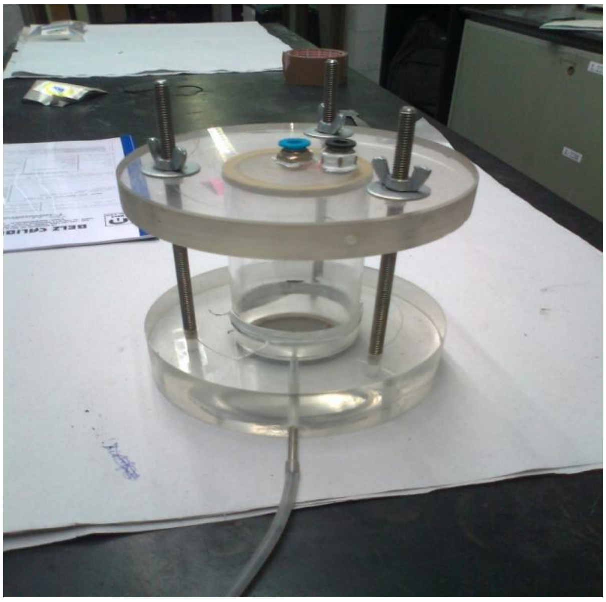


Fig. 7: 6cm module

- **5cm. * 5cm. Dead End (Suction) Unit:** The membrane module was prepared by fixing (using silicone gel) one membrane on each side of the square support with inbuilt flow channels. The module was connected to a stainless steel pipe through which permeate could come out due to suction through the membranes. The pipe was further connected to a polymer tubing which passes through a peristaltic pump. Connections were made across the manometer in order to measure the pressure across the membrane. The membrane module was submerged in a 2L. beaker filled with humic acid (10mg/L). The pump speed was fixed at 10rpm. and it was switched on for collection of permeate in a continuous mode. The permeate was collected in a measuring cylinder and the volume collected in a known time period was noted. Permeate was collected over 5 min interval in test tubes fora duration of 2 h and the samples analyzed spectrophotometrically.
- In case of phenol, the beaker was filled with phenol (5mg/L) and the same procedure described above followed.

4.2.3. Trans- membrane Pressure is the net driving pressure on the membrane. This is the effective pressure for forcing water through the membrane. A clean membrane will have a relatively low TMP, whereas a fouled membrane will have a relatively high TMP, depending on the severity of fouling. When TMP reaches 15-20 psi, a chemical cleaning is recommended.

Fig. 8: 5cm * 5cm module

4.2.4. Batch Adsorption Tests

12 conical flasks were filled with humic acid (10 mg/L.) and to two flasks 0.05g adsorbent was added. Similarly, two sets of each feed concentration were prepared (0.1, 0.2, 0.3, 0.4, 0.5 respectively).The flasks were kept in the Scigenics Biotech Orbitek shaker for a contact time of 5 hrs. at a speed of 160 rpm at 25^{o}C temperature. After 5 hrs., the flasks were taken out and the content of each flask was centrifuged at 8000 rpm for 15 mins. Then the liquid content from the centrifuge tubes was filtered through a 0.45µm filter. After the filtration, the permeate was transferred in different test tubes and the absorbance measured.

4.2.5. Sample Analysis

The concentration of humic acid was determined by directly recording the absorbance at a wavelength of 254nm using a Aquamate UV Visible spectrophotometer. Samples containing phenol were treated prior to absorbance measurement. The pH was adjusted to 7.9 (by adding phosphate buffer to lower the pH or ammonium hydroxide to raise the pH). Subsequently, 0.1 ml. of 4- aminoantipyrene and 0.1ml. of potassium ferricyanide were added. After 15mins., the absorbance was measured at a wavelength of 500nm using a Aquamate UV Visible spectrophotometer. Calibration curves with known sample concentrations were prepared for both humic acid and phenol prior to the adsorption and filtration experiments.

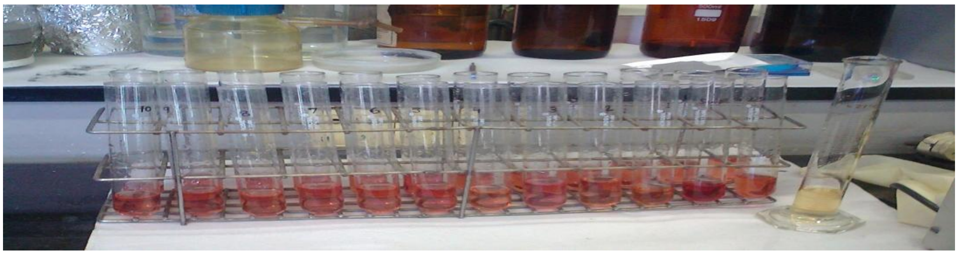


Fig. 9: Spectrophotometric method for detection of phenol

4.2.6. Sonication vs. Weight Loss Analysis

In the 1880's, Jacques and Pierre Curie made the observation that when certain asymmetric crystals such as quartz and sodium potassium tartrate (Rochelle salt) are compressed, they generate an electrical charge. This property would become known as the piezoelectric effect (piezo being the Greek word meaning "to press"). Conversely, when these same crystals are stimulated with electrical current, they contract. By rapidly alternating the electrical current, the crystal rapidly contracts and expands and thus creates a mechanical vibration. Thus, without the use of motors, electrical energy can be converted into mechanical vibration. Ultrasonics applies this physical property by creating high frequency mechanical vibrations by stimulating crystals with high frequency oscillating electrical currents.[https://www.rpsonication101.htm]

An incoming electrical current is converted to a high frequency current which is then used to stimulate the piezoelectric crystals. The crystals are attached to either a probe that can be immersed into a liquid or to a pan as with ultrasonic water baths. In either case, the oscillating crystals impart vibrational energy into the liquid.

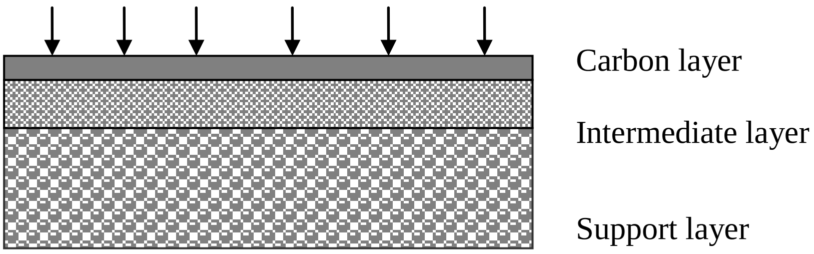
For the experiment, the fresh carbon coated membranes were dipped in a beaker filled with water and the beakers were kept in the ultrasonic water bath supplied by Toshibha, India. The sonication vs. weight loss tests was helpful in analysing the binding of carbon layers to the supports. The lesser time the carbon layer takes to get removed completely, the lesser is its binding ability to the supports. Sonication also gives the advantage of regenerating the membranes by cleaning of the clogged pores.

5. Results and Discussion

5.1. Organics removal through different membranes

Permeate through each membrane was collected and absorbance was measured for knowing the % removal of different organics from their aqueous solutions. The membranes were tested in two modes viz. straight (where the feed was in contact with the carbon layer) and reverse (where the feed was in contact with the support layer) (Figure 10). The concentration of phenol/ humic acid (whichever filtered) in permeate was calculated by the standard curves (Figure).

Straight (feed in contact with carbon layer)



Reverse (feed in contact with support layer)

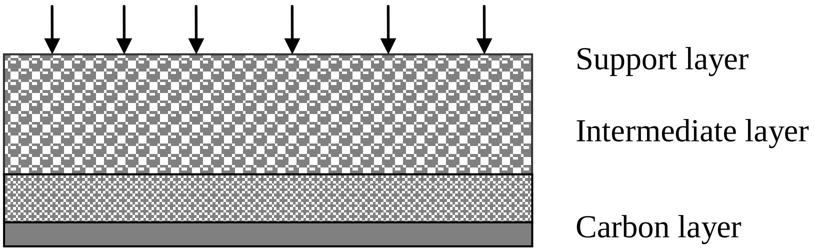


Fig. 10: Modes of testing the membrane

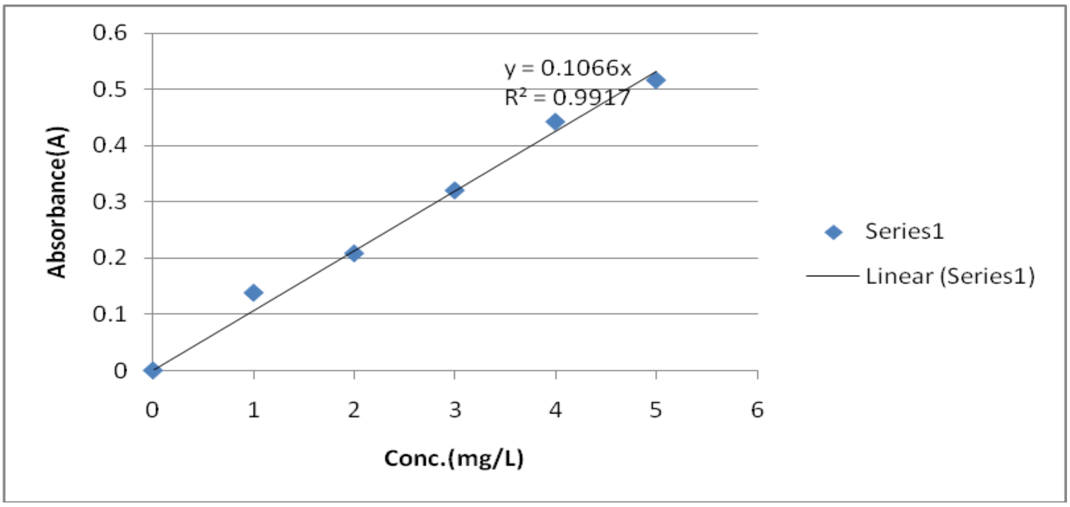


Fig. 11: Standard Curve- Phenol

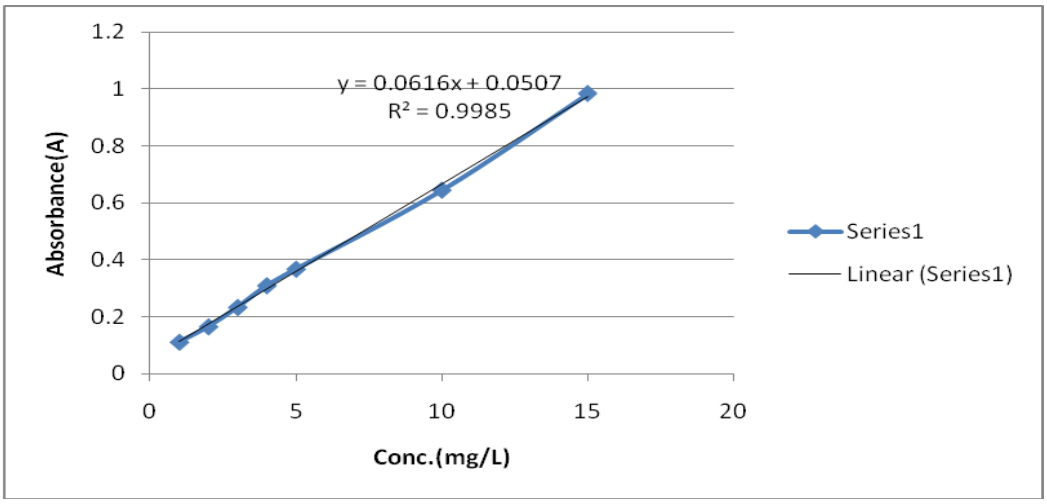


Fig. 12: Standard Curve- Humic acid

5.1.1. Removal of Humic Acid

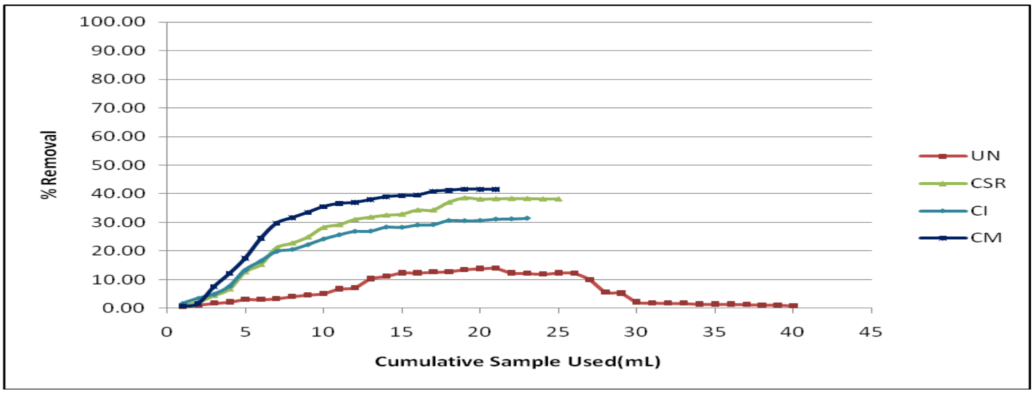


Fig. 13: Removal of humic acid (10mg/L) through 25 mm. membranes (Straight)

Among the small membranes, the commercial activated carbon (Merck) showed the best results. The %removal through each carbon membrane reached a constant after around 20mL feed was filtered. Almost every membrane showed some removal, so all the membranes were tested further.

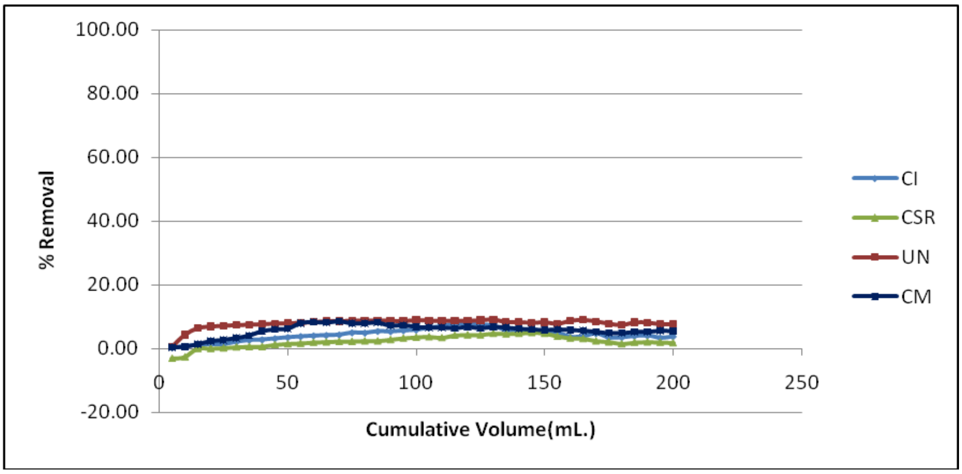


Fig. 14.Removal of humic acid (10mg/L) through 25 mm. membranes (Reverse)

When the membranes are kept in reverse, the removal was lower than in the straight mode. Also, the removal was similar for both carbon coated and uncoated membranes. In some of the experiments, it was observed that some fraction of carbon initially comes out along with permeate. So, the permeate absorbance should be taken only when no more carbon particles are observed.

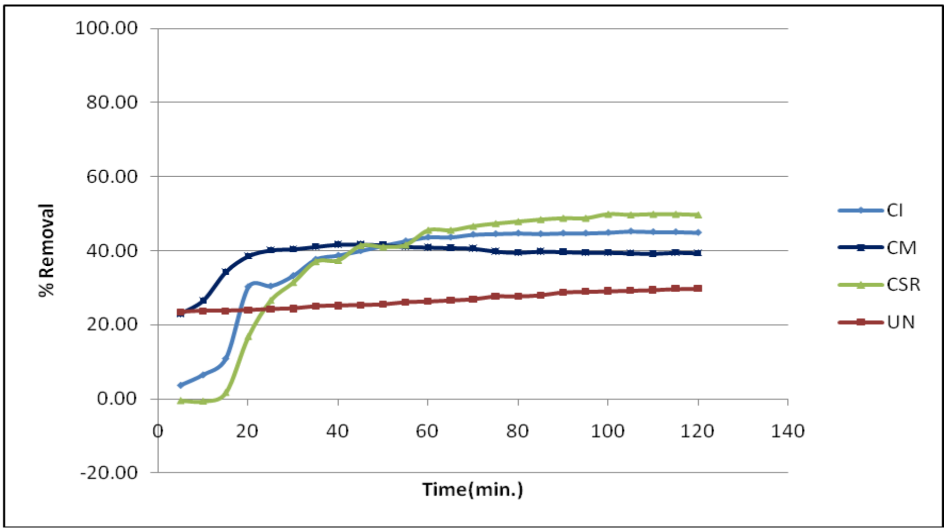


Fig. 15: Removal of Humic acid through 6cm. Circular membranes (Straight)

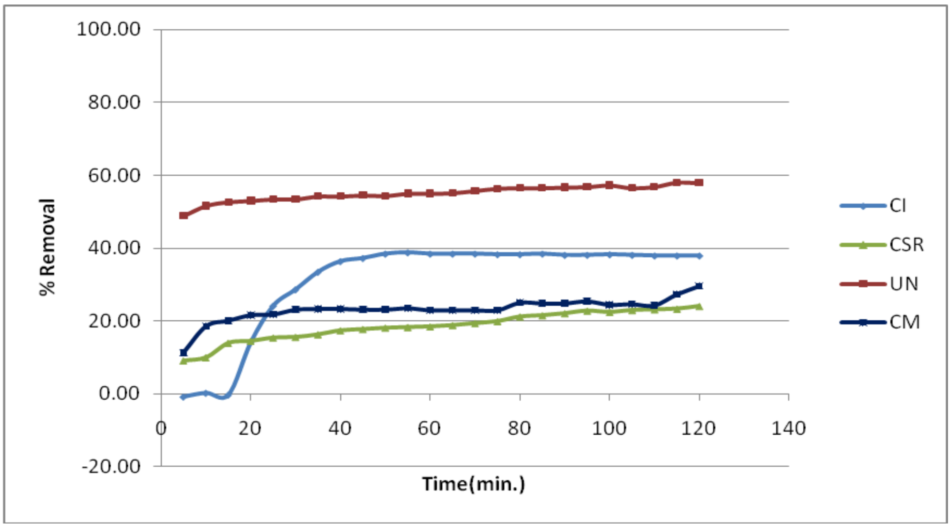


Fig. 16: Removal of Humic acid through 6cm. Circular membranes (Reverse)

Figures 15 and 16 show the results of humic acid removal using a larger filtration area. The uncoated membrane placed in reverse displayed the highest removal. The problem faced with this module was that during assembly, the porous membranes or their coating had a tendency to crack. To avoid this problem, the submerged configuration using the 5 * 5 cm^2 membrane module was tested.

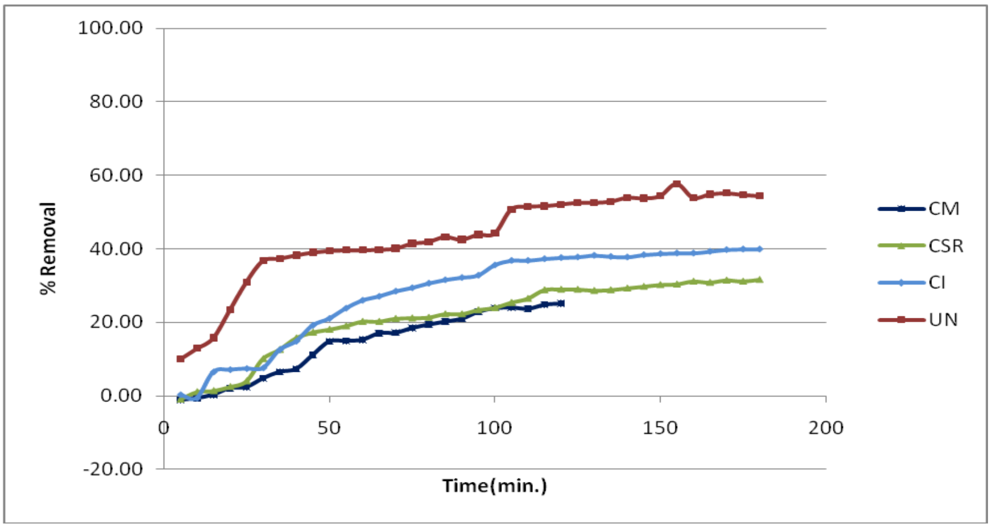


Fig. 17: Removal of Humic acid (10mg/L) through 5cm * 5cm membranes (Straight)

In the submerged configuration, the uncoated membrane displayed the best results in the straight mode (Figure 17). The reason may be that the humic acid particles are big enough to be retained by the filter. It is evident from the batch adsorption results (Section 5.5, Figure 32), that the uncoated membrane shows an adsorption of about 10-11%. So, the rest of the removal of humic acid could have been due to filtration. Of the carbon membranes tested, Merck coated membrane (CM), showed cracks in the carbon coating, as soon as the module was submerged in the humic acid feed. Lesser or no carbon removal was observed in case of Innova and SR coated membranes. The results for Innova and SR carbon membranes are better due to this reason as well.

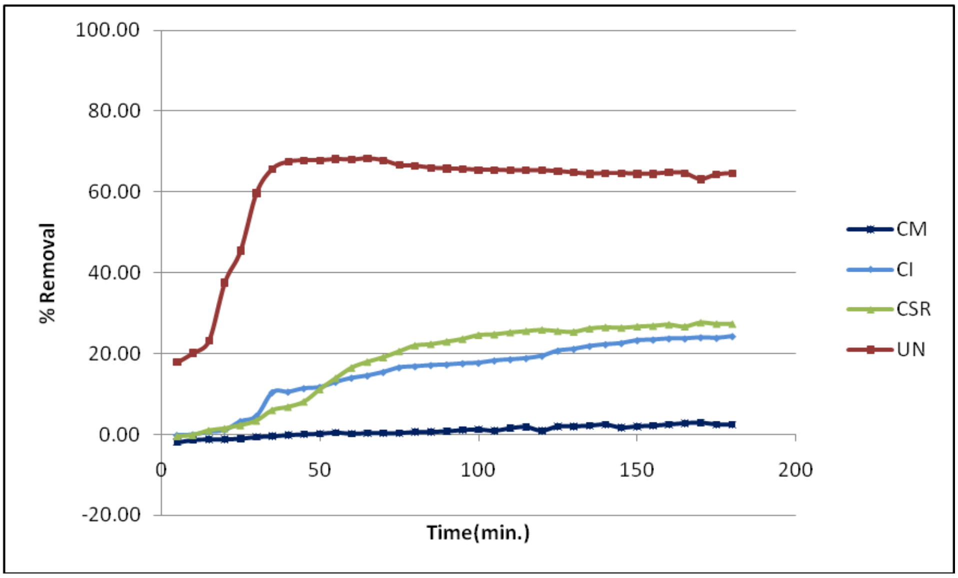


Fig. 18: Removal of Humic acid (10mg/L) through 5cm * 5cm membranes (Reverse)

In case of the membranes placed in reverse (Figure 18), the highest removal (68%) was once again obtained with the uncoated membrane. The removal is marginally higher than in the straight mode (< 60%, Figure 17). So, the uncoated membrane in reverse appears to be the best for humic acid removal.

5.1.2. Removal of Phenol:

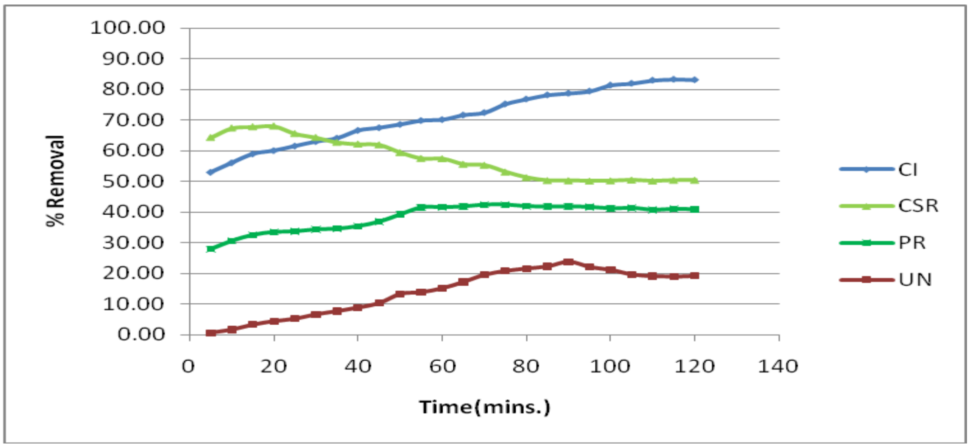


Fig. 19: Removal of phenol (5mg/L) through 5cm * 5 cm membranes (Straight)

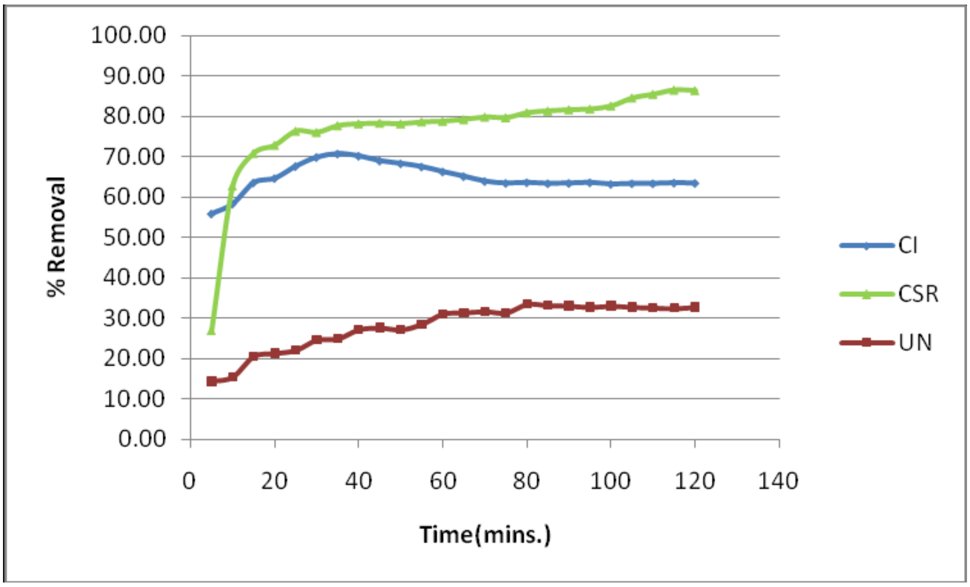


Fig. 20: Removal of phenol (5mg/L) through 5 * 5 cm membranes (Reverse)

Figure 19 and 20 shows the phenol removal profiles for the membranes in the straight and reverse mode. Unlike with humic acid, the performance of the carbon coated membranes was observably superior to that of the uncoated membrane. In the straight mode, the Innova coated membrane (CI) shows highest removal (50-80%) while in the reverse mode the SR carbon coated membrane (CSR) showed the highest removal (30-90%). Surprisingly, there was a decrease in removal with CSR in the straight mode. The reason for this is not clear and needs to be investigated.

5.2. Permeate flux

5.2.1. Humic Acid Filtration

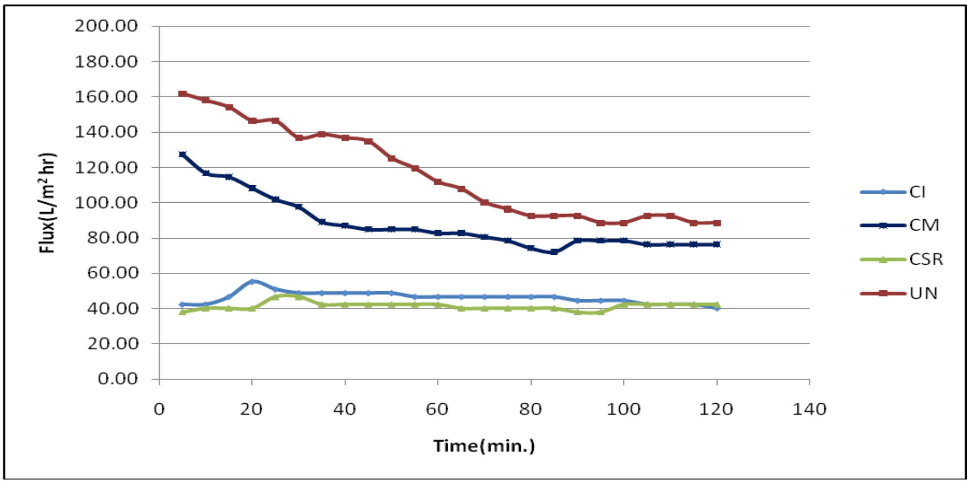


Fig. 21: Permeate flux for humic acid feed (10 mg/L) using 6cm circular membranes (Straight)

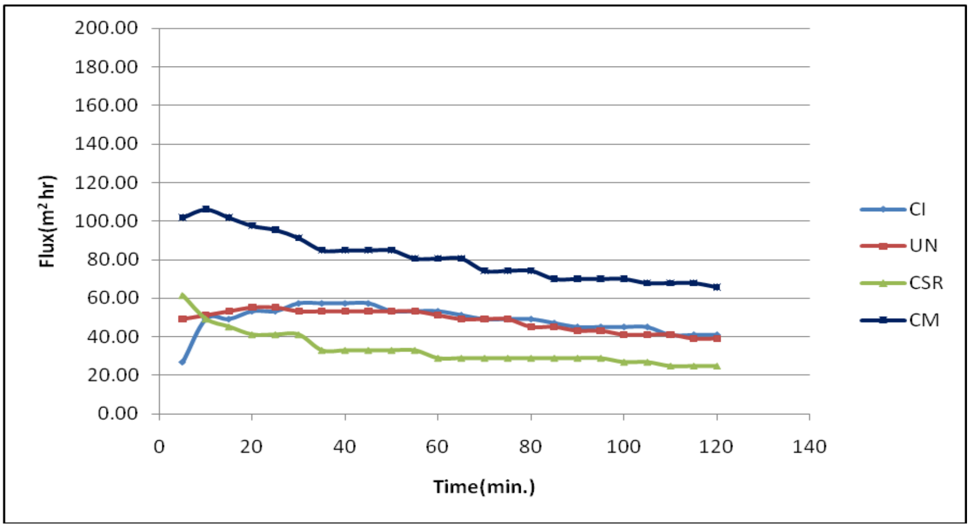


Fig. 22: Permeate flux for humic acid feed (10mg/L) using 6cm circular membranes (Reverse)

Figure 21 and 22 shows the flux profiles for humic acid in the closed dead-end filtration cell. There was no clear trend; further, as mentioned earlier (Sec. 5.1.1), the membranes tended to crack during the cell assembly. Thus, further experiments were done using the submerged membrane module.

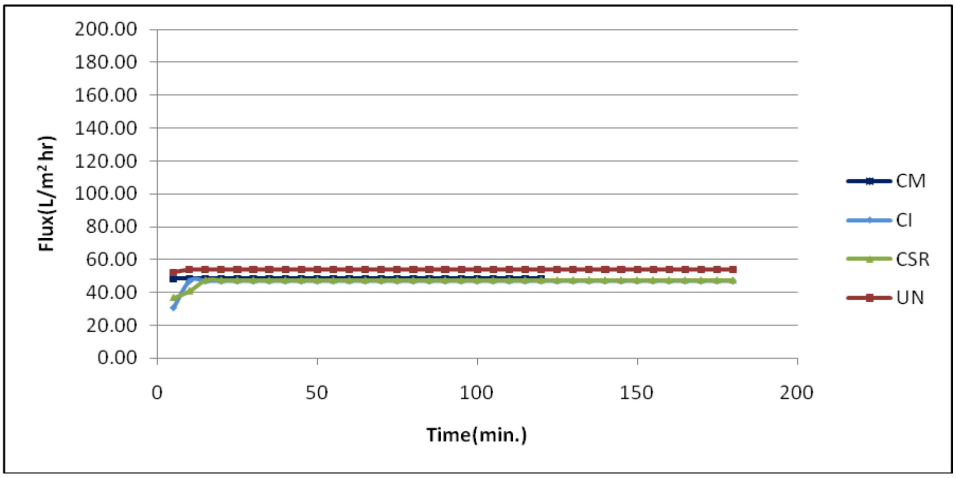


Fig. 23: Permeate Flux for humic acid feed (10mg/L) through 5cm * 5cm membranes (Straight)

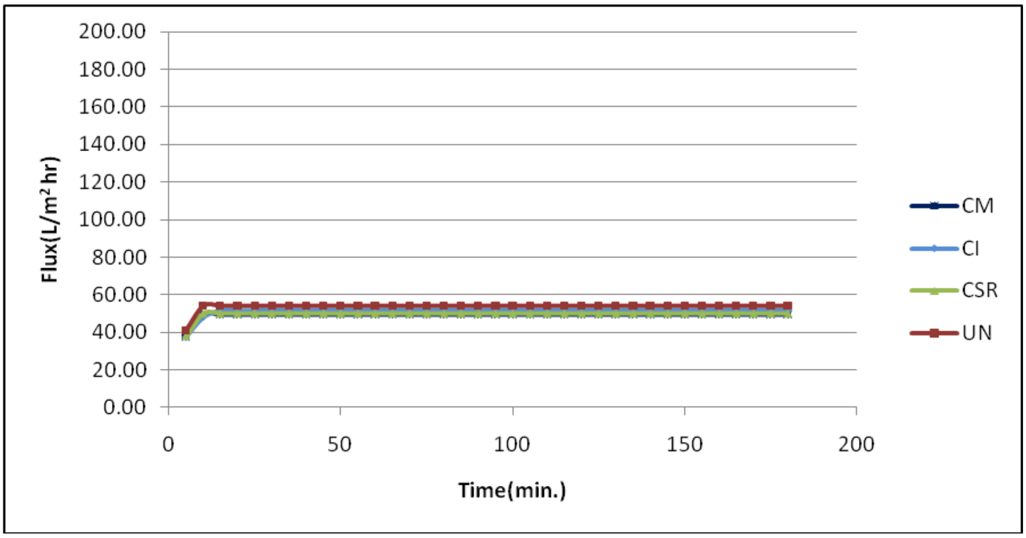


Fig. 24: Permeate Flux for humic acid feed (10mg/L) through 5cm * 5cm membranes (Reverse)

The flux profiles with the submerged membrane modules are shown in Figure 23 and 24. The flux was stable and almost identical for all membranes in the straight and reverse configuration. Since high removal combined with high, stable flux is desired, among the membranes tested, the uncoated membrane in reverse configuration appears to be the most suited for removal of humic acid.

5.2.2. Phenol Filtration

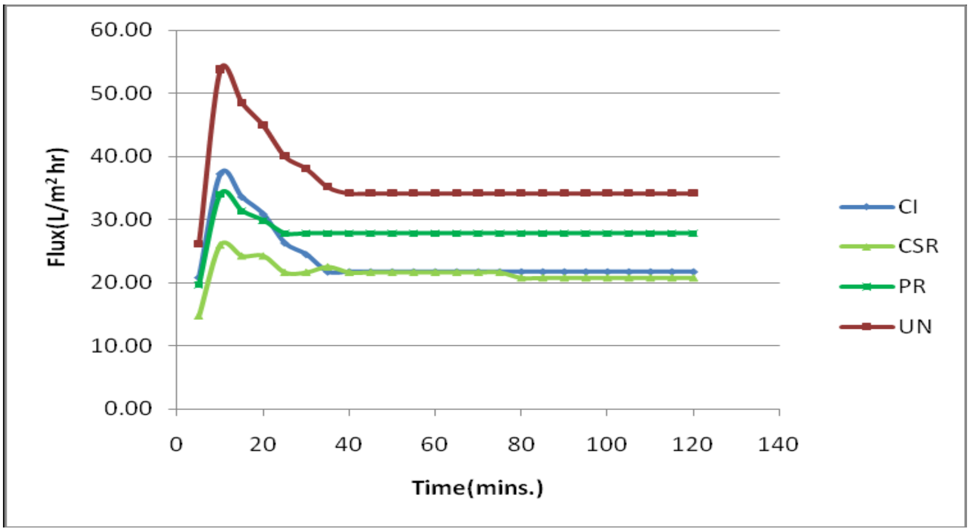


Fig. 25: Permeate flux for phenol feed (5mg/L) through 5cm * 5 cm membranes (Straight)

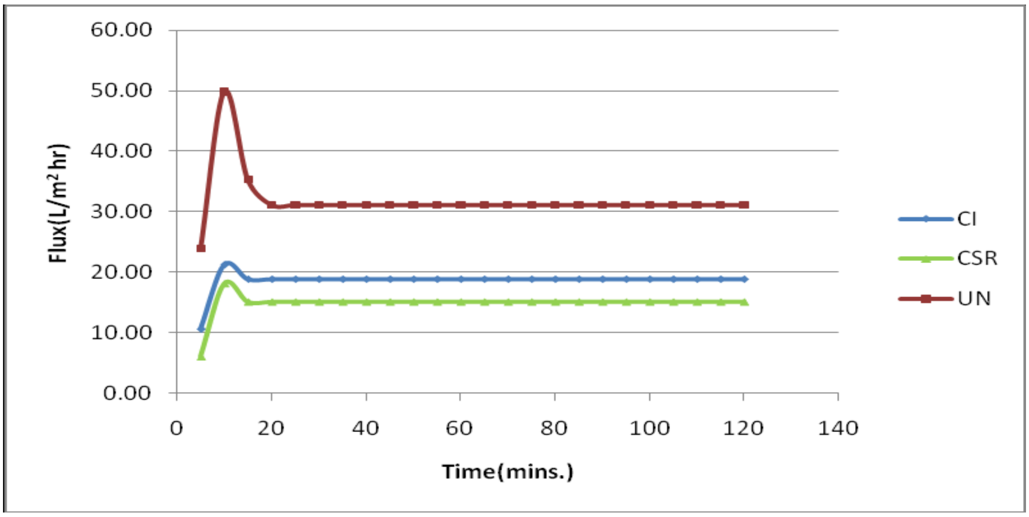


Fig. 26: Permeate Flux for phenol feed (5mg/L) through 5cm * 5 cm membranes (Reverse)

The flux profiles for phenol in the straight and reverse configurations are shown in Figures 25 and 26. The flux is marginally higher in the straight configuration. In both configurations, the uncoated membrane displays the highest flux. However, the corresponding phenol removal is low (as shown in section 5.1.2, Figures 19, 20). Among the carbon membranes, the flux is identical for CI and CSR in the straight configuration; in the reverse configuration, the flux with CI is only marginally higher. Thus based on the data obtained, CI in straight configuration appears to be most suited for phenol removal.

5.3. Trans- membrane Pressure

A clean membrane generally shows a low TMP whereas a fouled membrane shows a relatively high TMP since it offers increased resistance to flow. As the TMP increases, the permeate flux decreases. This section presents the TMP profiles obtained during filtration of humic acid and phenol.

5.3.1. Humic Acid Filtration

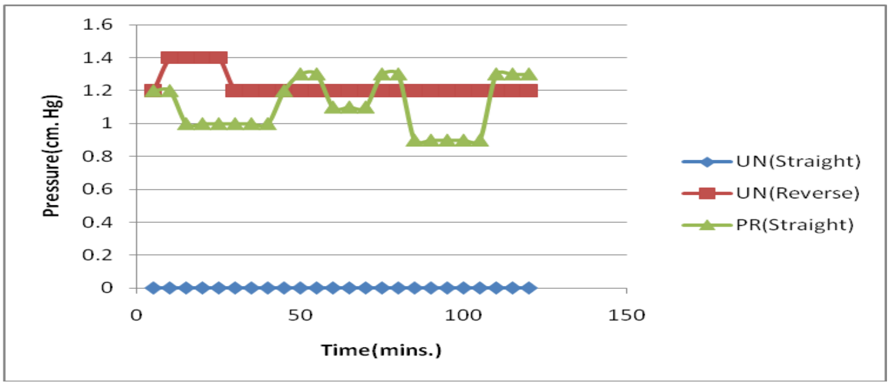


Fig. 27: TMP for humic acid feed (10mg/L) using 5cm * 5 cm membranes

As observed from Figure 27, the uncoated membrane (straight) shows the lowest TMP. Though TMP data for CI and CSR are not available, the same is available for filter coated with carbonized binder (PR). This profile shows some variation over time. Additional experiments are required to fully understand the TMP build-up.

5.3.2. Phenol Filtration

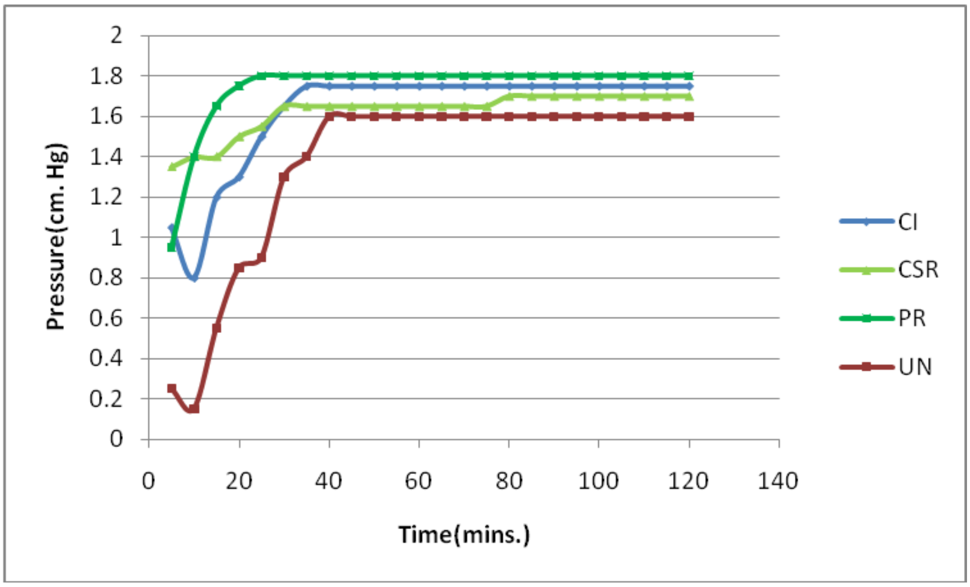


Fig. 28: TMP for phenol feed (5mg/L) using 5cm * 5 cm membranes (Straight)

As observed from Figure 28, the TMP values are almost identical (16-18 mm Hg) for all membranes in the straight configuration. The uncoated membrane shows a similar rise in the reverse configuration as well (Figure 29); however, the TMP rise is higher with CI and CSR in the reverse mode.

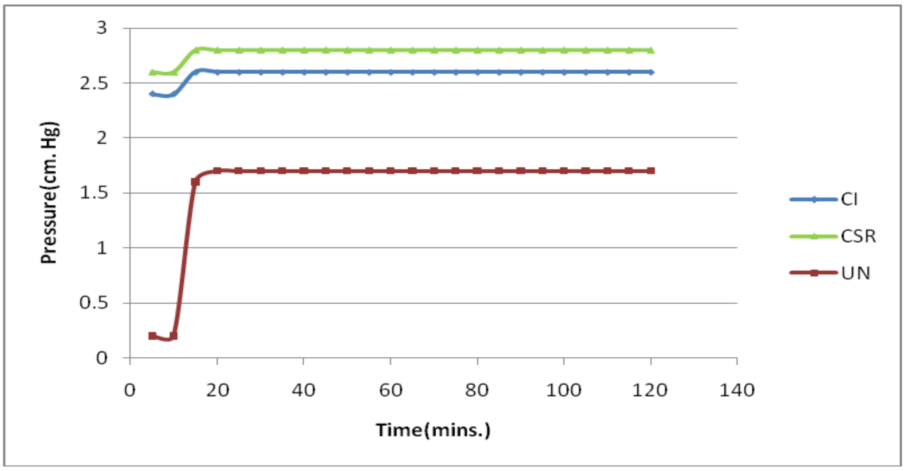


Fig. 29: TMP for phenol feed (5mg/L) using 5cm * 5 cm membranes (Reverse)

5.4. Carbon and membrane Characterization

5.4.1. Pore Size Analysis

Mercury porosimetry has been proven to be a very useful technique to relate the pore sizes of different membranes as well as to compare the pore size distribution of used and fresh membranes. The results are summarized in the table:

Table 3: Pore size analysis of membranes

Type of membrane	Porosity (%)	Mean Pore Diameter (μm)
Support (Fresh)	43.02	0.08
Support (After humic acid filtration)	35.8	0.07
PR (Fresh)	34.54	9.89
PR (After humic acid filtration)	31.37	4.72
CI (Fresh)	34.87	18.51
CI (After phenol filtration)	29.06	9.48
CI (After phenol filtration and sonication)	36.04	4.63
CSR (Fresh)	34.87	18.51
CSR (After phenol filtration)	33.95	15.06
CSR (After phenol filtration and sonication)	40.45	2.25
CI (Fresh, after sonication)	44.85	0.12
CSR (Fresh, after sonication)	40.22	7.44

It is evident from the results above that the porosity of the used membranes is lower than that of the unused ones. So, it appears that, some pores must have been clogged by the humic acid or phenol that has been filtered. When the used membrane was placed in water and sonicated for 15 mins in order to clean the clogged pores, the carbon layer was removed that causes most of the separation and the organics adsorbed also could have entered the water. So, the pore size increased as compared to the used membranes.

5.4.2. Surface Area Analysis

The surface area of the activated carbons and the binder used in this work are given in Table 4 Merck carbon has the maximum surface area as compared to the other two carbons and as such shows better removal in batch adsorption studies (section 5.5, Figure 30). But the binding of Merck carbon to the fly ash support is not as good as compared to the lower surface area Innova and SR carbons. Thus the physical integrity of the CI and CSR membranes was observably better. Further, surface area increases after carbonization (as seen for the carbonized binder + Innova and binder+ SR). Carbonization leads to the removal of unburned carbons and volatiles, thus, it increases the surface area.

Table 4: Surface area of activated carbons and binder

Component	Surface Area (m^2/g.)
Merck (activated carbon powder)	921
Innova (activated carbon powder)	255
SR (activated carbon powder)	340
Carbonized Binder	12
Carbonized (Binder+ Innova)	461
Carbonized (Binder+ SR)	417

The surface area of the carbon membranes, before and after use is shown in Table 5. As expected, there is a decrease in the surface area after phenol adsorption. Sonication of the used membrane does not appear to regenerate the used carbons. When the membrane is sonicated in water for a period of 15 min, the carbon layer gets removed completely and thus the surface area is reduced.

Table 5: Surface area of carbon membranes

Type of membrane (crushed form)	Surface Area (m^2/g.)
Support layer	4.25
Uncoated membrane (UN)	3.38
Carbonized Binder	34.64
CSR (Unused)	14.41
CSR (Used with Phenol)	12.815
CSR (Used with phenol, after sonication)	9.965
CI (Unused)	26.06
CI (Used with phenol)	10.76
CI (Used with phenol, after sonication)	10.30

5.5. Batch Adsorption Studies

Batch adsorption studies (Figures 30-32) were carried out to get an idea about the adsorption potential of the different materials used in the preparation of the filters. Also, adsorption ability of the chunks of support and uncoated filter (which gave the best results in case of humic acid removal) was checked out.

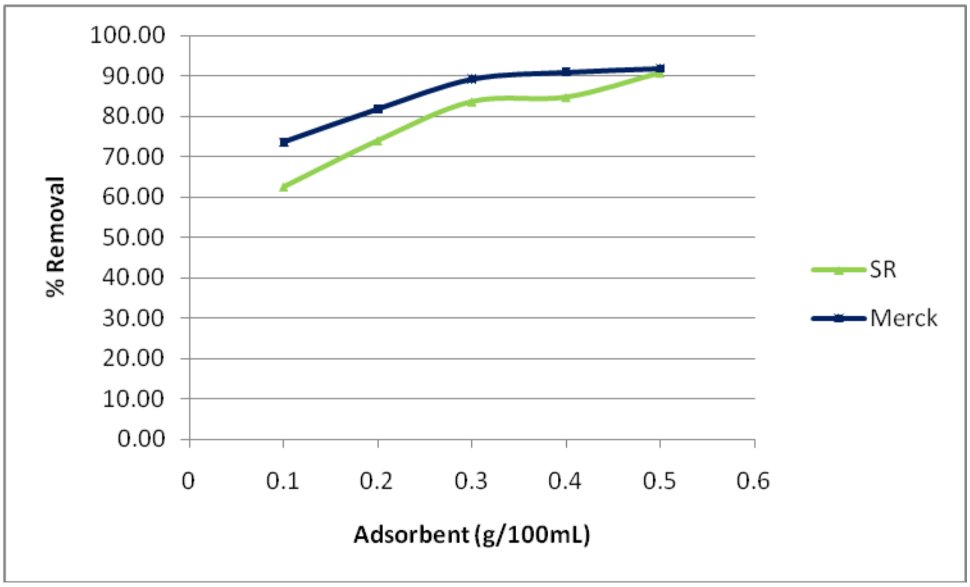


Fig. 30: Adsorption on activated carbons (SR and Merck)

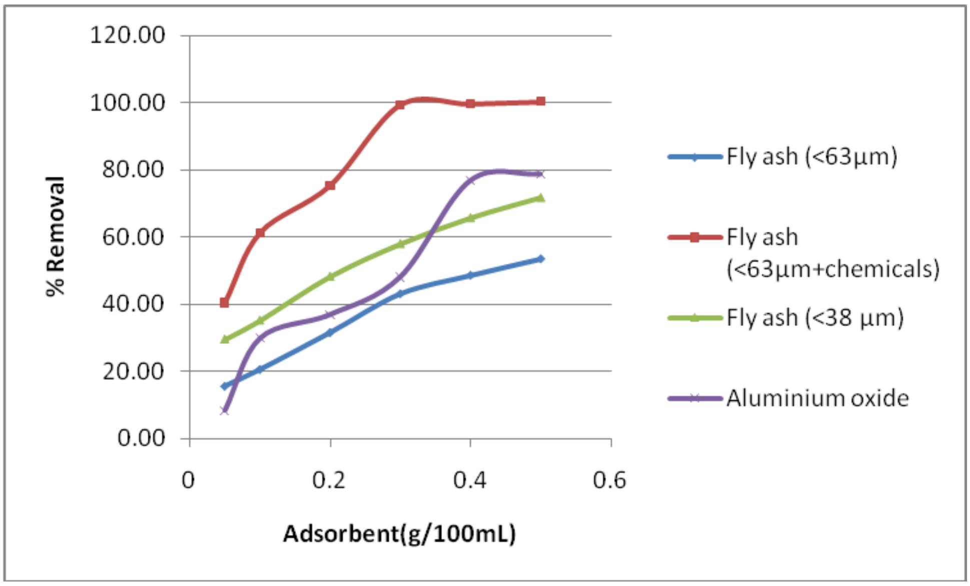


Fig. 31: Adsorption on membrane components (fly ash (<63µm), fly ash (<63µm+ chemicals), fly ash (<38µ), aluminium oxide)

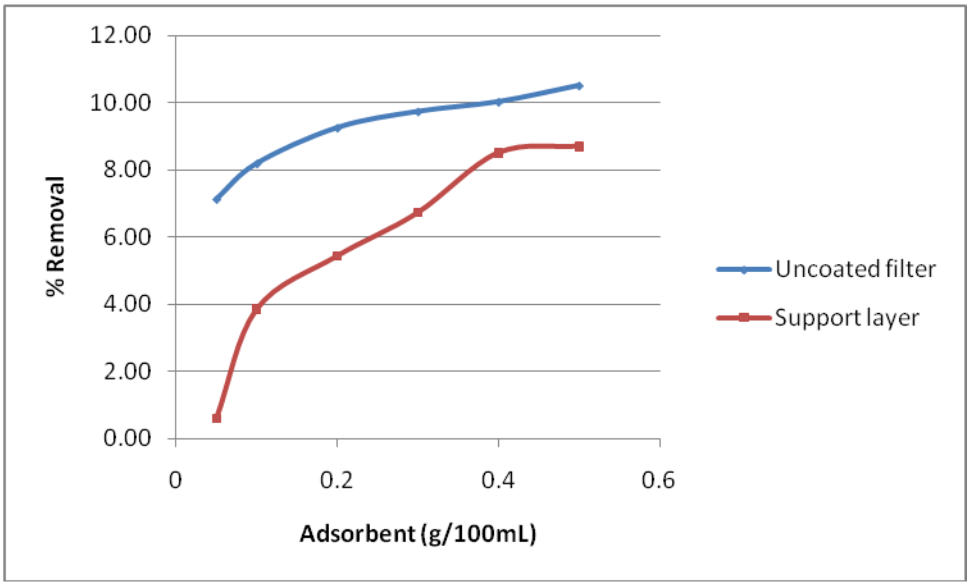


Fig. 32: Adsorption on membranes (uncoated filter, support layer)

Both Merck and SR activated carbons showed high humic acid adsorption (Figure 30). This is in spite of the significant difference in surface area (921 m^2/g for Merck vs 340 m^2/g for SR). The results with Innova activated carbon were not conclusive since the humic acid concentration increased with increasing activated carbon dosage. This was verified to be due to leaching of some component(s) from the carbon itself that caused interference in the humic acid analysis. So the adsorption results for Innova activated carbon have not been included. FTIR analysis of the Innova carbon is underway to find out the components causing the interference.

As shown in Figure 31, the various fractions of fly ash being used for filter preparation also adsorb humic acid. In particular, the fly ash + chemicals combination used for filter making almost completely adsorbs humic acid. This was due to the presence of alumina (which is a good adsorbent) in this mixture. However, the sintered filters show very less adsorption (< 10%) (Figure 32).

5.6. Sonication vs. weight loss

This analysis gives an idea about the removal of the separation layer (carbon layer) with time when the membrane is submerged in water and kept for sonication.

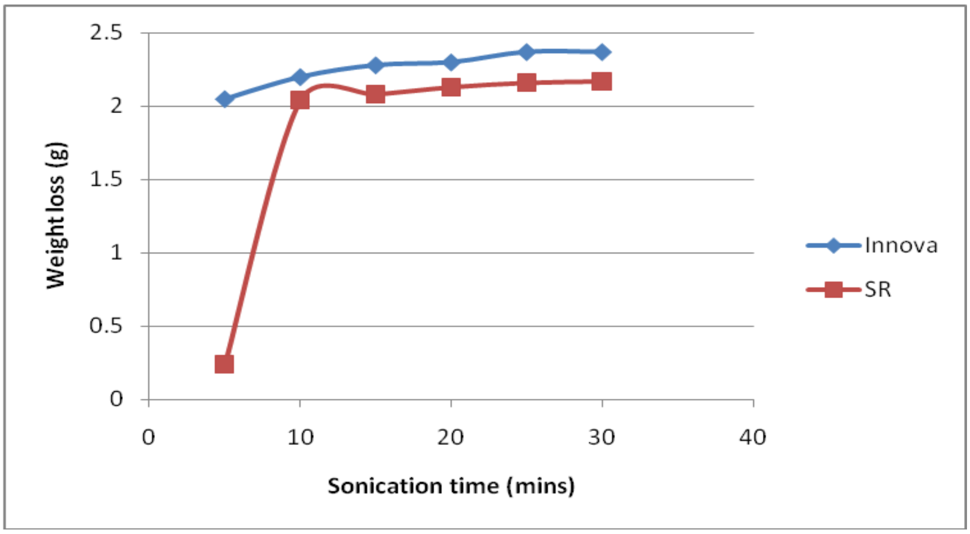


Fig. 33: Sonication vs. weight loss

Figure 33 shows that the carbon layer gets removed immediately when subjected to ultrasonic vibrations in case of Innova. The SR coating gets removed slowly. So, the binding of SR carbon to the support is better than the Innova carbon.

6. Conclusions

This work proves that carbon coated hybrid membranes can be used for removal of low and high molecular compounds from both aqueous streams. The conclusions are as follows:

- Carbon membranes prepared with lower surface area Innova and SR carbons (CI and CSR) have better binding between the carbon and flyash support. These membranes are more suitable for treating of aqueous streams, compared to membranes prepared with high surface area Merck carbon (CM).
- The 5cm * 5 cm submerged membrane module is suitable for testing the prepared carbon membranes. It avoids the operational issues encountered with testing in a closed filtration cell; further, the flux is stable over time.
- The membrane configuration (straight or reverse) appears to have an effect on the removal of organic pollutants. Of the membranes tested, Innova coated membrane (CI) in straight configuration appears to be most suited for phenol removal. For humic acid removal, the carbon coating appears unnecessary and the uncoated membrane in reverse configuration is most suitable.

Thus under the conditions of this study, the carbon membranes prove better for removal of low molecular weight compounds (viz. phenol) while the uncoated membranes prove better for removal of high molecular weight compounds (viz. humic acid).

7. Future Prospects

- Filtration tests can be carried out for a longer duration to check out the fouling of the membrane.
- Regeneration of the membranes and extraction of the adsorbed organics, if achieved, would prove to be highly useful and the membrane would be able to function for a much longer duration.
- Mass transfer studies can be carried out.
- Modifications in the pore size and carbonization techniques can be tried out in order to achieve complete removal of the organics.
- Carbon nano particles can also be tried out for the adsorption studies.

8. References

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