STUDIES ON DESALINATION AND DEOILING OF WASTEWATER FROM THE OIL FIELDS: OPTIMIZATION OF SEPARATION METHOD AND IMPROVING THE QUALITY OF WATER

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“Statement of Originality”

I, **Riku Dutta** registered on **05. 01. 2017** do hereby declare that this thesis entitled **“Studies on desalination and deoiling of waste water from the oil fields: optimization of separation method and improving the quality of water”** contains literature survey and original research work done by the undersigned candidate as part of Doctoral studies.

All information in this thesis have been obtained and presented in accordance with existing academic rules and ethical conduct. I declare that, as required by these rules and conduct, I have fully cited and referred all materials and results that are not original to this work.

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…Dedicated to the budding Scientists

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Abstract

All forms of life present on the earth, from the lowest living things to the most sophisticated and advanced human systems, depend on water for their living. A major constraint perhaps the most significant factor hindering growth in many regions of the world is the shortage of fresh drinking water, scarcity of water for use in industry and agriculture, and for a plethora of other activities where water is inevitable. Harmful chemicals and volatile substances released from industries such as oils, arsenic, fluorides and mercury has increased at an alarming rate. Sands, silts and other such substances although do not have any direct effect on the human health but alters the natural property of water. There are various sources of this oil-contaminated waste water that contaminates the fresh water reserves. Some of the most common sources include: 1) Produced water from the oil exploration fields, 2) Petrochemical industries, refineries, 3) Metal processing industries, 4) Automotive and 5) Chemical manufacturing industries viz. textile industries, heavy metal industries, paint industries, leather industries, food processing industries. The use of conventional methods of water treatment like skimming, floatation, gravity settling, filtration etc. are inefficient in separating oils from oil-water suspensions.

Absorption has been found to be the most efficient method for treating oil contaminated wastewater. Various materials having hydrophobic character has been widely used in the removal of oils from wastewater. Various naturally occurring absorbents has also been utilized in this process of wastewater treatment like kapok fibre, cotton fibres, bagasse and other agricultural wastes, however, these absorbents have not been extensively used because of their low hydrophobic character and poor oil/water selectivity. Numerous natural materials have also been studied to determine their oil absorption capacity. These include activated carbon, wool fibres, zeolites, straw, etc. But due to their low absorption properties and poor reusability they are not abundantly used in wastewater treatment.

Polymeric absorbents have proven to be the utmost effective strategy to eliminate oils and other organic impurities from contaminated water. This work investigates the efficiency of Poly (ethylene-co-vinyl acetate) based absorbents in removing oils and organic solvents from wastewater. Further it also investigates the use of NaCl as porogen to improve the porosity of the absorbents which further increases the absorption capacity of the absorbent. Another aspect of this work is related to the use of nanoclay to prepare poly (ethylene-co-

vinyl acetate) based absorbents which also showed excellent absorption capacity in various oils and organic solvents.

Poly (ethylene-co-vinyl acetate) or EVA is a thermoplastic copolymer consisting of different compositions of ethylene and vinyl acetate. Depending on the ethylene and vinyl acetate (VA) content this polymer exhibits different properties like melting point, crystallinity, stiffness and polarity. EVA has been widely used as an encapsulation material having superior properties in wire coating, drug delivery and footwear applications due to its higher tensile strength, wear and tear properties with low hardness.

The primary body of this thesis is divided into six chapters. The introduction part is included in **Chapter 1** outlines the various methods used for wastewater treatment, materials used in preparing absorbents for absorption of oils from wastewater, materials used in the current research work and their properties. The methods, results and discussion of the current investigations have been discussed in **Chapter 2, Chapter 3, Chapter 4 and Chapter 5**. The conclusion and future scope of this thesis are discussed in **Chapter 6**.

Chapter 1: Introduction

This chapter deals with the general introduction and literature review of the current work. The importance of treating oil-contaminated wastewater has been discussed in this chapter. The various methods for treating oil-contaminated wastewater have also been outlined in this chapter. The basic concept of absorption, materials investigated for preparing absorbents and characteristics of a good absorbent has been discussed in this chapter. The various components used in this work to prepare the oil absorbents and their physical and chemical properties has also been discussed in detail. Finally, the objective of the current investigation is presented.

Chapter 2: Removal of organic solvents and oils from wastewater by absorption with crosslinked Poly (Ethylene-co-vinyl acetate) modified by cetyl alcohol

In this first investigation on the oil absorption capacity of Poly (ethylene-co-vinyl acetate), a novel crosslinked Poly (ethylene-co-vinyl acetate) (EVA) based absorbent was prepared by the grafting of maleic anhydride (MA) and cetyl alcohol (CA) in the presence of benzoyl peroxide (BP). Although EVA has been widely used in various applications like drug delivery, encapsulation, and footwear industry, however, its application in environmental remediation has not been studied in detail. In this study, melt mixing was carried out in the

Brabender mixture at 120^0C. The grafted polymer was post-cured in the hot air oven at 100^0C for 24 hours. The post-cured sorbent showed excellent absorption capacity in Toluene (2200%), Gasoline (1720%), Crude Oil (1105%), and Kerosene (390%). The contact angle measurement reveals its hydrophobic nature (123^0). The absorption properties of this hydrophobic composite remain stable even after 10 absorption/desorption cycles with absorption capacity remaining constant. The crosslinked polymer was characterized by FTIR, XRD, TGA, and SEM.

Chapter 3: Development of Porous Crosslinked Absorbents and Studies on Their Oil Removal Efficiency

In this novel study, an attempt has been made to prepare porous crosslinked poly (ethylene-co-vinyl acetate) polymer (C-EVA). The porous C-EVA was prepared by grafting of maleic anhydride and cetyl alcohol onto the polymer backbone with addition of NaCl as porogen in the brabender mixture at 120^0C and 80 rpm. This was followed by leaching of NaCl with water extraction to generate a highly porous polymer structure which was evident from its SEM micrographs. The polymer was found to have excellent swelling capacity in various oils and organic solvents and showed good selective absorption capacity. The reusability of the synthesized polymer was studied and it was found that it could be reused for more than 30 absorption desorption cycles without undergoing much change in its absorption capacity. The cross-linked polymeric composite was further characterized by FTIR, TGA, XRD, and SEM.

Chapter 4: Development OF NANO ABSORBENT USING Poly (ethylene-co-vinyl acetate)

To enhance the elimination of oils and other organic solvents from waste water, poly (ethylene-co-vinyl acetate was blended with organically modified montmorillonite (OMMT) nanoclay following a green pathway by melt blending in the Brabender plasticoder. The nanocomposites thus prepared were found to have excellent absorbing capability in various oils and organic contaminants. To further increase the absorption capacity of the nanocomposites NaCl was added as porogens in the melt mixing process, which was followed by leaching of NaCl in water to generate a highly porous nanocomposite material. The absorption test also revealed excellent absorption efficiency in various oils and organic solvents with absorption capacity of 40 g per gram of absorbent in dichloromethane (DCM) and 9 g per gram in gasoline. The nanocomposites also demonstrated excellent recycling capability and could be reused for more than 30 absorption-desorption cycles. FTIR, XRD, SEM, TEM analysis was conducted to delineate the structure and morphology of nanocomposite.

Chapter 5: Desalination of wastewater using Ion exchange method

In this study, a novel integrated ion exchange resin system has been developed to remove salts from waste water. Amberlite IR 120 and amberlite IR 400 has been used as the cation exchange and the anion exchange resins respectively which exchanges the cations and the anions from the wastewater and consequently makes the water free from salts. The adsorption isotherms for Langmuir as well as Freundlich model were studied and the adsorption kinetics thus established. Amberlite IR 120 and Amberlite IR 400 showed excellent adsorption potential of 161.29 mg/g and 233.64 mg/g respectively. The regeneration of the resins was also studied and it was found that the resin system could be used multiple times in the desalting process. The resins were further analysed by FTIR and EDX.

Chapter 6: Conclusion

This chapter highlights the summary of the overall work under investigation as well as the future scope of the current investigation.

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List of Abbreviations and Symbols

°C	Degree centigrade
WRA	Water resources assessment
USEPA	United States Environmental Protection Agency
CTAB	Cetyltrimethylammonium bromide
TDS	Total dissolved solids
NORM	Naturally occurring radioactive material
API	American Petroleum Institute
MF	Microfiltration
NF	Nanofiltration
UF	Ultrafiltration
DTG	Differential thermal analysis
TOC	Total organic compound
FTIR	Fourier transform infrared spectroscopy
g	Gram
PU	Polyurethane
PAN	Polyacrylonitrile
BMA	Butyl methacrylate
MMA	Methyl methacrylate
KBr	Potassium bromide
MWNT	Multiwalled nanotubes
kV	Kilo volt
WCA	Water Contact angle
EVA	Ethylene vinyl acetate

m	:	Meter
LDPE	:	Low density polyethylene
mg	:	Milligram
min	:	Minute
mL	:	Milliliter
MMT	:	Montmorillonite clay
MPa	:	Mega pascal
EVAgMA	:	Maleic anhydride grafted ethylene vinyl acetate
NaOH	:	Sodium hydroxide
NaCl	:	Sodium chloride
OMMT	:	Organically modified montmorillonite
g/g	:	Gram per gram
MA	:	Maleic anhydride
CA	:	Cetyl alcohol
DMF	:	Dimethyl Formamide
DMSO	:	Dimethyl sulphoxide
DCM	:	Dichloromethane
ONGC	:	Oil and Natural Gas Corporation
PVC	:	Polyvinyl chloride
VA	:	Vinyl acetate
UV	:	Ultraviolet
rpm	:	Revolutions per minute
RW	:	Residual weight
SD	:	Standard deviation
SEM	:	Scanning electron microscopy

C-EVA	:	Crosslinked Ethylene Vinyl acetate
µm	:	Micrometer
TD	:	Decomposition temperature at different weight loss
TEM	:	Transmission electron microscopy
Tg	:	Glass transition temperature
TGA	:	Thermogravimetric analyzer
Ti	:	Initial decomposition temperature
Tm	:	Maximum pyrolysis temperature
APTES	:	Aminopropyltriethoxysilane
ODA	:	Octadecylamine
Hg	:	Mercury
Al	:	Aluminium
Pb	:	Lead
wt%	:	Weight percentage
XRD	:	X-ray diffraction
θ	:	Diffraction angle
mg/l	:	Milligram per liter
HCl	:	Hydrochloric acid
EDX	:	Energy-dispersive X-ray

CHAPTER I

INTRODUCTION

1.1 Water: A Vital Resource

All life forms present on earth, from the simplest and the modest living things to the most complex and advanced human systems, depend on water in one way or another. A major constraint perhaps the most significant factor hindering growth in many regions and countries of the world is the shortage of fresh water for drinking, for use in industrial and agricultural activities, and for a plethora of other activities where water is most essential. As the population has increased, the demand for water has also risen enormously, and although the world's freshwater reserves are extensive, they are distributed unevenly and have limited practical use. As a result, the shortages that are already impacting many locations are projected to expand and become substantially more frequent during the next century. Climate change is anticipated to worsen these shortages in many locations. According to the report of the United Nations, 2018 water stress has affected more than 2 billion population residing in different countries. Global freshwater consumption has increased four times in the last 100 years owing to population stress, industrialization, and change in consumption patterns. According to the United Nations (UN) World Water development report (WWDR) 2021, the rate of increase in this water consumption can be estimated at 1% per year from 1980 onwards.

Under such circumstances, increasing knowledge and information of the world's water reserves and resources is critical for human well-being and environmental conservation. In making informed judgments on the sustainable management of "water resources" accurate knowledge on their current state and trends is highly required. Information and data is therefore essential for water resource planning, design of plans and projects, environmental impact assessment, project analysis and operation, and for forecasting or discharging cautionary warning of extreme and severe events such as floods and droughts. Hence, in order to develop and manage water resources effectively, water resources assessment (WRA) is a must.

In addition to several nutrients essential for sustaining life like iron, phosphorus, nitrogen, etc., water also consists of several substances hazardous for living organisms that have a detrimental effect on the environment as a whole. Substances like oils, arsenic, fluorides and mercury have led to a serious health concern not only on plants and animals but also on human health. Harmful chemicals and volatile substances released from industries has increased at an alarming rate. Sands, silts and other such substances although do not have any direct effect on the human health but alters the natural property of water. It is, therefore, necessary to develop water quality standards for a wide range of purposes. It has been estimated by the World Water Assessment Report 2017 (WWAP, 2017) that 80% of all industrial derived and municipal derived wastewater is released globally into the total environment without any pretreatment, which leads to detrimental and negative consequences on human health and ecosystems. In the least developed countries, this ratio is found to be much higher due to poor sanitation and wastewater treatment infrastructure. This annual volume of wastewater produced can recover approximately 380-400 billion m^3 of water. [1]

One of the most significant sources of this wastewater is the water that evolves from the oil and gas related production activities that account for a larger fraction of the contaminated wastewater. This wastewater or produced water may contaminate both the underground as well as surface water if allowed to interact with each other. Therefore, from the environmental perspective, different countries have implemented various norms for the discharge of produced water. The offshore oil and gas discharge limit of produced water in Australia has been set at 50 milligrams per liter [2] . The United States (US) Environmental Protection Agency (USEPA) has set up norms to dispose only 42 milligrams per liter per day of oil and gas and the monthly disposal criteria is set at an average of 29 milligrams per liter [3]. Even the Central Pollution Control Board of India has set the limiting value of oil and grease concentration as 5 milligrams per liter for disposals from petroleum oil refineries [4]. Since a large volume of this water is generated annually from the entire globe, many water-scarce countries have been enforcing focused efforts to come up with cost-effective and efficient methods of treatment in order to protect their natural freshwater sources and to utilize the treated wastewater in other industrial and human activities. Produced water is actually a blend of various organic as well as inorganic materials. The nature of this water depends on numerous factors ranging from the geological location of the producing fields to the type of hydrocarbon being produced from these fields. From the broader perspective, the major components present in the produced water are:

a. Oil compounds (dispersed or dissolved)

b. Minerals of subsurface formations dissolved in the water

c. Chemical (both organic and inorganic) compounds used in the production activities

d. Solids produced (waxes, asphaltenes, formation solids etc.)

e. Dissolved gases

To comply with the strict regulations of the Environment protection agencies and also to reuse the wastewater for beneficial applications many resources have stressed on treating oily saline wastewater produced from the oil fields.

1.2. Oil contaminated and saline wastewater: type, sources and composition

Three main kinds of oil contaminated wastewater exist in nature: a) free oil floating on the water's surface, b) emulsions, and c) mixtures of free-emulsified oil and water. In the free oil-water system, oil droplets are larger in size (more than or equal to 150 µm), which limits their probability of mixing with the aqueous phase. As a result, a free separate oil layer occurs above the aqueous phase due to the density differential between the two phases. In mixtures and emulsions, the majority of the oil droplets are relatively smaller in size, ranging from 20 to 150 nm and below 20 nm, respectively, this promotes the miscibility of oil particles with the water [5,6].

Table:1.1 Different forms of wastewater according to oil droplet size

Size of oil droplets (µm)	Waste Water type
>150	Free oil-water system
20-150	Dispersed oil in water (mixtures)
<20	Emulsion

For the emulsion kind of oil contaminated wastewater, minute oil droplets are spread out throughout water. Water acts as the medium of dispersion and remains in the continuous phase, while the dispersion phase is oil. To fulfil discharge standards, the oil must be separated and eliminated from the water. In the case of emulsions, the oil in the water is often waste oil, therefore maintaining the water's quality is more crucial than maintaining the oil's product quality. The emulsion's consistency or stability is determined by the range of repulsive forces that exist between the droplets, as indicated by the system's zeta potential. For example, the distributed oil droplets in an oil-in-water emulsion which is stabilized by the presence of a surfactant, display net negative charge at the droplet surface (Lewis, 1932). According to the theory put forward by Helmholtz on electrical double layer, the counter ions existing in the bulk solution are attracted to these closely distributed negatively charged particles along the interface. This eventually results in the development of a zone of oppositely charged ions, resulting in the formation of an electrical double layer as shown in Fig. 1.1 [7]. The electrokinetic potential decreases with increasing distance from the oil surface to the bulk water phase, and at a sufficient distance in the bulk solution, it is assumed to be zero. This electrokinetic potential is dependent on the thickness that exist in the double layer, which is responsible for the repulsion between the oil droplets and hence inhibits individual oil droplet to coalesce. This repulsive electrokinetic potential is represented by a scientific factor termed as zeta potential [8], which represents the electrical potential difference existing within the surface having a considerably tightly bound ion layers on the dispersed surface of the particle and the neutral electrical region in the solution [9]. This factor is considered as a significant indicator for delineating the stability of an emulsion. The physical stability of the emulsions depends largely on its zeta potential where the emulsions tend to demonstrate high stability with a large negative or positive zeta potential value owing to its electrostatic repulsion. However, the emulsions with smaller values of zeta potential shows a poor physical stability due to Van der Waals force of attraction which causes the droplets to attract each other leading to particle aggregation. This aggregation destabilizes the stabilized emulsions. Thus, treatment of this emulsified waste water largely depends on the state in which oil in water exists, the oil droplets size and the internal composition and nature of the effluent stream that solely controls the surface characteristics and the stability of mixture.

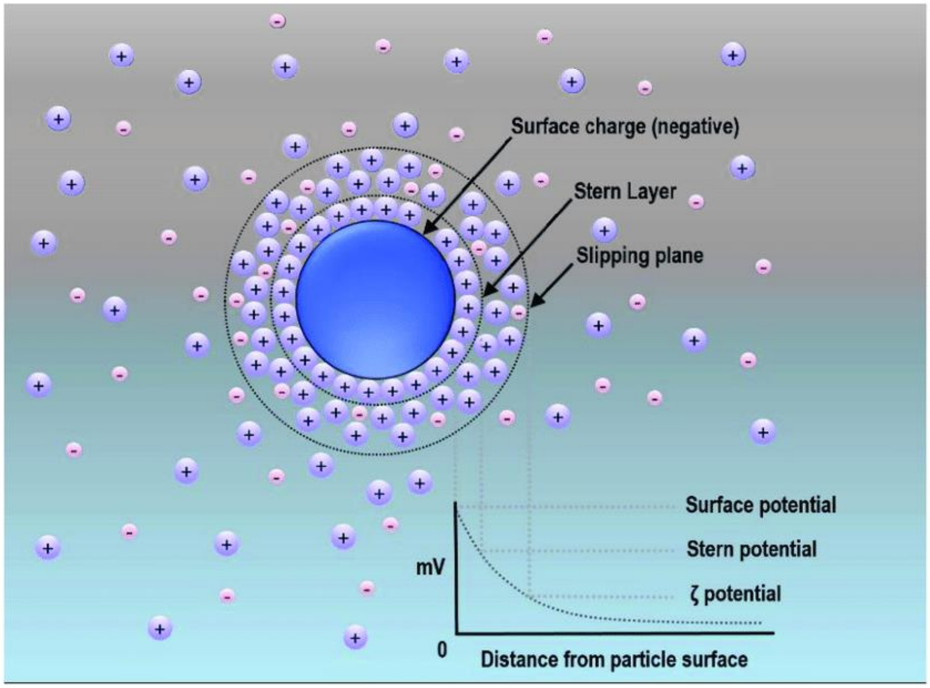


Fig:1.1 Pictorial representation explaining electric double layer

There are various sources of this oil contaminated waste water that contaminates the fresh water reserves. Some of the most common sources include:

1) Produced water generated from the oil exploration and production fields

One of the major sources of oil contaminated wastewater is the water that is generated during the drilling operations in oils and gas wells. This oil contaminated water (also known as produced water) carries various organic and inorganic pollutants from the subsurface along with huge amount of oil [10]. Due to several stringent norms of discharging, this produced water cannot be directly released to the environment. Due to several operations associated with production of oils and gas such as water injection into the formations for secondary recovery or fracture stimulation for enhanced oil recovery process, several substances mix with this produced water, further degrading its quality. Generation of produced water (PW) continues throughout the entirelife of the well.

The concentration of various impurities present in this produced water is generally well and area specific. However, it majorly contains a) Salts which is commonly termed as salinity which is eventually responsible for the TDS (Total dissolved solids) or the electrical conductivity, b) Oils and grease which is measured by a analytical test which determines the amount and nature of organic compounds and their families, c) Different organic and inorganic constituents (magnesium, calcium, barium, sulfates etc. that are responsible for hardness and scaling in water), d) Chemicals used in various associated activities like water injection, fracture stimulation, Enhanced oil recovery (e.g., surfactants, colloids, biocides etc.), e) Naturally occurring radioactive material (NORM) [11].

2) Petrochemical industries, refineries

Oil-contaminated wastewater is produced at the oil refineries as the crude oil containing produced water and other contaminants from the drilling operations gets treated [12]. This emulsified wastewater from the refineries could not be separated easily from the crude oil. However, it is essential to separate this wastewater from the crude oil before feeding into the refineries or it may lead to malfunctioning of the pumps and various flow channels. If this wastewater discharged from the petrochemical industries including refineries can be treated, it may be reused as a source of water for various industrial as well as other potential services.

3) Metal processing industries

The metal processing and handling industry is identified as one of the most oil contaminated wastewater producing source, where the water released from them mostly consist of cutting oils, grinding oils, coolant oils and lubrication fluids with a concentration ranging from 100–20000 mg/L [13].

4) Automotive

It has been estimated that around 40,000 gallons of water is required in the manufacturing of a single vehicle. Water is essential in manufacturing different components of automotive. Hence, in order to remain sustainable and safeguard the water sources, the water from these industries must be separated from the contaminants before disposing to the environment. Coolant oil waste, baths, plating operations, paint overspray and rinses are some of the sources of oil contaminated wastewater generated from these industries [14].

5) Chemical manufacturing industries such as textile industries, heavy metal industries, paint industries, leather industries, food processing industries [15,16], restaurants [17], automobile service stations, garages [18,19]maritime transport and oil spill accidents [20,21]are some other important sources of oil contaminated waste water. Fig: 1.2 shows various sources of oil contaminated wastewater in emulsified form.

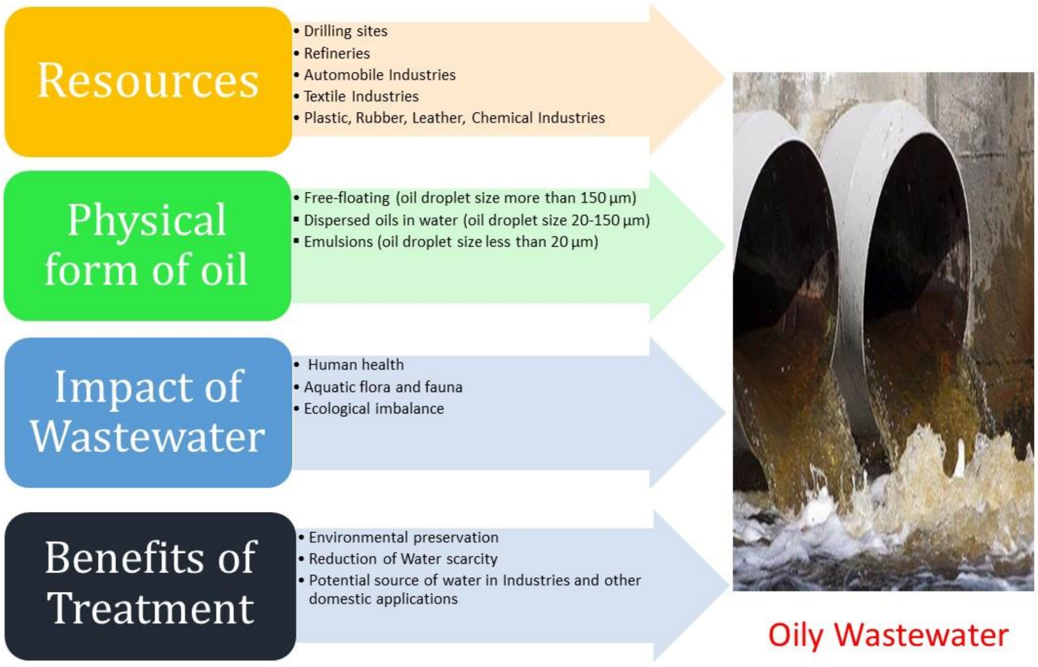


Fig. 1.2 Significance of oil contaminated wastewater

Several components present in the oil contaminated wastewater viz. soaps, emulsifiers, dirt, detergents, silt etc. stimulates the formation of stable emulsions which makes the separation process complex and tedious. A major percentage (around 25%) of the oil polluted waste water discharged from the industries remains in the form of emulsions which makes the oil-water splitting more troublesome [22]. The use of conventional methods of water treatment like skimming, floatation, gravity settling, filtration etc. are inefficient in separating oils from oil-water suspensions. Due to the complex nature and composition of the emulsified wastewater generated by various domestic and industrial set up, it has become difficult to select the proper treatment method for eradicating oil contaminated contaminants from the water. Therefore, considering the increasing demand to meet the various water discharge limits mandated by various stringent legislations (Table: 1.2), global research is focusing on developing adequate treatment technologies for effective emulsion disruption as well as simultaneous oil-water separation [23]. Various innovative treatment methods for treating oil-contaminated water before discharge to the environment are being investigated. Some of such methods include flotation, electrochemical treatment, chemical coagulation, biological treatment, adsorption, membrane separation process, among many others. The next sections will stress on the various treatment methods employed for separating oils from water and will point out the various conclusions that researchers obtained from their study.

Table: 1.2 Discharge limit of dispersed oil in water under various conventions

Region	Convention/Law	Discharge limit of dispersed oil in water	References
North Sea region	Oslo-Paris (OSPAR) convention	30 mg/L	[24]
Sea, offshore and onland fields	Paris Convention	➢ Sea: 40 mg/L ➢ Offshore/On-land fields: 5 mg/L	[25]
United States	EPA	Maximum 72 mg/L	[26]
India	Central Pollution Control Board	10 mg/l	[27]
China	China National Standard (2018 version)	<15 mg/L	[28]
Malaysia	Malaysia Environmental Quality and standard	➢ 5 mg/L within specified catchment areas ➢ 10 mg/L, other than the specified areas	[29]

Environmental pollution has become a matter of concern from the last decade and several stringent norms on the disposal of wastes to the environment have come up recently. One of the most talked about sources of environmental pollution has been the contaminated water produced from the oil and gas wells during hydrocarbon exploration [30]. This water termed as produced water contains huge quantity of organic and inorganic elements together with various suspended particles, oils and grease [31,32]. Now in order to make this produced water beneficial and support human as well as aquatic life, this water needs to be treated so that the various salts, organic and inorganic elements get separated from the water. The characteristics of this water produced from the hydrocarbon extraction depends on numerous factors that includes method of drilling, the geographical location, nature of the reservoirs and the geochemistry of the formation layers [32]. Saline nature of the produced water depends on the formation layer from where extraction is performed. The main constituents which determine salinity in water are sodium and chloride along with potassium, magnesium, calcium and sulphates. Salinity levels in this water various significantly depending on the geographical location as well as depending on the lifetime of the well. Sometimes salinity of produced water has been found to be as high as 2,00,000 mg/l based on the geography and class of the extracted hydrocarbon [33].

Dissolved compounds which are inorganic in nature present in produced water are mainly cations and anions, radioactive elements like thorium, uranium heavy metals and heavy metals etc. A wide variety of cations as well as anions are present in the produced water. Cations and anions are effective in altering the nature and chemistry of water in terms of salinity, buffering and scale developing ability. Sodium and chloride mainly contribute to the water salinity as compared to other cations and anions [34].

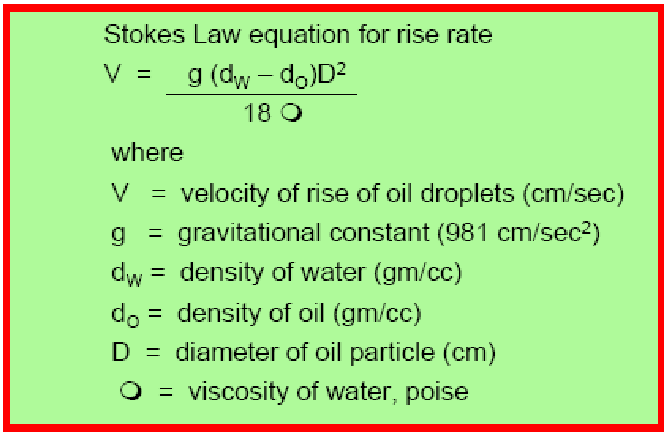
Trace quantities of heavy metals like copper (Cu), chromium (Cr), lead (Pb), cadmium (cd), mercury (Hg), zinc (Zn) and silver (Ag) are present along with produced water. The concentration of these metals is related to the age of the well and the geology of formation. Radium is the most widely available naturally occurring radioactive material (NORM) that exists in produced water. Radium ions are co-precipitated along with other scales from the produced water [35].

1.3 Separation methods of oil contaminated and saline waste water

Oil contaminated saline waste water discharged from various sources viz. oil spills, refineries, drilling operations and various chemical and processing industries are treated by several techniques for oil water separation (OWS). Some of such techniques which are currently being used include gravity separation or vortex separation, coalescence, coagulation, flocculation, air flotation, chemical treatment, biological treatment, adsorption etc.

1.3.1 Gravity separation

In gravity separation methods like API separators, Stoke's law is utilized as the governing principle. The rising velocity of the oil droplets at which it rises to the surface of the solution is the main guiding principle in such oil-water separators, which is influenced by the density difference and size of the liquids (oils) and the water. This separation is a most used, simple and low-cost separation method but requires lengthy settling time, calm environment, and larger footprints. In centrifugal separation methods liquids are separated by density differences using centrifugal forces, where the liquid with lesser density would concentrate and will be gathered within the middle of the device's rotational axis. Advantages of this method include less space requirement, maximum speed and high throughput capacity. However, higher energy consumption is a disadvantage as compared to gravitational separation [36].



Stokes Law equation for rise rate

$$V = \frac{g\,(d_W - d_O)D^2}{18\,\bigcirc}$$

where

V = velocity of rise of oil droplets (cm/sec)

g = gravitational constant (981 cm/sec^2)

d_W = density of water (gm/cc)

d_O = density of oil (gm/cc)

D = diameter of oil particle (cm)

$\bigcirc$ = viscosity of water, poise

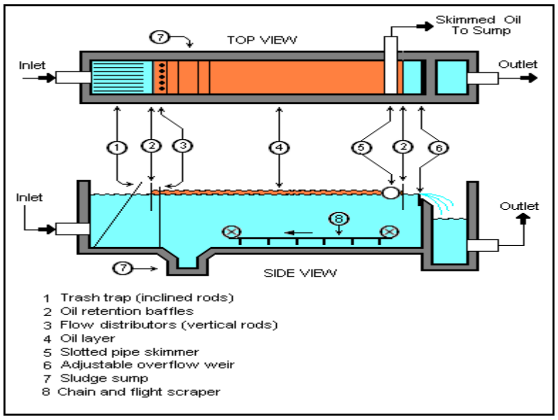


Fig. 1.3 Sectional view of API Separator

1.3.2 Coalescence OWS

In this process, a coalesce media is used to pass the sludge which results in coalescence of the oil droplets. The method of coalescence is effective where concentrations of oil are higher with different oil particle sizes depending particularly on the media used for coalescence. The significant lacuna of this technology is poisoning caused by particle adherence to the media, which significantly reduces its efficiency [37,38].

1.3.3 Coagulation and flocculation

Most separating technologies, like flotation and sedimentation, are incapable of removing colloidal and emulsified particles due to their smaller particle size. These systems must drive them to create larger, floc-like particles in order to eliminate them. This is accomplished by a process known as coagulation-flocculation, which involves adding some chemicals to water in a flocculator. Coagulation occurs when iron (Fe) or aluminium (Al) salts, viz. aluminium or copper sulphate, ferric sulphate, ferric chloride, ferric sulphite, or polymers, are added to water. Such chemicals are termed as coagulants possessing positive charge. The negative charges present in the dissolved and suspended elements in the water are stabilized by the positive charge present in coagulant throughout the reaction, causing the particles to bind together or coagulate (this process is occasionally termed as flocculation) to generate flocs. The heavier, bigger floc particles soon sink to the bottom of the water supply. This process of settling of heavier particles is known as sedimentation [39,40].

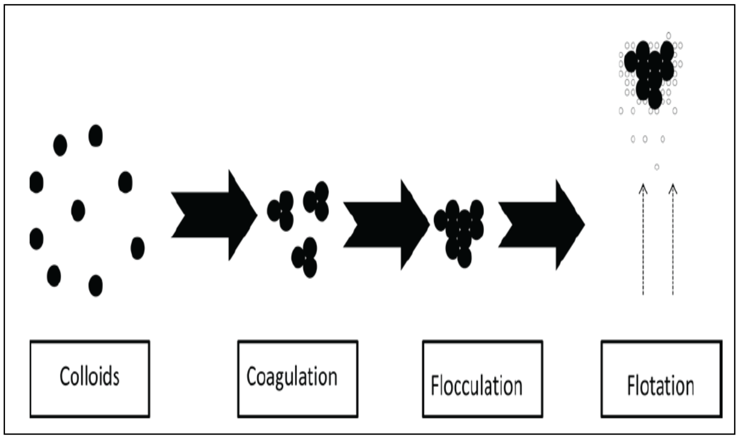


Fig. 1.4 Process of Coagulation, Flocculation and Flotation

1.3.4 Floatation

Similar to separation methods by gravity, where variations in density of the species to be separated is the main driving force, flotation methods also operate under the Stoke's law. The elementary principle underlying this fundamental law is that when the gas bubbles get attached to the scattered smaller particles, agglomerated heavier and low-density particles are produced [41]. As a result, these heavier particles remain floated on the surface due to lack of sufficient buoyancy force as the density has decreased considerably. These methods are also operated effectively for the separation of dispersed finer particles. Due to the recent advancements and innovations, jet flotation technologies having lower cost of energy are also becoming a potential technology for the separation of dispersed as well as emulsified particles present in water. The disadvantages that exists in floating systems include costly maintenance and repair concerns caused by the equipment remaining immersed in waste water for extended periods of time. Additionally, it becomes quite challenging to handle the suspended particles (oil, and other items) that remains floated on the surface[42].

1.3.5 Electrochemical treatment

One of the most competent and efficient methods for treating emulsified oil contaminated wastewater is electrochemical treatment, which makes use of a number of technologies, including electrocoagulation, electroflotation, electrochemical oxidation, and electroFenton process. The technologies listed above utilize an electrochemical reactor with appropriate electrodes, where the demulsification process is carried out by exerting an external potential difference (PD) between the electrodes. The success of these treatment processes is based mainly on the physicochemical characteristics and natureof the waste water and also depend largely on the electrode material. Electrocoagulation has been considered to be most effective for treating waste streams consisting high volume of suspended solids, colloids and oils. The fundamental idea behind electrocoagulation is to produce coagulants in situ electrochemically by electro-dissolving the suitable anode (sacrificial electrode). When there is a potential difference between the electrode pairs, the metal ions generated from the anode dissolve into the cell's wastewater and are then instantly bound to the OH^- ion that is discharged to create insoluble hydroxides. (Eq. 2.1., 2.3.). These metal hydroxides are continuously generated from the sacrificial metal anode in the region of the electrodes and operate as a highly efficient coagulant. The anode-generated cationic metal ions neutralize the surface charge present in the colloidal droplets, reducing electrostatic repulsion between the droplets. Consequently, the van der Waals force of attraction becomes more prominent, resulting in coalescence and flotation. The flocs generated form a sludge layer, which is then separated from the aqueous phase by settling or electroflotation. In contrast, the bubble slug that forms on the electrode surfaces (produced H_2) during electroflotation in conjunction with electrocoagulation in the cell helps the oil-water emulsion get demulsified and aids in the movement of the coalesced droplets to the solution's surface from where they may be readily skimmed mechanically. Therefore, the electroflotation method enables the effective separation of sludge from the solution's surface [43,44].

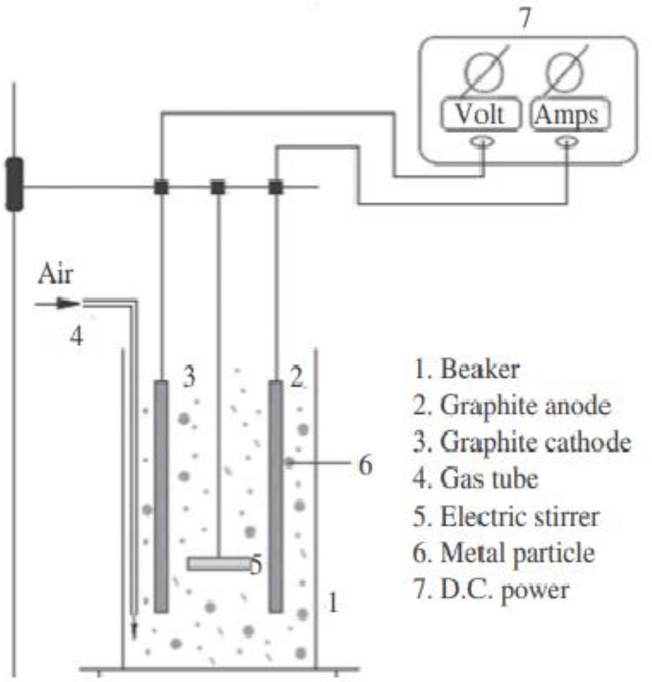


Fig. 1.5 Apparatus used for electrochemical treatment [45]

Yavuz et al. (2010) [46] treate oil refinery wastewater using various electrochemical method viz. electrochemical oxidation (direct and indirect) using diamond anode doped with boron; direct electrochemical oxidation utilizing a electrode which is metal oxide mixed with ruthenium; electro-Fenton and electrocoagulation with the help of iron electrodes. From their investigation they concluded that utilizing electrodes of iron reported the most effective results of removal of phenol (98.74% and 75.71%) whereas chemical oxygen demand (COD) was observed to be 6 and 9 min respectively.

1.3.6 Biological treatment

Biological treatment is the application of microbial metabolism for separation of dissolved colloidal organic contaminants from the wastewater. These applications has shown certain impressive results in the recent times. In many instances, combination of various microbes has been applied to the water for eliminating various hazardous contaminants from the wastewater. As the nature and behavior of different microbes under different environmental condition could not be precisely controlled, therefore the biological treatment methods has not been developed for use in water treatment applications. However, in recent times due to the focused research that has been undergone on the efficiency of this technique, notable results have come up. From the experiment conducted by Song et al. (2011) [47] by combining a total lipase cell with lipase from fungus and Yarrowia lipolytica (ascomycetous yeast) to oil contaminated wastewater, it was established that for 72 hours of treatment of the whole-cell, 96.9% and 97.6% of oil and COD were removed. A typical strategy is biological remediation using the microbial metabolism technique, in which bacteria use harmful contaminants as nutrition and energy sources to multiply and thereby organic contaminants are eliminated from the waste stream by either total or partial breakdown into non-toxic compounds [48–50]. However, as a natural process utilising indigenous bacteria, bioremediation is regarded as a very cost-effective and ecologically responsive solution with respect to degradation of resistant oil contaminated wastewater. However, as the conditions of the pollution sites vary abruptly these technique does not show consistent results and their outcome becomes unpredictable which leads to ineffective eradication of the oil pollutants. Numerous biological agents, including hydrocarbonoclastic bacteria, enzymes, and biosurfactants, are capable of completely mineralizing complex organic contaminants and impurities into water, carbon dioxide (CO_2), inorganic chemicals, and cell protein [51,52] . In another study with pseudixanthomonas sp. RN402 it was found that RN402 can degrade various oils as well as organic solvents completely. Bacteria have been discovered to be key degraders in oil spilled aquatic habitats, capable of eliminating both the aliphatic and aromatic hydrocarbon portions of petroleum while simultaneously producing the lucrative by-product lipase [53] Various species of yeast such as Candida lipolytica, Rhodotorula mucilaginosa, Trichosporon mucoides Geotrichum sp., and species of fungi such as Aspergillus, Pencilliumare, Cephalosporium, etc. have also shown great potential for hydrocarbon digestion. The use algal biomass has also been of wide acceptance in bioremediation in the recent times due to its advantage in effectively reducing global warming by absorbing natural CO_2. Conventionally, activated sludge technologies are used to biologically treat industrial effluents. In this process, a dense microbial culture in suspension is suspended in the activated sludge present in the aerated sedimentation tank, where it is employed to break down organic contaminants in the waste stream. Santo et al. (2013) [54] used biological activated sludge technique for deoiling of wastewater from the petroleum refineries. They found that 94–95% of COD, 85–87% total organic carbon (TOC), and 98–99%

of total solids in suspension (TSS) are eliminated from the water. However, due to thickening and foaming difficulties, the traditional activated sludge method cannot carry out the effective hydrocarbon biodegradation since oil-polluted wastewater is often low in nitrogen and phosphorus contents [55]. Additionally, the higher level of salt content present oil contaminated wastewater occasionally inhibits the correct metabolism of the microorganisms in the activated sludge process, triggering plasmolysis and impairing endogenic respiration [56–58] .The biological filter or biofilter approach, which allows a biofilm to develop by cultivating and reproducing the hydrocarbonoclastic microbe on the filter material inside a reactor, is also frequently investigated (Fig. 1.6).

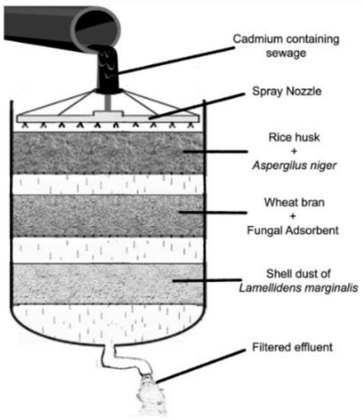


Fig. 1.6 Schematic of biofilter [59]

In recent times more mature technology has been incorporated into the biological treatment. The research fraternities have developed a number of unique membrane bioreactors, such as the microporous membrane bioreactor (MBR), immobilized biological aerated filter (I-BAFs), up flow anaerobic sludge bed- biological filter (UASB-BF), etc. [60,61].

1.3.7 Membrane treatment for emulsified oil contaminated wastewater

Membrane separation has been found to be most coveted technology for emulsified oil contaminated wastewater treatment in recent decades. Technology involving membrane such as microfiltration (MF), nanofiltration (NF), Ultrafiltration (UF) has been effectively applied in the deoiling of wastewater. Microfiltration (MF) as well as ultrafiltration (UF) are the more suitable options for membrane-based separation since the oil droplet size in an emulsified oil contaminated waste stream ranges between 1 and 10 m[62]. Fig. 1.7 represents a conventional UF membrane-based system for deoiling of oil contaminated wastewater.

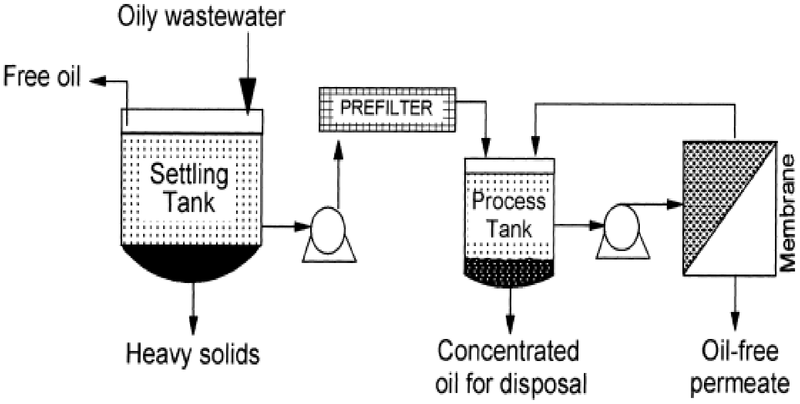


Fig: 1.7 Schematic representation of conventional membrane treatment set up for deoiling of wastewater [63]

There are various advantages of membrane application:

1. The treatment method could be used in various industrial segments.
2. The treated and purified water or the permeate is much homogenous even with significant alteration of the influent since the membrane behaves as a barrier to the eliminated components.
3. Less contamination due to non-application of harmful chemicals.
4. Smaller footprint of related equipment of membrane.
5. Low energy cost as compared to thermal methods.
6. The process can be easily operated without the engagement of highly skilled operators.

For the treatment of oil contaminated wastewater, membranes having molecular weight cut-offs (MWCO) ranging from 20-50 kDa are commonly recommended. However, in the case of saline emulsified waste stream reverse osmosis (RO) or nanofiltration (NF) can also be utilized to process such saline oil contaminated wastewater [64]. In this context, membrane distillation (MD) may be another promising option [65–67]. Hua et al. [68] used cross-flow microfiltration (MF) technique having pore size of 50 nm to separate oils from waste water. Their results showed that various parameters have affected the permeate flux to different levels. Under all conditions, about 92.4% of the total organic compound (TOC) has been removed. For the successful treatment of an emulsified oil-contaminated waste stream, membranes constructed of various polymers, primarily polysulphone (PSf), polyethersulphone (PES), regenerated cellulose (RC), polyvinylidene difluoride (PVDF), and polyacrylonitrile (PAN), are frequently used [69] There are certain limitations related to the membrane technology:

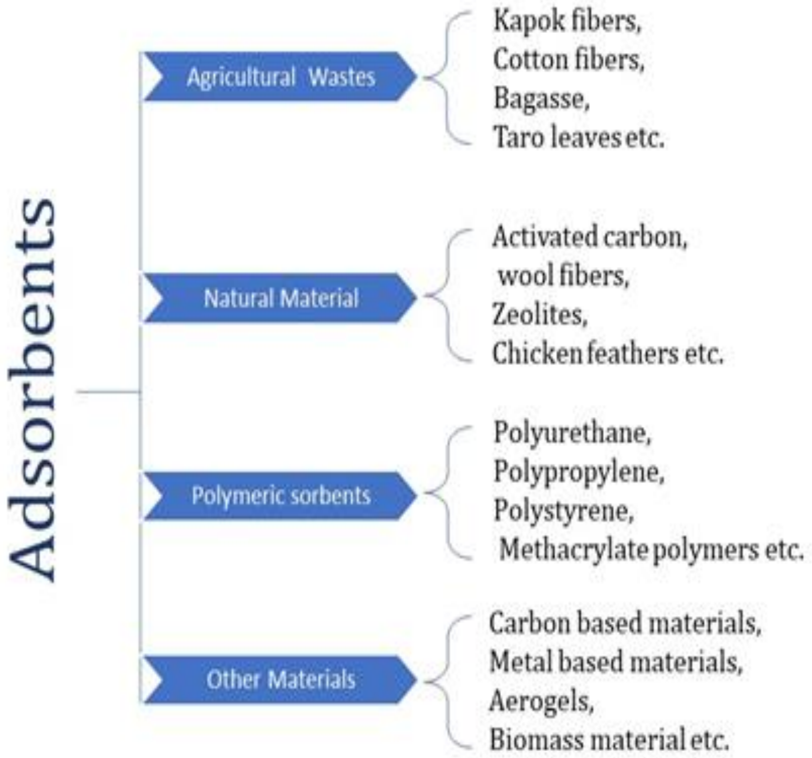
1. The scaling up of the setup is almost linear to the influent volume. As a result, the cost of operation increases when applied to larger waste water stream.

2. Fouling and degradation of the membranes occurs periodically after regular use and hence they have to be substituted frequently. As such the operation cost esclates.

However, with these disadvantages, integrated membrane technique used in conjunction with other methods of separation has shown excellent results commercially with installations of 3000 and above polymeric UF/MF and over 75 inorganic/ ceramic items worldwide. Dynamic membranes are another innovative development in the realm of membrane materials. Their main advantage is their capacity to be produced using a modest filtering process using low-cost components. As soon as the membrane fouls, the deposited foulant film can be eradicated with the subsequent deposition of a fresh dynamic layer. Several polymeric or inorganic materials are employed to provide supports for developing dynamic membranes, such as porous tubes of stainless-steel, polymer based membranes, porous ceramic and sintered polymer tubes made of Polyvinyl chloride (PVC), Polyethylene (PE), etc. [70]. For the development of dynamic membranes, a variety of polymeric or inorganic materials have been used as supports, including sintered polymer tubes composed of PVC, PE, porous ceramic, and polymeric membranes [70].

1.3.8 Adsorbents

Adsorption is a mechanism of transferring pollutants from one phase to another, which necessitates additional methods for removal from the environment. Adsorptions between adsorbate suface and adsorbent surface are categorized into two types: a) physisorption and b) chemisorption. Physisorption is the process where the adsorbate gets attached to the adsorbent surface where the major driving force that exists between the two is weak van der Waals contact. Chemisorption refers to adsorptions that involve a chemical interaction which developes between the adsorbate surface and adsorbent surface. Electrostatic adsorption signifies the process where adsorbent and adsorbate having opposite charges attract each other. Adsorption energy is typically used to determine the kind of adsorption [71]. Various materials having hydrophobic character has been widely used in the removal of oils from wastewater. Various naturally occurring absorbents has also been utilized in this process of wastewater treatment like kapok fiber [72,73], cotton fibers [74,75], bagasse [76,77] and other agricultural wastes [78–81], however, these



absorbents have not been extensively used because of their low hydrophobic character and poor oil/water selectivity. Numerous natural materials have also been studied to determine their oil absorption capacity. These include activated carbon [82,83], wool fibers [84,85], zeolites [86,87], straw [88], etc. But due to their low absorption properties and poor reusability they are not abundantly used in wastewater treatment [30].

Polymeric absorbents have proven to be the most effective strategies to eliminate oils and other organic pollutants from contaminated water. Some of these polymeric materials are discussed below:

1.3.8.1 Polyurethane

Polyurethane have been extensively researched, and modern manufacturers have gained good control over its properties like size and uniformity of the pores present, volume of pores and so on. PU foams have several known applications like cushioning of furniture and cars, packaging material, fire retardant material, insulation, etc. The processing and properties of PU have been continuously developed and researched because of its versatile properties [89]. In order to adsorb oils effectively, polyurethane foams need to have an open cell structure and high interconnections between the pores so that it can retain maximum oil within its porous structure. Assuming that the polyurethane matrix has no effect of swelling within the matrix, the retainment of oil within the pore structure is dependent on: a) the force that attracts oil to the pores, b) the volume of pores, and c) the interconnections that exists between the pore spaces. Based on the PU material selected interconnections and pore volume remains as a predetermined property. Wu et al. studied the absorption of sponges prepared from polyurethane modified with silica sol. They found that the material absorbs about 100 g/g when dipped in motor oil [90]. Li et al. modified polyurethane foam with bird’s feather by graft polymerization and found that the material exhibited good oil absorption potential of 41 g/g when used with kerosene [91,92]. Su et al. also synthesized PU foams having a WCA (water contact angle) of 152^0 which efficiently separates oil from oil-water environment [93]. Investigations are also conducted on preparing composite polyurethane sorbents. In one of such study graphene sheets were incorporated into polyurethane and the sorbent thus formed showed excellent absorption capacity of 99% for oil/water mixtures [94].

1.3.8.2 Polystyrene oil sorbents

Polystyrene is an aromatic thermoplastic polymer that is hard and brittle in structure. It has a low melting point and used in various applications like packaging material (as in case of peanuts, DVDs, CDs etc.), bottles, containers, tumblers, trays, disposable cutlery etc. In recent years, polystyrene has found considerable attention as an oil adsorbing material. Polystyrene fibers were prepared by electrospinning by Lin et al. which are nanoporous in structure and having potential of removing oil in remediation process [95]. Polystyrene and polyacrylonitrile (PAN) was combined by electrospinning in another study performed by Li et al. and concluded that the material had excellent sorption efficiency in pump oil (195 g/g) [96]. The developed material exhibited good mechanical properties and strength and high buoyancy. Composites made from polystyrene and divinylbenzene was also reported to have oil sorption capacity of 23 times the initial weight of the material. Lin et al. modified the polystyrene morphology with various polymers and solvent composition in the electrospinning process and concluded that the porosity of the polystyrene fibers is one of the integral factors to ascertain the absorption efficiency of the prepared composite [97]. Fig. 1.8 shows a schematic illustration of electrospinning process to generate hydrophobic polystyrene fibers.

1.3.8.3 Oil sorbents prepared from polyethylene and polypropylene

A majority of the oil absorbing material which are available commercially are synthesized from a) polyethylene and b) polypropylene. Saleem et al. developed oil sorbents from waste and discarded polyethylene and concluded that the sorbent has high adsorption capacity as well as high rate of oil uptake [98,99]. Polypropylene and kapok fiber was blended in a 50/50 ratio by Lee et al. in a needle striking process and results showed good adsorption properties [100]. Similar combination of polypropylene, kapok fiber and milkweed fibers also demonstrated high sorption capacity [100]. Results derived from a recent study where polypropylene mats were manufactured by electrospinning; it was concluded that the mats can separate water from fuel with eliminating efficiency upto 99% [101]. It has been clearly established from studies that the sorption potential of polypropylene is related mainly on the fiber diameter, porous nature of the sorbent and properties of the oil under consideration [102].

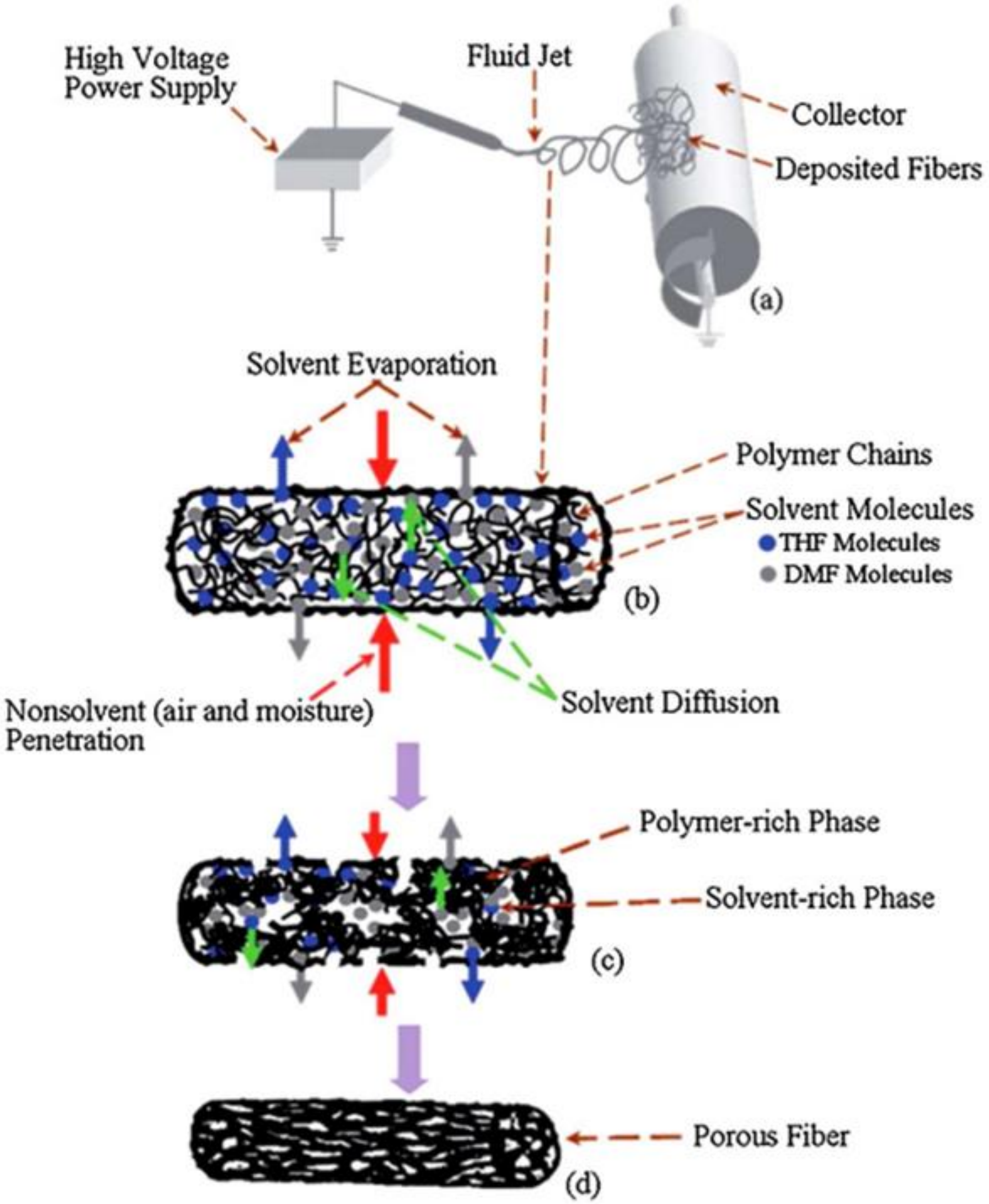


Fig: 1.8 Schematic illustration of electrospinning process to generate hydrophobic polystyrene fibers [92].

1.3.8.4 Polyacrylates oil sorbents

Polyacrylates are salts, esters (RCOOR′) and conjugate bases of acrylic acid and various monomers can be derived depending on the structural form of acrylic acid. Some of such acrylate monomers include: methacrylates, methyl acrylates, ethyl acrylates, butyl acrylates, butyl methacrylates etc. Feng and Xiao [103] synthesized fibers of co-polymers (butyl methacrylate and lauryl methacrylate) and found impressive results on its oil adsorption capacity. A ternary copolymer synthesized from styrene, butyl methacrylate and steryl methacrylate for investigating the efficiency in oil spills was developed by Feng et al. [104] Butyl methacrylate used as a monomer was combined with styrene to form a porous copolymer which revealed oil adsorption capacity 9 g/g when tested in crude oil [105] . Similar binary copolymer was prepared with butyl methacrylate (BMA) and monomers of methyl methacrylate (MMA) by polymerization process (suspension emulsion polymerization) which also showed higher oil absorption potential [106]. Steryl methacrylate and butyl methacrylate were copolymerized to form microspheres of high porous structure having oil absorption potential up to 28 g/g in case of diesel oil and has the potential to be reused for 12 cycles [107]. Fibrous methacrylate electro spun mats produced by suspension polymerization also showed good potential for oil absorption.

1.3.8.5 Adsorbents based on other polymer materials

Adsorbents based on several other polymers were also investigated at different times for its absorbing capacity. Bukharova et al. utilized polyethylene terephthalate (PET) in absorbing oil which unfolded a new avenue in utilization of waste plastic in oil absorption [108]. Butyl acrylate monomers and styrene were electro spun to obtain fibrous membrane capable of adsorbing high viscosity oils [109] Composites prepared from polydimethylsiloxane (PDMS) reinforced with multiwalled nanotubes (MWNT) showed adsorption capacity of 6-12 g/g [109]whereas in another study polydimethylsiloxane coated cotton sorbents showed adsorption capacity up to 30-65 times of the sorbent weight [110].

1.3.8.6 Ion Exchange Resins

The application of Ion exchange resins has gradually increased in water treatment applications. Most synthetic ion-exchange resins are actually solid organic polymers carrying an electrostatic charge that is neutralized by a particular counter ion which is oppositely charged. Ions exchange resins may be cation exchanger having positively charged mobile ions or anion exchanger with having negatively charged ions. Bernabe et al. [111]had prepared resins from poly (acrylamide-co-methacrylic acid) and estimated the adsorption capacity for Hg (II), Pb (II), and Al (III) ions. Heshmati et. al [112] developed ion exchange resins from polyamidoxime and studied its removal efficiency in case of Th (IV) with respect to pH, time of agitation and dosage. Yasemin et. al [113] investigated the eradication of sulphate ions present in water by means of ion exchange resins and reported that the resin could remove 60% of sulphate from the processed water. Amberlyst A21 ion exchange resin was used by Guimaraes and Leao [114] for removing sulphate and found the adsorption capacity as 11.6 mg sulphate per ml of resin. Most of these resins are generally based on the extent of cross-linking between polystyrene and divinylbenzene copolymers having functional groups responsible for the exchange of ions. Porosity of resins is an important factor which is controlled by a typical cross-linkage from 0.5% to 20%. Resins with a low cross-linked nature exhibits a gel structure (microporous), whereas those with a high degree of cross-linkage exhibits a macroreticular resins (macroporous). Some of the bulk properties of the resins like rate of swelling, swelling capacity, equilibrium rate of adsorption and selectivity are controlled by porosity. Generally, with the decrease in cross-linking percentage, the moisture content, the loading capacity, the equilibrium rate and the capacity to holdlarger ions increases. Non-cross-linked polymeric resins are seldom used as they are chemically, mechanically and thermally unstable in nature [115].

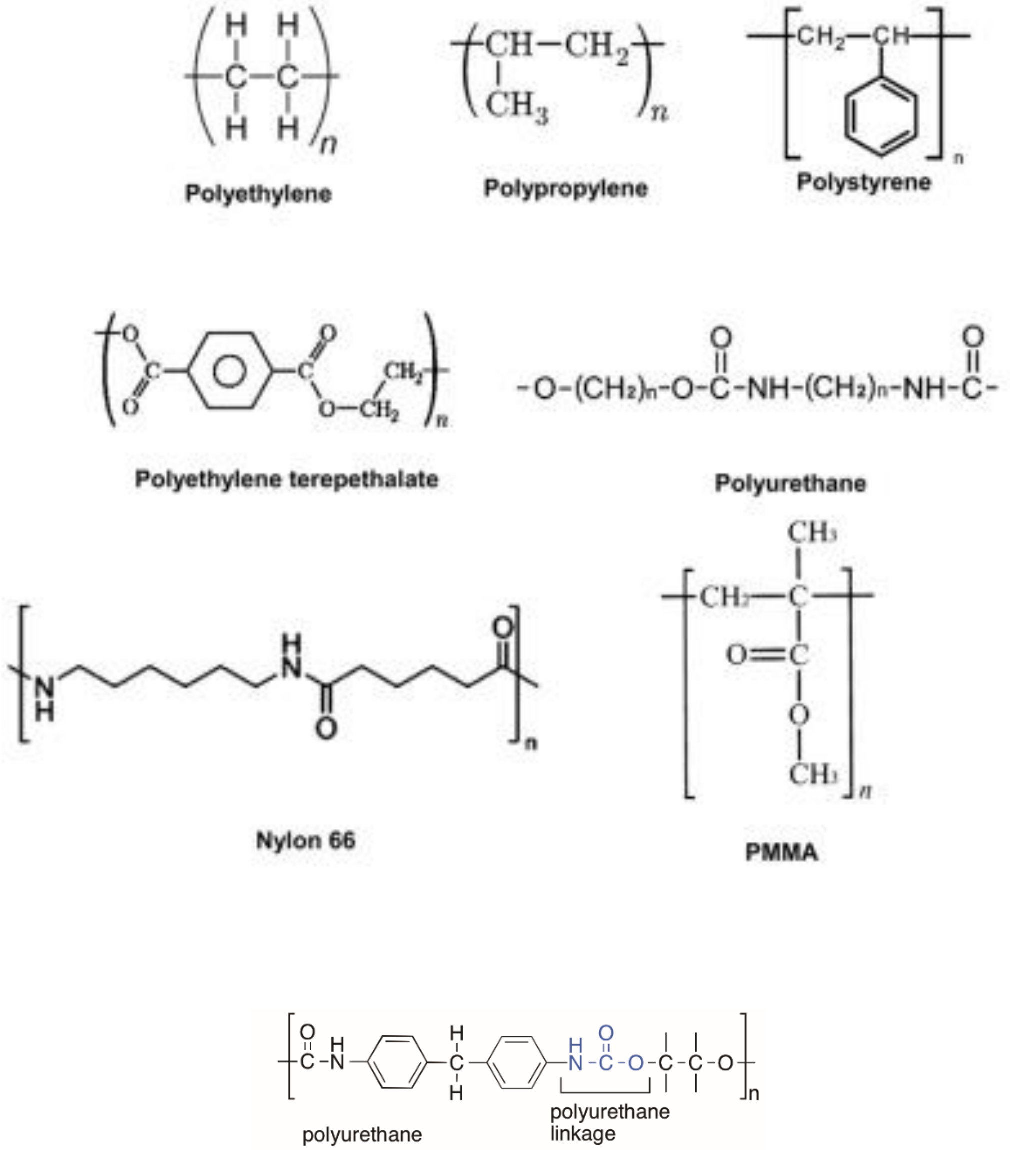


Fig: 1.9 Various Polymeric materials for oil adsorption

1.3.9 Strategies adopted for synthesis of polymeric oil sorbents

Several strategies are adopted during the synthesis of polymeric sorbents which are described below:

1.3.9.1 Chemical conversion

This preparation method involves various chemical modifications of the polymers under various conditions. Atta et al. [116] conducted chemical conversion of polyethylene teraphthalate (PET) waste with the aid of trimethylolpropane (TMP), polyol oligomers evolved. These oligomers were subsequently reacted with the help of 2,4-toluene diisocyanate which eventually led to the development of various polyurethane foam material for oil adsorption study.

1.3.9.2 Grafting

In this method of fabrication, polymer chains are attached onto a surface. Grafting method is used to alter the chemical reactivity of the surface on which they are attached. In our present study, poly(ethylene-co-vinyl acetate) has been successfully grafted to maleic anhydride with the use of benzoyl peroxide as an initiator. The polymeric absorbent thus formed displayed excellent absorption capacity in oils as well as organic solvents. Tanobe et al. [117] grafted polystyrene with waste polyurethane foams and studied its effect on oil absorption. Results from the study indicated that grafted foams had better sorption capacity, better absorption kinetics and better reusability. In another such investigation, methacrylic acid was grafted to polypropylene fibres using a crosslinking agent. The absorption in this study was found to be 20.8 g/g.

1.3.9.3 Gamma Radiations

Here, low doses of gamma radiations are applied to fabricate oil sorbents that possess good oil absorbing properties. Sheets of unused plastic made from polypropylene (PP) and polyethylene (PE) were exposed to small doses of gamma radiations which revealed good sorption efficiency for crude oil. Gamma radiations of lower doses resulted in lower degree of crosslinked structure which enabled sorption of crude oil into the polymeric network [118].

1.3.9.4 Mechanical methods

Hydrophobic fibers were prepared from polystyrene waste by utilizing peels of citrus as solvent by simple mechanical means without involving any chemicals by Sharma et al [119]. These fibers showed good absorbing properties.

1.3.9.5 Porous films

a) Dry stretch process

In this process, pores are induced by stretching the polymer and extending in the machine direction [120].

b) Particle stretch process

Here, the nanoporous polymers is blended with particulate material and pores are induced on the material when the force applied during stretching fractures the polymer and particulate interface [120].

c) Wet process

In this wet extraction process, extrusion is conducted in a mixture of polymer material and oil which are mixed in a certain weight ratio. During extrusion, the oil is eventually removed to generate a porous polymeric sorbent [121].

1.3.10 Properties of a good adsorbent

The adsorption capacity of a sorbent is defined as the ratio between the difference in weight of the sorbent before and after adsorption and the weight of the sorbent before adsorption in g/g.

Some of the essential properties that a good adsorbing material must possess are discussed in brief.

1.3.10.1 Solubility between the adsorbate and the adsorbent

This property relates to the structure of the adsorbate and the adsorbent. The chain structure of both the adsorbate (oil) and adsorbent (polymeric composite) must be mutually compatible with each other.

1.3.10.2 Surface area

Higher the surface area higher is the area available for adsorption. Thin adsorbents having good mechanical strength are more suitable for adsorption.

1.3.10.3 Porous structure

Pores and void spaces on the surface of the adsorbent will provide an additional driving force for adsorption. Viscous oils frequently block an adsorbent's surface pores, inhibiting consequent adsorption which are to be driven by the inner adsorption sites. In such circumstances, the performance or ability to adsorb largely depends on the size and accessibility of the pore spaces.[122]. Modified Darcy’s law which is derived for fluid flow in unsaturated and porous media lucidly delineates this phenomenon:

$$j = -D\frac{\delta c}{\delta s} \text{...} 1.4$$

where j represents mass flux passing through the porous structure; δc represents gradient of concentration; δs represents the distance changed; and D denotes the capillary diffusivity which is established by the equation 1.5.

$$D = \rho_{liquid}\, K\, \frac{\delta h}{\delta c} \text{ ……………………………..} 1.5$$

where the constant K is known as the hydraulic conductivity and delineated by the equation 1.6

$$K = \frac{\rho g}{\mu}\frac{1}{8}\sum_i \frac{\pi n_i r_i^2}{A} \cdot r_i^2 \qquad \text{………………….} 1.6$$

In Eqs. (1.4) and (1.5), δh is known as the hydraulic potential; μ denotes the viscosity that the adsorbate (liquid) possess; g signifies acceleration due to gravity on the earth’s surface; ρ is the density of the adsorbate (liquid); n_i denotes the total pores having size of r_i radius; A is the area in total exposed to adsorption.

Here ‘k’ which is the intrinsic permeability and represented by the final half of Eq. (1.6) absolutely depends upon the pore radius ‘r_i’ of the pores:

$$k = \frac{1}{8}\sum_i \frac{\pi n_i r_i^2}{A} \cdot r_i^2 \qquad \text{………………….} 1.7$$

Darcy’s law elucidates that the porous media will have a lower volumetric flux with a smaller size of the pore r_i. The viscosity and volumetric flux are indirectly related. When the operation involves adsorbate with high viscosity, a larger diameter pore size is required which induces the flow of the adsorbate within the adsorbent. The pore surface is clogged by the highly viscous adsorbate when the cohesive force existing between the oil molecules exceeds the driving pressure gradient between the oil and the adsorbent surface. Now since the adsorbent is undersaturated, as the distance between the oil and solid interface increases into the adsorbent, capillary diffusivity drastically reduces and the adsorbent becomes drier. Due to the combined effect of this gradient drop, restriction in radius and viscosity, there generates a resultant force effective along the direction at which the force of cohesion acts, eventually ceasing the viscous fluid flow into the adsorbent.

1.3.10.4 Wetting Characteristics

Wettability of an adsorbent is the ability by which a liquid adheres to the solid surface. Wettability determines the hydrophobic or hydrophilic character of a material when water is used as the liquid. The wettability is frequently measured by the means of contact angle. The angle created by the liquid droplet with the exposed surface of the solid through the liquid is defined as the contact angle. Surface energy along with surface morphology are two surface related properties which is responsible for the wetting characteristics of the of a material [123,124]. The effect of surface energy on wettability depends more significantly on its rather than the surface tension (ST) of the liquid. Higher the γc value, higher will be the surface energy that exists per unit area.

As the critical solid surface tension (ST) (γc) becomes higher than the surface tension exhibited by the liquid, the liquid wets (adheres) to the surface of the solid. When γc value (critical solid surface tension) of the adsorbent lies within the surface tension (ST) of water (about 60-65 mN/m) and oil (generally 20 mN/m however is influenced by the nature and composition of the oil), the adsorbent is said to be hydrophobic or oleophilic.

The relation that exists between the water contact angle (WCA) and the interfacial surface tension is explained by the young’s equation [123–125]:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} cos\theta \text{………………………}2.5$$

If we consider a smooth surface which is static without any intermolecular interactions, the contact angle is given by θ whereas γ_{SV}, γ_{SL} and γ_{LV} are the interfacial tensions. Hydrophobic character similar to water is exhibited when the contact angle exceeds 90^0. However, when the contact angle (θ) of water approaches 0^0, the liquid wets the surface of the solid and spreads over it indicating a hydrophilic or oleophilic nature [126].

1.3.10.5 Buoyancy, density and surface area: Conditions fluctuate over time during oil recovery, and the characteristics of oil change subsequently. The density as well as viscosity of the oil and the adsorbent alter as it evaporates and emulsifies, thus impacting buoyancy. During oil recovery, a lot of the naturally buoyant organic materials lose some of their original buoyancy owing to these changes, making it tough for them to stay floating. The adsorbent may, however, be prevented from making contact with the oil if the viscous and heavier oils has a light and buoyant material that floats on its surface. As a result, effective adsorbents must be capable of sustaining buoyancy both before adsorption as well as after it. The surface area accessible for adsorption determines the adsorption nature of the sorbents. As a result, there is a proportional relationship between the adsorbent's adsorption capability to the surface area it can invade [127,128]. Materials having a higher ratio between surface area and volume make potential candidates for adsorption as the adsorbates can bind to a larger number of adsorption sites.

1.3.10.6 Geometry, saturation, strength and durability

3D porous structured adsorbents have grown in popularity in recent times as a way to elevate the surface area to volume ratio [129,130]. However, handling of these low-density 3D porous structured adsorbents is a matter of concern when subjected to the harsh environmental conditions during oil-water separation. Therefore, earlier investigations have reported using 3D porous templates merely as a support system [131,132]. Aerogels from soy protein is one of such examples [133]. Other such materials include melamine sponges [134], kapok wadding [135], polypropylene foam [136], polyurethane sponge [137], etc., and various such natural as well as synthetic biopolymers [138]. The adsorbing materials which are prepared using this heterogenous system are found to possess better wetting properties. Hence, to create effective 3D porous structured adsorbents, the diffusivity and the permeability of the material should be known precisely. These materials thus utilize their properties viz. high surface area to volume ratio, durability and strength for absorbing various absorbate on to its surface.

1.3.10.7 Retention capacity and recyclability

For effective recycling capabilities, it is necessary to have good oil retention qualities. The capacity to adsorb effectively and even rapidly may be found in various materials. However, to prevent the premature drainage, the absorbent must possess a good oil retention capability. This property plays a significant role in eliminating oil from a oil-water mixture. Materials with poor oil retention property will lead to secondary waste hazard or contamination due to leakage of oils and spills. Since an adsorbent will be applied in dynamic environmental conditions, it must possess good strength to withstand the various pressures, otherwise, it will be subjected to physical deformation. This deformation will exert an external pressure on the pore spaces which will squeeze out the oil from its internal network. Absorbents which are made from organic materials often show this phenomenon. As evident from Darcy’s law discussed earlier, the drainage phenomenon gets slowed down in case of pores with smaller diameter thus elevating the oil retention property. However, during absorption, the speed with which the absorbate invades the absorbent surface also depends on its pore size. In some cases, the adsorbent’s external surface gets occupied by viscous oils, particularly in cases where smaller pore spaces exists, which subsequently stops the adsorption into the internal network.

[139] which is often inefficient to eliminate the entire oil from the absorbent. Therefore, other extraction methods like thermal heating and extraction by acetone or other organic solvents are applied to eliminate residual oil from the absorbent. Although most of the oils could be extracted from the absorbent using organic solvents thus increasing its oil absorbing efficiency, the handling and disposal of the organic solvents, as well as oil and solvent mixture, becomes another concern that increases the secondary hazardous wastes. Therefore, a small decrease in the absorbing efficiency is acceptable until the absorbent exhibits a stable oil absorbing potential during continuous cycles of absorption and desorption. In summary, all these properties must be optimized in such a manner that the absorbent exhibits a good oil retention capacity along with an excellent recycling property.

1.4 Basic components of Poly(ethylene-co-vinyl acetate) based adsorbents and ion exchange system

- Poly(ethylene-co-vinyl acetate) which provides the polymeric backbone for the adsorbent.

- Benzoyl peroxide, acts as an initiator.
- Maleic Anhydride, which acts as a crosslinker.
- Cetyl alcohol which provides long chain carbon structure to the polymer backbone.
- Sodium chloride which is used as a porogen.
- Nano-fillers (Montmorillonite clay) for enhancing the properties and nature of the adsorbent.
- Ion Exchange resins (cation exchange and anion exchange) which provides the sites for ion exchange.

1.4.1 Poly (ethylene-co-vinyl acetate)

Poly (ethylene-co-vinyl acetate) or EVA is a thermoplastic copolymer of ethylene and vinyl acetate. Depending on the ethylene and vinyl acetate (VA) content this polymer exhibits different properties like melting point, crystallinity, stiffness and polarity.

The various properties exhibited by poly (ethylene-co-vinyl acetate) are discussed in brief [140].

1.4.1.1 Physical properties

EVA resembles low density polyethylene (LDPE) in structure being opaque at vinyl acetate content ~ 5% and appears to be crystal clear rubbery material at higher vinyl acetate content. Although in thin sections, due to low vinyl acetate content the material appears to be opaque, however in thin films they reveal transparent nature owing to their low degree of crystallinity. Even the density of EVA also depends on its vinyl acetate content. The surface hardness of Ethylene vinyl acetate, EVA copolymers is dependent on two main factors viz. molecular weight and degree of crystallinity. Hence as the vinyl acetate concentration rises the hardness of EVA copolymers decreases significantly. The thermal behavior of EVA copolymer changes with the rise in temperature. As the temperature increases the polymer softens and viscosity tends to decrease. When the threshold temperature is achieved, the melting of the crystalline region starts further reducing the viscosity. However, this behavior depends on the vinyl acetate amount of the copolymer.

The effect of vinyl acetate percent of other mechanical properties is explained in the stress-strain diagram in Fig. 9. At lower vinyl acetate content the stress-strain graph exhibits a yield region similar to LDPE. However, at higher % Vinyl acetate (VA) it exhibits higher elongation and strength with subsequent disappearing of the yield region. The EVA becomes more rubbery in nature at this point. The flow behavior of EVA copolymers is non-Newtonian ie shear increases as viscosity decreases as like most thermoplastics. The relation is depicted in Fig. 10.

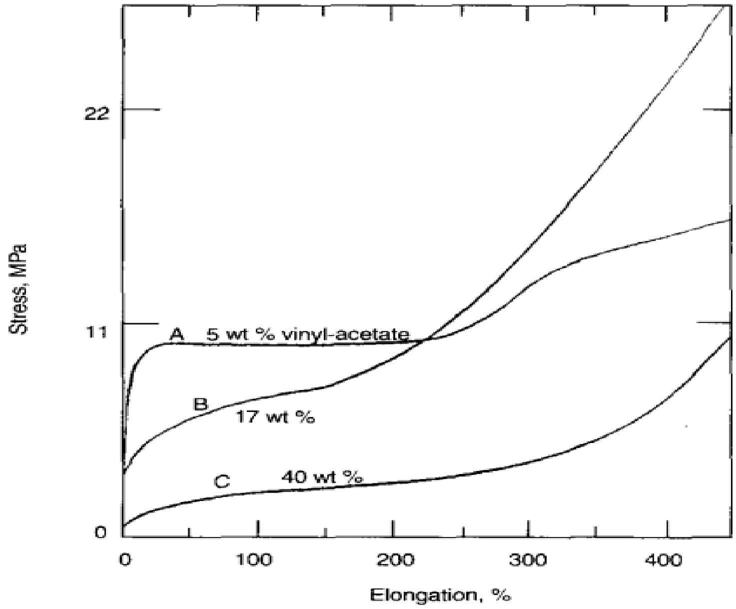


Fig. 1.10 Stress-Strain diagrams of EVA copolymers at different vinyl acetate content

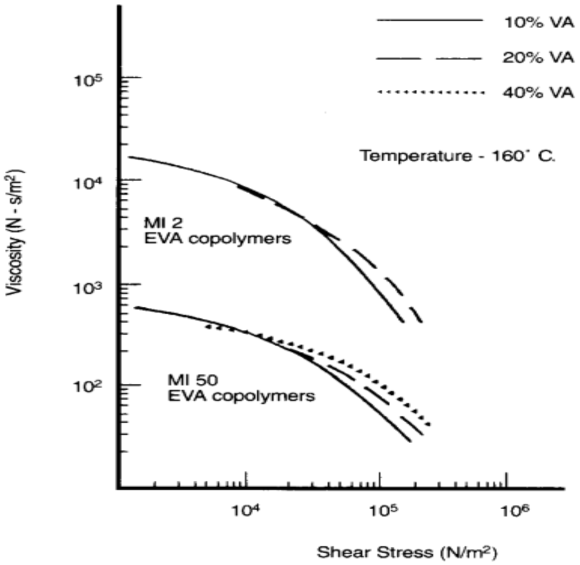


Fig. 1.11 Shear stress vs Viscosity curves for EVA copolymers

1.4.1.2 Chemical properties

With an increase in the vinyl acetate amount in EVA copolymers, a subsequent increase in polarity of the molecules is observed. This increase in polarity reduces the strength to resist various chemicals. Hence EVA copolymers readily reacts with different organic solvents and organic acids. The EVA copolymers tend to be very permeable to gases and moisture due to their more polar nature. They are thermally less stable; however their stability can be enhanced by crosslinking in the presence of peroxides as free radical sources.

1.4.1.3 Electrical properties

EVA copolymers exhibits poor dielectric nature due to the existence of polar vinyl acetate groups and therefore cannot be used in advanced electrical applications.

1.4.1.4 Applications of Poly (ethylene-co-vinyl acetate)

A wide number of literatures is available on the use of EVA as a drug delivery substance. These include drug delivery in cervical cancer [141]oral delivery of antifungal and anti-microbial [142], controlled release of dopamine [143], and delivery of levodopa for a continuous extended period (Sabel et al.,1990) among various other chemicals used in pharmaceutical Science. The most common industrial processing technique which is used for the synthesis of various EVA-based products is the hot-melt extrusion process which is a combination of melting, blending, and shaping and also a solvent free process that is compatible with various polymeric applications [145,146].

EVA has been widely used as an encapsulating material because of its superior properties like high transmission value, good toughness at low temperature, UV resistance, and high-volume resistivity [147]. Klampaftis et al. [148] have reported that luminescent material added to the EVA layer as encapsulating material resulted in improving the efficiency of silicon solar cell. Yuwaween et al. [149] modified EVA encapsulating film using esterified bacterial cellulose nanofibers and observed the increase of mechanical, as well as barrier properties of EVA encapsulating film. Even various studies have also been conducted to investigate the causes and effects of EVA encapsulation degrading behavior in U.V radiations [150]

EVA has also been used to develop microcellular foams blended with polybutadiene rubber (BR) for footwear applications having higher tensile strength, wear and tear properties with low hardness. [151] Bahattab et al. [152]have also reported the synthesis of crosslinked EVA/LDPE/metal hydroxide composites for wire and cable applications because of higher mechanical and other physical properties with easier processing. Bidsorkhi et al. [153]prepared EVA nanocomposites where halloysite nanotubes (HNT) are dispersed in the EVA matrix and found that as the HNT concentration increases the tensile strength of the EVA nanocomposites also gets increased.

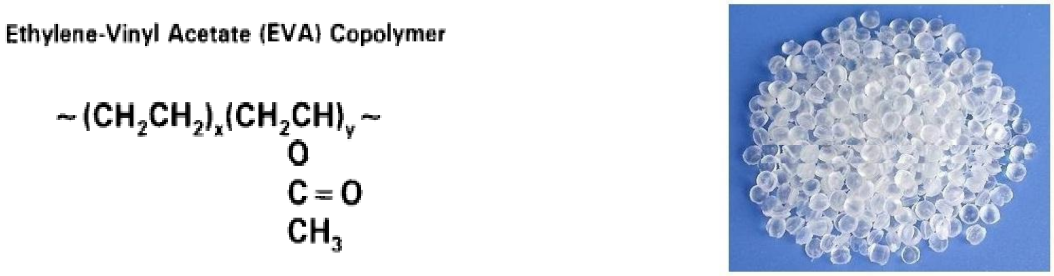
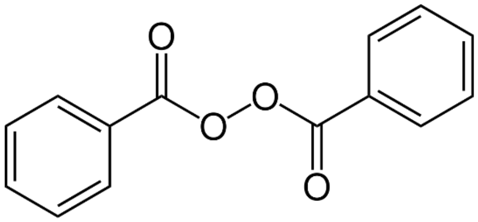


Fig. 1.12 Structure and photograph of Poly(ethylene-co-vinyl acetate) (EVA)

1.4.2 Benzoyl Peroxide

Benzoyl peroxide (B.P) is an organic peroxide with chemical formula $C_6H_{10}O$. It is developed from the reaction between benzoyl chloride and hydrogen peroxide in which two benzoyl groups are linked to each other by a peroxide group. It appears to be white solid granules with a faint odor. It has poor solubility in water but soluble in various organic solvents like ethanol, acetone etc. Benzoyl peroxide is mainly used in the polymer production. It is utilized as a radical initiator that induces chain-growth polymerization reaction as in the case of polyesters and poly(methylmethacrylate) (PMMA) resins. It is used as a safe replacement of methyl ethyl ketone peroxide which is itself hazardous in nature[154]



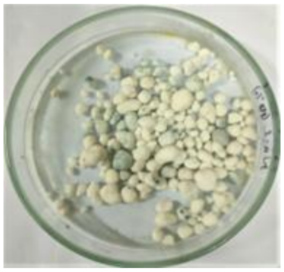


Fig. 1.13 Structure and photograph of Benzoyl Peroxide

1.4.3 Cetyl Alcohol

Cetyl alcohol has been found to be a significant raw material in the manufacture of surfactants. It is a straight compound consisting of 16 carbons. The most noteworthy advantage of cetyl alcohol is its potential to elevate the viscosity as well as stability oil oil-water emulsions. Hence, it is an indispensable ingredient in the manufacture of cosmetic creams and other pharmaceutical ointments [155]

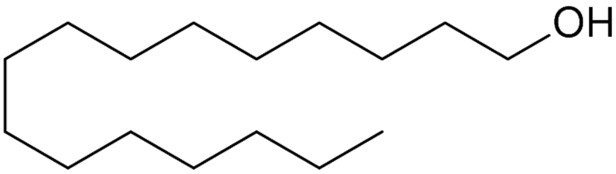


Fig. 1.14 Structure and photograph of cetyl alcohol

1.4.4 Maleic Anhydride

Grafting of maleic anhydride into polyolefins is one of the oldest and proven techniques to prepare a compatibilizer. The high activity exhibited by the anhydride group and low cost of maleic anhydride makes it as one of the most significant functional crosslinkers in industry. The incorporation of the optimum amount of maleic anhydride into the composite system improves the mechanical strength of the composite along with other properties. Hoang et al. studied the effect of adding maleic anhydride (MA) grafted ethylene vinyl acetate (EVAgMA) copolymer on nanocomposites synthesized from silica and EVA and found that the tensile and thermal properties were improved drastically on addition of 1% EVAgMA. [156]

1.4.5 Sodium chloride (NaCl)

NaCl has been extensively used as porogens in tissue engineering to improve the porosity of scaffolds. Tran et al. [157] developed an effective facile method to improve the control on the NaCl size distribution (13.78±1.18 µm) from the traditional method having size (13.89±12:49 µm) and fabricated scaffolds with improved interconnectivity and microchannels. Yu et al. [158]studied the effect of variant pore sizes and porosity created by the different particle sizes of NaCl porogens on the mechanical properties and microstructure of poly-Ɛ-Caprolactone-hydroxyapatite composites and concluded that the use of varied particle size of porogens in HA-PCL scaffolds results in altered porous features and mechanical properties. Xia et al. [159]had studied the effect of Nacl porogens on the pore structure of silk fibroin (SF)/Hydroapatite (HA) composites and results from this study indicated that the increase in NaCl content, particle size distribution, and particle size of NaCl porogens have significant improvement in pore connectivity and mechanical properties of the synthesized composite.

1.4.6 Nano-fillers (Montmorillonite clay)

Nanocomposites are the class of composites made up of reinforcing nanomaterial into the polymeric matrix. By incorporating nanomaterials into the polymeric matrix, improvement in mechanical strength, thermal stability, flame resistance, and excellent water and chemical resistance properties can be achieved. The reinforcing action of filler is related to numerous variables, including nature and type of nanofiller, polymer matrix characteristics, polymer and filler concentration etc. Clays, nanocellulose, carbon nanotubes, graphene, halloysite etc. have been utilized to create nanocomposites with various polymers.

Among the various nanoclays, Montmorillonite (MMT) is a extensively used nanoparticle for numerous applications. It has 2:1 phyllosilicate structure, with an alumina sheet (octahedral) sandwiched between two sheets of tetrahedral silica. The tetrahedral silicate layer is made up of SiO_4 groups that are connected together to form a hexagonal network of Si_4O_{10} repeating units. The layer width is about 1 nm, and the lateral dimension may range from 300 Å to several microns.

Under specific experimental circumstances, the interlayer space of clay may be expanded, and polymer chains can penetrate deep inside these gallery layers of clay [160,161]

1.4.7 Ion Exchange Resins

Ion-exchange resins are developed from synthetically polymerized organic compounds that possess positive ($^+$) or negative ($^-$) charged sites capable of attracting oppositely charged ions from their surrounding solution. [115] The electrically charged sites generally contain sulfonic acid or carboxylic acid salts and sometime quaternary ammonium salts. Polymers with acid groups are capable of exchanging positive charged ions like hydrogen ions and metal ions and are classified as cation exchangers whereas those with ammonium groups are capable of exchanging negative charged ions such as hydroxide or halide ions and are termed anion exchangers [162]. Amberlite IR 120 is one of such cation exchange resin which is used in a wide range of demineralization, dealkalization and deionization application. It is a gel type with strong acidic nature made from sulfonated polystyrene. It is used for demineralizing water mainly in the H^+ form. Amberlite IR 400 is a microporous strong basic anion exchange resin with polystyrene divinyl benzene polymer matrix used for industrial demineralization applications. In industrial applications, ion exchange resins are generally used for water softening operations for the elimination of calcium, magnesium, manganese and, ferrous salts present in the water. In chemical study, these resins are applied for the removal of ionic substances whereas in chemical synthesis these ion exchange resins are utilized as important catalyst preferably in esterification reaction and hydrolysis.

1.5 Objectives and Plan of work

One of the emerging challenges that the earth is facing currently is the scarcity of safe water to drink, for use in industry and agriculture, and for a plethora of other activities where water is essential. The repercussions of these aggravated water scarcity have detrimental effects not only on the human population but also on the flora and fauna. In addition to several nutrients essential for sustaining life like iron, phosphorus, nitrogen, etc., water also consists of several substances hazardous for living organisms that have a detrimental effect on the environment as a whole. Substances like oils, arsenic, fluorides and mercury have led to a serious health concern not only on plants and animals but also on human health. One of the most significant sources of this wastewater is the produced water that evolves from the oil and gas extraction activities that accounts for a larger fraction of the contaminated wastewater. This waste water (produced water) generally contains oils as the primary pollutant. Sometimes salinity of the produced water has been found to be as high as 2,00,000 mg/l on the basis of geography and nature of the extracted hydrocarbon which is regarded as another threat in discharging the wastewater. Different researchers has undergone various works to treat the contaminated water and remove the pollutants. The researches have studied the application of various biological as well as physiochemical processes to eradicate the oils and salts from the contaminated water. Out of the various methods employed for the treatment of water, adsorption has come up as the most promising and simple method of treatment.

Various polymeric adsorbents has been studied regarding its efficiency to eradicate oils and other contaminants from waste water. One of the most significant factor which requires attention is the blending technique of the polymer and its composites. The solution blending process involves lots of organic solvents. Because of its high toxicity, minimum use of organic solvents is recommended by the environmentalist. The melt blending process is the best method to overcome the hazard associated with solution blending. Here heat is used to blend the components and to get a homogeneous mixture.

In polymeric adsorption, the chain structure of both the adsorbate (oil) and adsorbent (polymeric composite) must be mutually compatible with each other. As the rule of like dissolves like goes, the prepared polymer must consist of a long aliphatic chain mainly nonpolar in nature to attract the long-chain oils like gasoline, crude oil, kerosene and other organic solvents towards it. Hydrophobicity is another important parameter in this regard so that the oils could be absorbed into the polymer network due to the hydrophobic nature of the polymeric network. Pores and void spaces on the surface of the adsorbent will provide an additional driving force for adsorption. Moreover, to eliminate the high level of salts from the contaminated water, the Ion-exchange resins could be utilized which are synthetically polymerized organic compounds that possess positive or negative charged sites capable of attracting oppositely charged ions from their surrounding solution.

Under this background and considering the various aspects the objectives have been set up. The aim is to prepare a polymeric adsorbent by blending a novel polymer with a long chain molecule in the presence of a cross-linker and an initiator. Although, Poly (ethylene-co-vinyl acetate) has been used in several applications, however there is a dearth of report on its use as an adsorbent. The compatibility of nanocomposites with the polymer will also be studied thus determining the oil adsorption potential of the nano adsorbent. Moreover, to reduce the salinity of the contaminated water, a suitable ion exchange resin system has to be used which will exchange all the ions from the water thus desalting it. The melt mixing technique has been used as a green method in the process. Attempts have been initiated to enhance the physiochemical properties and adsorption capacity of the adsorbents through incorporating different additives and using specific processes.

The plan of the work has been designed as per the following

1. Collection of contaminated water samples from the oil fields.

2. Selection of suitable polymer, different types of crosslinker, and initiators and optimization of their loading in the polymeric matrix to evaluate the best properties.

3. Preparation of polymeric adsorbent using Poly (ethylene-co-vinyl acetate), maleic anhydride as a crosslinker, benzoyl peroxide as an initiator and cetyl alcohol and to evaluate its performance in oil adsorption.

4. Preparation of EVA based adsorbents using NaCl as a porogen to enhance the porosity of the adsorbent and nanoadsorbent by incorporating nanoclay using the melt blending technique and evaluating its oil adsorption capacity.

5. Study on desalination of the contaminated wastewater using ion exchange resin system.

6. Characterization of the composites using various chracterisation techniques.

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CHAPTER 2

REMOVAL OF ORGANIC SOLVENTS AND OILS FROM WASTEWATER BY ABSORPTION WITH CROSSLINKED POLY (ETHYLENE-CO-VINYL ACETATE) MODIFIED BY CETYL ALCOHOL

2.1 Introduction

During the last decade, environmental pollution has got an increasing public concern and the government has come up with stringent rules to address this issue. One such pollutant produced at an alarming rate is the water contaminated during drilling operations for hydrocarbon extraction. The huge amount of produced water must be safely disposed of in accordance with the numerous regulatory requirements. Thousands of new oil and gas wells are drilled each year all over the world, resulting in millions of barrels of generated water. As oil fields produced water containing a significant amount of oil and grease and numerous organic and inorganic elements and other suspended particles, it cannot be directly disposed of immediately or pumped into the subsurface for secondary recovery according to environmental regulations [1]. To utilize this water for various industrial applications, these pollutants must be eliminated. During the last few decades, many researchers have investigated several methods of separating these organic pollutants from the water. Naturally occurring absorbents such as kapok fiber, cotton fiber, bagasse, and other agricultural wastes have been investigated to determine their absorption efficiency but these absorbents have shown low hydrophobic character and poor oil/water selectivity. [2-5]

Various natural materials have been studied to determine their oil absorption capacity. These include activated carbon [6,7] wool fibers [8], zeolites [9,10], straw [11], etc. However, these materials were not abundantly used as oil absorbents because of their low absorption properties, and poor reusability. Polymeric absorbents and organogels have proven to be the most effective strategies to eliminate oil and other organic pollutants from contaminated water. Nam et al. [12] studied the absorption of polymer absorbent based on polyolefin and reported that the absorbent had an excellent absorption capacity of 40 g/g in crude oil. Yan et al.[13] used biomorphic MgO fiber with hollow structure as inorganic components to make acrylate composites. The composites had high absorbency for chloroform (28.22 g/g), carbon tetrachloride (25.23 g/g), toluene (15.13 g/g), and gasoline (10.44g/g) however its reusability was less. Kizil et al. [14] investigated the absorption capacity of poly(alkoxysilane)s on oils and several other organic solvents. The organogel was synthesized by the bulk polymerization method using 1,3-benzenedimethanol and alkoxysilanes at 160^0C without adding any catalyst. The poly(alkoxysilane) was reported to absorb about 7.25 g/g of their weight in various organic solvents like dichloromethane (DCM) but its absorption capacity reduces to about 0.5 g/g in oils like gasoline and diesel. Polyurethane (PU) absorbents are also predominantly used in the field of oil absorption due to their promising qualities which include corrosion and wear resistance, microstructure, and lower density. Zhang et al. [15] synthesized an excellent oil absorbent from MnO_2 nanowires/PU foams, with PU sponge being porous was used as the substrate whereas nanowires from MnO_2 were the modifiers. The material was found to be having excellent absorbing capacity of 36.42 g/g in chloroform, 14.66 g/g in toluene, and 4.54 g/g in edible oils. Wang et al. [16] adopted a feasible method to fabricate a PU sponge reinforced with carbon nanotubes (CNTs) that shows superhydrophobic and superoleophobic properties. It was found from the study that the prepared sorbent absorbed various organic solvents and swelled up to 34.9 times its initial weight. Sykam et al. reported a simple low-cost absorbent with exfoliated graphite that can absorb organic solvents up to 40-120 g of its own weight[17]. Son T. Nguyen et al. [18] prepared a novel absorbent using cellulose fiber from waste paper. Methyltrimethoxysilane (MTMS) functionalized absorbent was then prepared to increase its hydrophobic nature. The MTMS-coated recycled aerogel from cellulose had a high contact angle of 143° and 145° in water. The aerogel had high swelling abilities of 18.4, 18.5, and 20.5 g/g for different crude oils measured at 25°C, respectively however from the second cycle of application, the absorption capacity of this absorbent reduces drastically thus indicating its poor recycle efficiency. Chatterjee et al. [19]reported a novel adsorbent from graphene oxide nanocomposite which showed an absorption capacity of more than ten times the adsorption capacity of commercial activated carbon. Zheng et al. [20] investigated the compatibility of cellulose-based polymer for oil absorption. An environment-friendly freeze-drying process was used to fabricate cross-linked hybrid aerogels from a synthetic polymer (polyvinyl alcohol) and cellulose nanofibril (CNF), which were subsequently modified with methyl trichlorosilane by thermal chemical vapor deposition method [20]. A magnetic cellulose/TiO_2 aerogel with high porosity and exhibiting good swelling properties was prepared by Chin et al. [21] where TiO_2 was used as a surface coating.

In a recent study, a sorbent was prepared by the process of grafting methacrylic acid onto polypropylene fibers with divinylbenzene used as a cross-linking agent. The sorbent evinced a good absorbing efficiency of 20.8 g/g in various organic solvents [22]. A novel sorbent from natural sponge was synthesized by Heidari et al. [23] showing excellent hydrophobicity and oil/water absorption capacity of 11.92 g/g. In another study, a magnetic poly (styrene-divinylbenzene) foam with an oil-absorbing capacity of roughly 23 times its own weight was also reported [24]. Oil absorbency for crude oil was found to be around 9 g/g in a porous copolymer made with monomers of styrene and butyl methacrylate [25]. In another novel study using polyethylene terephthalate (PET), [26] although the absorption capacity of the sorbent was found to be about 1.5-2.5 g/g, however, this study opened new avenues for the research on waste plastic as a potential oil absorbent. Magnetic sponges were fabricated from composite polydimethylsiloxane PDMS/MWNT which could absorb 6–12 g/g of its own weight [27]. In another recent study, Wang et al. [28]reported a polyacrylonitrile/reduced graphene oxide porous composite capable of absorbing oil from 42.8 to 177.2 times its own weight. Cross-linked poly(tetrahydrofuran) was found to be having promising swelling abilities in one of the studies where the polymer demonstrated an absorbing capacity of 18 g/g in dichloromethane and 10 g/g in toluene [29]. In another recent study, Prakash et al. studied the oil recovery efficiency in degummed silk fibers. The fibers showed performance efficiency of 559% in engine oil, 517% in diesel, and 389% in petrol and could be reused for 10 separation cycles with more than 50% efficiency [30]. Krishnan et al. studied the absorption capacity of 3D-poly (styrene-methyl methacrylate)/divinylbenzene-2D-nanosheet composite polymeric networks in various oils and organic solvents. The prepared absorbent could absorb 12 g/g of chloroform and about 6g/g of oils [31].

The present study delineates the grafting of Poly (ethylene-co-vinyl acetate) (EVA) by maleic anhydride (MA) and cetyl alcohol (CA) in the Brabender mixture using Benzoyl peroxide (BP) as the reaction initiator. Since the last decade, the use of EVA in the wire and cable industry [32], and the encapsulation of PV modules [33] have been widely studied. More recently modified vinyl acetate copolymers have been found to be a good pour point depressant to enhance the properties of crude oil [34] However, as far as we are aware there is no record of the use of EVA copolymers as an oil absorbent and therefore in this study, we have attempted to investigate its oil absorption capacity in detail. In the present study, the absorption capacity of the synthesized EVA sorbent was investigated in various oils and organic solvents. It was found that unmodified EVA absorbs and swells in various solvents and disintegrates. However, when we have modified it using CA and MA, due to increase in crosslinking density it absorbs oils and organic solvents and remains stable. The swelling capacity of this sorbent was also explored in oil-water mixtures to demonstrate its efficiency even in practical oil spills. The re-usability of the sorbent was studied for up to 10 cycles and hence this EVA-based sorbent could be used as a novel and promising oil absorbent for water treatment and oil spill cleanup.

2.2 Experimental

2.2.1 Materials

The chemicals used in this study include Poly (ethylene-co-vinyl acetate) (EVA) (with 18% vinyl acetate content, melt index 15.08 g/10 min, and molecular weight 142849 Da) (Max Specialty Films limited), Maleic Anhydride (MA) (Merck), Cetyl Alcohol (CA) (Loba Chemie Pvt Ltd.), and Benzoyl Peroxide (BP) (G.S Chemical Testing Lab and Allied Industries). Solvents include toluene (Merck), dimethyl Formamide (DMF) (Merck), dimethyl sulphoxide (DMSO) (Merck), and various oils like Kerosene (locally collected), Gasoline (locally collected), and Crude Oil (ONGC).

2.2.2 Methods

2.2.2.1 Absorption Studies

The absorption studies of the prepared sorbents were performed by immersing sorbents in various oils and solvents viz. toluene, gasoline, crude oil, kerosene, DMF, and DMSO. A known weight of the sample (S_i) was taken and then immersed in 60 ml of oil or organic solvent taken in a beaker. The weight of the swelled samples (S_t) in the oil or solvent was measured at an interval of 2, 4, 8, 12, and 24 hours. The absorption percentage in oil/organic solvent was determined by the equation (1)

$$S\%\ (w/w) = \frac{S_t}{S_i}\, x100 \tag{1}$$

where S_t is the weight (g) of the swelled sample at the measured time interval (t) and S_i (g) is the initial dry weight of the sample. This process was repeated for all the prepared absorbents in the various oils and organic solvents under study.

2.2.2.2 Reusability

The reusability of sorbent was also evaluated by the absorption and desorption process. The sorbent was immersed in Toluene and allowed to swell for 24 hours to reach near its maximum swelling capacity. After 24 hours, the swollen sample was subjected to thermal heating at 50^0C for 1 hour for the desorption process. The desorption was verified by a comparison between the initial weight of the absorbent and its dry weight after desorption. This process was repeated for 10 absorption-desorption cycles.

2.2.2.3 Separation of oils from oil-water mixture

For demonstrating the direct removal of oils from the mixture of oil and water, 20 ml of gasoline and 20 ml of water were mixed to form an oil-water suspension. 0.3 g of the sorbent was dropped on the oil-water mixture and the absorption capacity was monitored as a function of time.

2.2.2.4 Kinetic Study

The kinetic study was performed by plotting the absorption capacities as a function of time [29,35]. The absorbents were immersed in various oils and organic solvents and their weight was noted at regular intervals (20, 40, 60, 80……mins). The first order absorption kinetics is expressed by the equation:

$$\frac{dW_t}{dt} = K(W\infty - W_t) \qquad (2)$$

where W_t is the sample weight after absorption at time t, and $W\infty$ is the sample weight after absorption at equilibrium.

Integrating Eq. (2), we get,

$$\ln W\infty/(W\infty - W_t) = Kt. \qquad (3)$$

If the graph obtained by plotting $\ln W\infty/(W\infty - W_t)$ vs t represents a straight line we can conclude that the absorption follows first-order kinetics.

The second-order absorption kinetics is expressed by the equation:

$$\frac{dW_t}{dt} = K(W\infty - W_t)^2 \qquad (4)$$

Integrating Eq. (4), we get,

$$\frac{t}{W_t} = \frac{1}{KW\infty^2} + \frac{1}{W\infty}t \qquad (5)$$

If the graph obtained by plotting t/W_t vs t gives a straight line we can conclude that the absorption follows second-order kinetics.

2.3 Characterization Studies on synthesized absorbents

EVAM1, EVAM2, EVAM3 and EVAP samples were characterized using Fourier transform infrared spectroscopy (FTIR) instrument (PerkinElmer, Frontier MIR-FIR) with a scanning range between 400-4000 cm^{-1}. X-ray diffraction (XRD) studies was conducted with X-ray diffractometer (Bruker Axs, Germany, scanning rate-10 min^{-1}) with angle varying from 70 to 500. The study on thermal behavior of the prepared composites was performed using Thermogravimetric Analysis (TGA) instrument (TGA-50, Shimadzu, Japan). Contact angle goniometer (Kyowa, DMs401) setup was used to evaluate the wettability parameter. The morphology of the prepared absorbent was investigated using a scanning electron microscopy (SEM) (JEOL, JSM Model 6390 LV) with a 15 kV accelerating voltage. For this work, the fractured surface of the composites was set on a brass holder and platinum sputtering was conducted.

2.4 Results and Discussion

2.4.1 Synthesis of EVA-based Absorbent

40 g of EVA was mixed with 2 g of Benzoyl peroxide and different weight percentages of MA and CA (Table1) and transferred into the chamber of the Brabender Plasticizer for melt mixing and grafting. This process of blending was carried out at a temperature of 120^0C for 10 mins at 50 rpm. The resultant mixture was then shifted to the desiccator to preserve the samples from moisture.

Table 2.1: Composition of different absorbent samples and their codes

Sample	**EVA (g)**	**MA (Wt.% of EVA)**	**BP (**Wt.% of EVA)	**CA (**Wt.% of EVA)
EVAP	40	0	5	—
EVAM1	40	3	5	6
EVAM2	40	5	5	10
EVAM3	40	10	5	15

2.4.2. FTIR Spectroscopy

FTIR Spectra of crosslinked EVA are shown in fig. 2.1. The characteristic peak of EVA at 2916-2919 cm^{-1} and 2849-2852 cm^{-1} [36] are observed which represents the C-H bond deformation (symmetric and asymmetric) of methane, methylene, and methyl groups in ethylene-vinyl acetate copolymer. The typical absorption peak of the carbonyl group (C=O) of Maleic Anhydride is observed at 1735 cm^{-1} [36]. A band at 1220-1238 cm^{-1} represents the asymmetric C-O-C deformation of the acetate group, while the band at 1016-1022 cm^{-1} represents the symmetric C-O-C group of acetate. The absorption band representing 720 and 610 cm^{-1} are the typical vibration groups CH_2 and C=O [36]. The characteristic peak at 1456 -1466 cm^{-1} corresponds to the deforming CH_2 group in the main chain. The absorption peak at 1371 cm^{-1} represents the methylene groups (deformation vibration in the plane of C-H in CH3) [38]. It can be clearly visible from the IR curves that the intensities of the MA characteristic stretching peak of C=O at 1857 and 1778 cm^{-1} disappeared which confirms the ring-opening reaction of maleic anhydride with the -OH group of cetyl alcohol which is also evident from the mechanism in scheme 1.

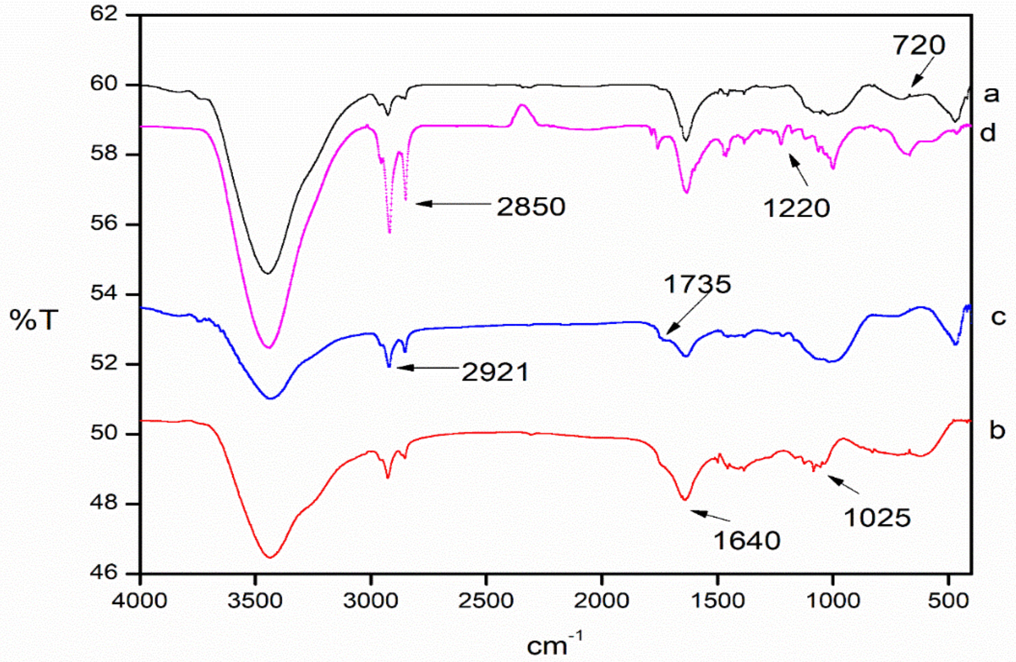
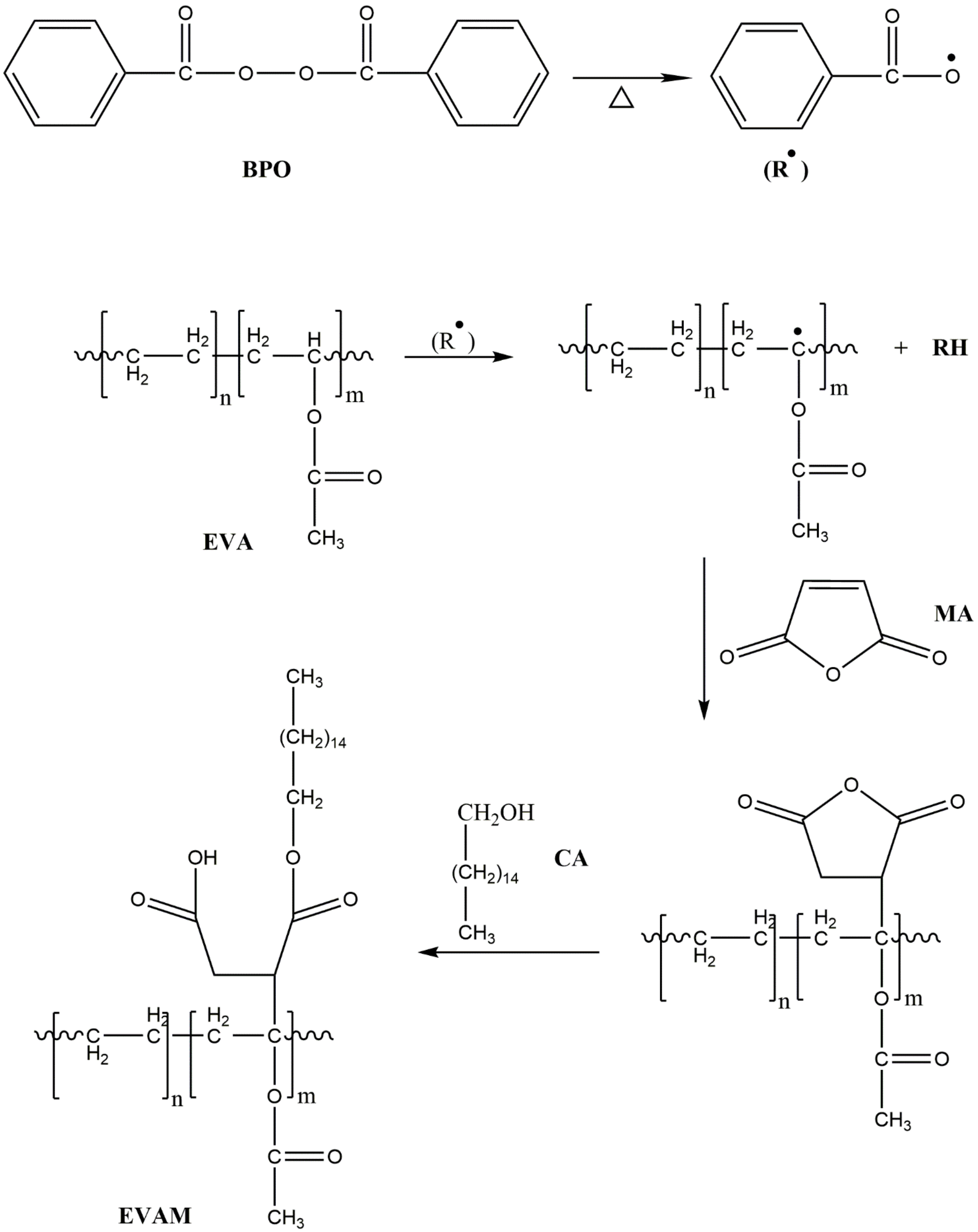


Fig. 2.1 FT-IR spectra of a) EVAM1 b) EVAM2 c) EVAM3 d) EVAP



Scheme 1: Plausible mechanism for grafting of MA and Cetyl alcohol on EVA.

2.4.3 X-Ray Diffraction

Fig (2.2) indicates the XRD pattern of EVAP, EVAM1, EVAM2, and EVAM3. XRD peaks at 21.1^0 2θ (110 plane) and 23.5^0 2θ (200 Plane) are observed in EVAM1 and EVAP which corresponds to the crystalline and amorphous regions of EVA respectively. This indicates that the crystalline behavior of EVA remains unaltered on varying the composition of the components. In addition to this, with an increase in MA and CA in EVAM2 and EVAM3, the intensity of diffraction peaks decreases as the restricted alkyl side groups have low crystallization ability onto the backbone of the synthesized copolymer.

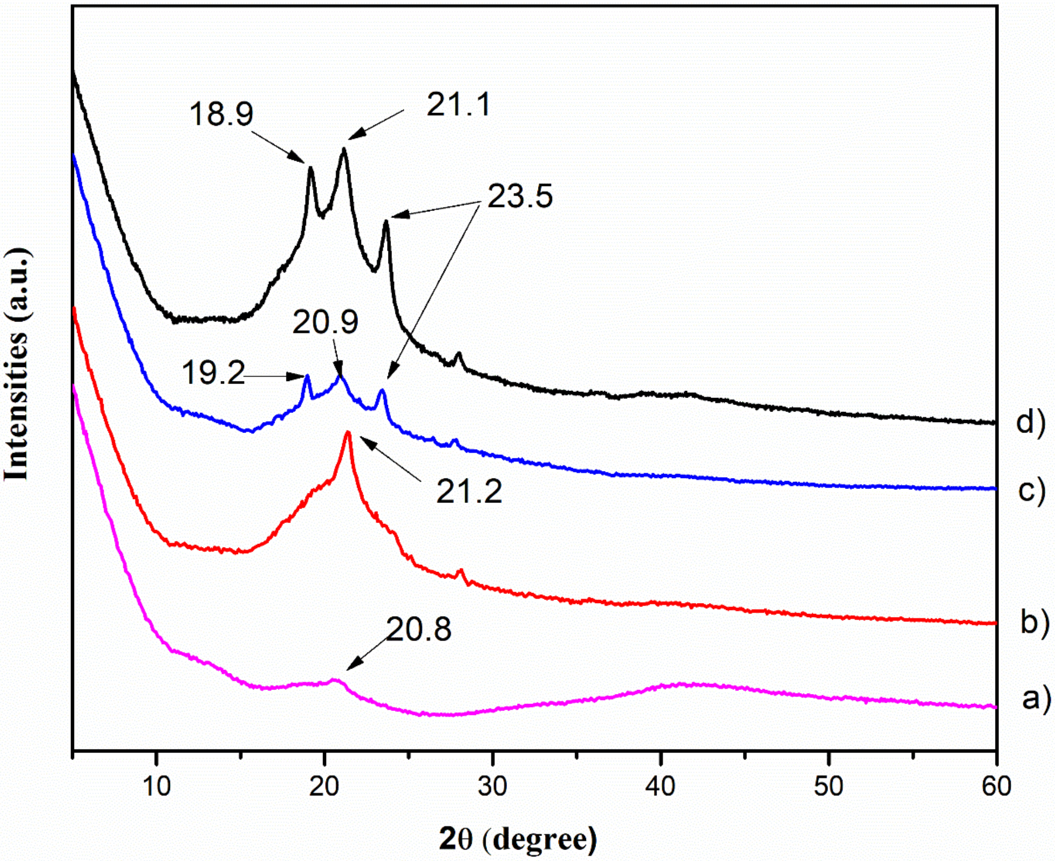


Fig. 2.2 XRD spectra of a) EVAM3 b) EVAM2 c) EVAP d) EVAM1

2.4.4 Thermogravimetry (TG)

The initial decomposition temperature (Ti), maximum decomposition temperature (T_m), decomposition temperature at different weight loss (T_D %), and residual weight (RW %) for the prepared absorbents are given in Table 2.2. TGA curves showed two-stage weight loss events. The initial weight loss occurring between 340 and 375^{0}C can be attributed to the autocatalytic deacetylation of vinyl acetate [37]. The second weight-loss event is associated with the chain scission of the polyethylene chains of EVA in the interval of 460 - 485^{0}C. The cross-linked copolymers EVAM2 and EVAM3 have a slight increase in degradation temperature because of their crosslinked network which plays a crucial role in elevating the thermal resistance of the cross-linked absorbents which is also evident in the scheme 1.

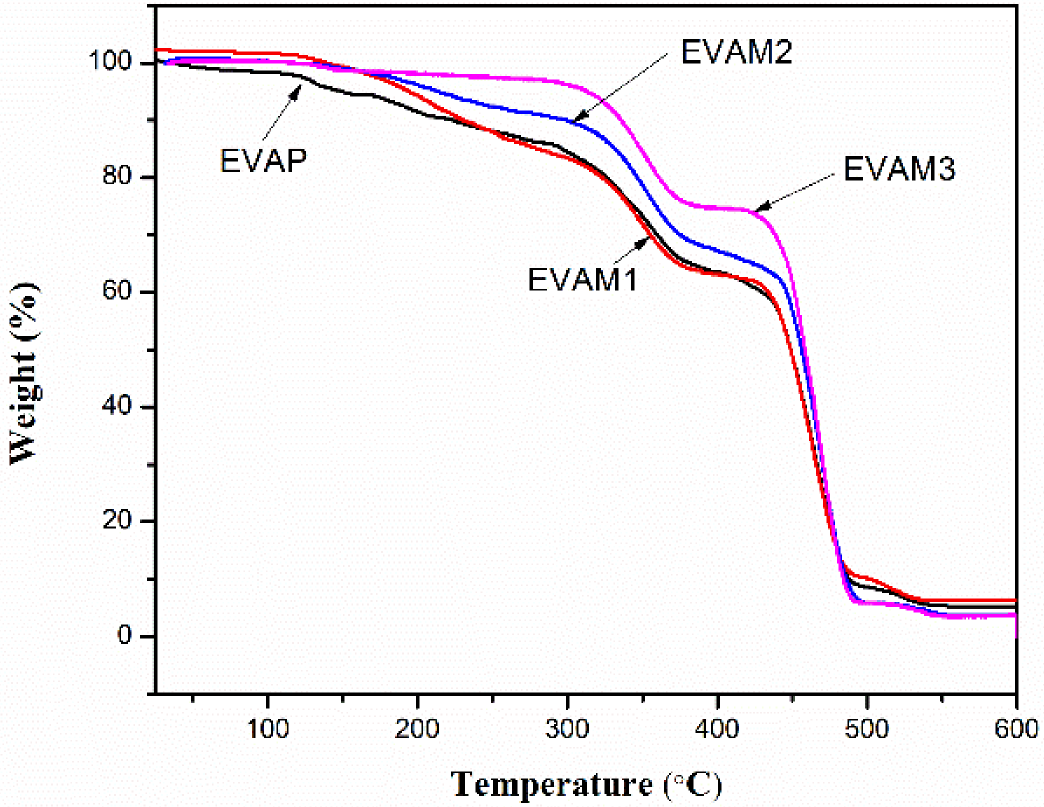


Fig. 2.3 TGA thermogram of EVAP, EVAM1, EVAM2 and EVAM3

Table 2.2: Thermal analysis of EVAM1, EVAM2, EVAM3, and EVAP.

Sample	**T_i[1]**	**T_m[2]**	**T_m[3]**	**T_D[4] (^{0}C) at different weight loss (%)**				**RW[5] % at 600^{0}C**
				20%	**40%**	**60%**	**80%**	
EVAM1	316	345	462	316	428	457	470	6.19
EVAM2	326	344	460	339	441	464	476	3.92
EVAM3	328	347	466	364	454	465	477	3.92
EVAP	312	332	458	320	427	456	470	4.88

[1] Initial decomposition temperature
[2] maximum pyrolysis 1st step

[3] maximum pyrolysis 2nd step
[4] decomposition temperature at different weight loss
[5] residual weight

2.4.5 Wettability Measurements

The wettability study in terms of contact angle is reported in Fig. 2.4. EVAM1 and EVAM2 show good hydrophobic character. EVA contains both hydrophobic ethylene groups as well as

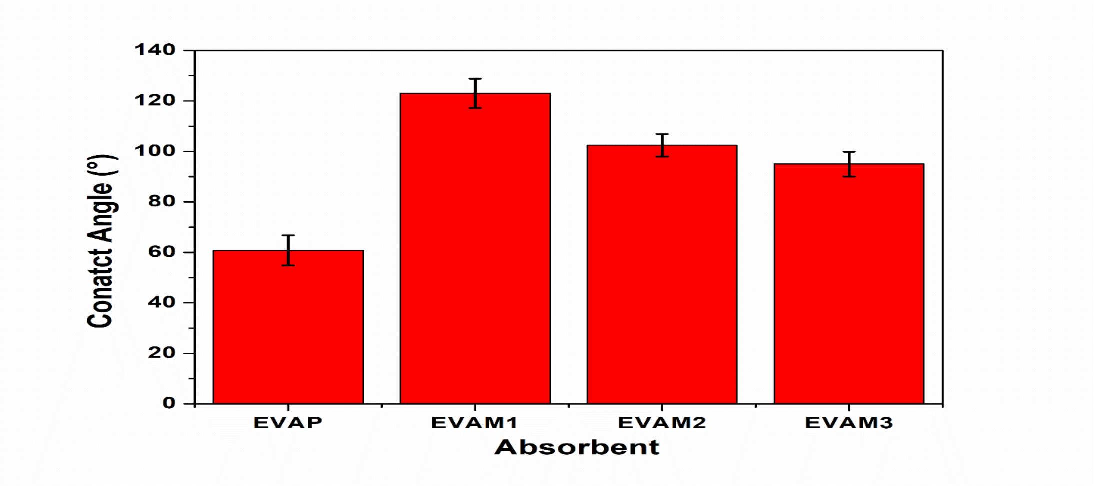
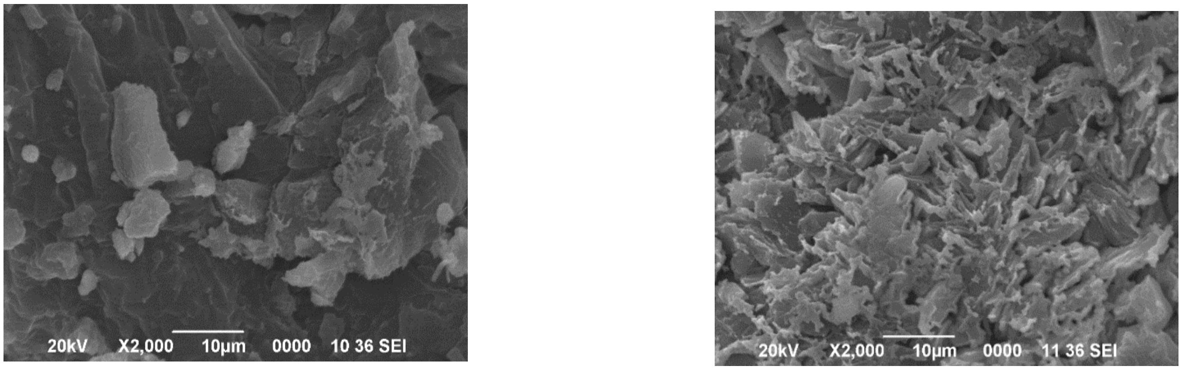


Fig. 2.4 Contact angle of EVAP, EVAM1, EVAM2 and EVAM3

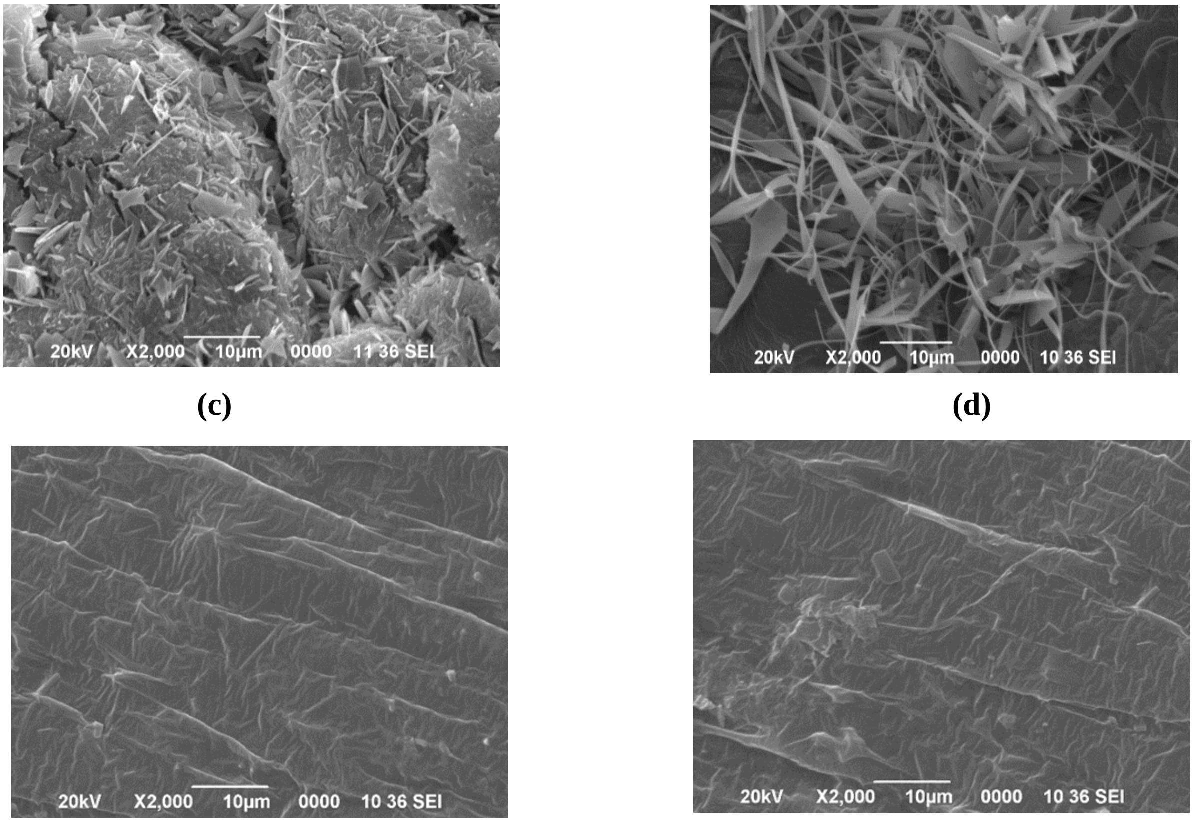
hydrophilic vinyl acetate groups. Due to the presence of hydrophobic ethylene groups, weaker adhesion interaction occurs between the ethylene groups and the water surface, and hence the hydrophobicity increases. With the incorporation of CA in the absorbents, the contact angle increases from 60.8 to 123^0 indicating an increase in hydrophobic nature. However, with a higher CA content (EVAM2 and EVAM3), contact angle decreases due to the presence of a higher amount of unreacted CA groups on the absorbent surface. Similar findings are also reported by J. Gu et al. [39]. But as the unreacted portions in EVAM2 and EVAM3 were removed using chloroform in a reflux reaction at 40^0C for 30 mins, more uniform morphology could be observed with contact angles of 125^0 and 126^0 respectively.

2.4.6 Scanning Election microscopy (SEM) Study

SEM micrographs of the synthesized sorbents with varying percentages of MA and CA are given in Fig 2.5. The micrographs of EVAP depict a rough surface with lumps which signify poor interactions among the various components. A better interaction could be observed in the morphology of EVAM1(fig. 4 b) along with pore spaces. The micrographs of EVAM2 and EVAM3 (fig. 5 c and fig. 5 d) depict a rough surface with needle-like structures which may be attributed to the unreacted portions as the MA% content and CA% content increase. These unreacted portions were removed using chloroform in a reflux reaction at 40^0C for 30 mins. The SEM images thus obtained show a more uniform morphology (fig. 2.5 e and 2.5 f) with no significant pore spaces as compared to EVAM1. This is mainly due to the increase in crosslinking density with the increase in MA and CA content. This results in a decrease in absorption capacity in EVAM2 and EVAM3 as evident from the absorption study.



(a) (b)



(c) (d)

(e) (f)

Fig. 2.5 SEM micrographs of (a) EVAP (b) EVAM1 (c) EVAM2 before reflux (d) EVAM3 before reflux (e) EVAM2 after reflux (f) EVAM3 after reflux

2.4.7 Oil absorption capacity

The equilibrium or maximum swelling capacity reaches within 24 hours for all these sorbents. The maximum absorption capacity of these sorbents in various oils and organic solvents is shown in fig. 2.6. The sorbents show excellent absorption characteristics in oils and organic solvents. Scheme 1 lucidly explains the mechanism of the grafting reaction. All the sorbents have high swelling capacity in toluene at room temperature. This is mainly due to the small molecule which can readily penetrate into the pores present in the polymer. On the other hand, the long-chain oils like gasoline, crude oil, and kerosene also showed good absorption into the polymer network due to the hydrophobic nature of the polymeric network. But absorption is low compared to toluene as longer molecular chains containing molecules are mostly adsorbed on the surface of the polymer and therefore blocked the adsorption of other molecules. On the other hand, since the prepared polymer consists of a long aliphatic chain (mainly from cetyl alcohol) as evident from the scheme 1, they are mainly non-polar in nature, and hence polar nature molecules like DMF, and DMSO exhibit lower absorption on the polymer (Scheme 1). Dutta et al. [35] in their work also found similar results where the prepared sorbent showed excellent absorption in non-polar organic solvents like chloroform (690-750%) and poor absorption in case of polar solvents. The acrylic ester resin composites prepared by Yan et al. [13] had also demonstrated high absorbency for chloroform (28.22 g/g), carbon tetrachloride (25.23 g/g), toluene (15.13 g/g), and gasoline (10.44g/g) and poor absorbency in polar solvents. The content of MA and CA in the prepared polymer has a potential effect on the absorption of both the organic solvents and crude oil. From Fig. 5, it is found that maximum absorption is achieved for EVAM1 as compared to EVAM2, EVAM3 and EVAP. EVAM1 showed the highest absorption percentage in toluene (2200%). Similar cross-linked poly(tetrahydrofuran) sorbents [29] also showed an absorption capacity of 18g/g in dichloromethane and 10 g/g in toluene. Cross-linked 3D-poly (styrene-methyl methacrylate)/divinylbenzene-2D-nanosheet composite polymeric networks has also reported to absorb 12 g/g of chloroform and about 6g/g of oils [31] Although, the only EVA-based polymer (EVAP) also gives good absorption but due to the lower crosslinking density of the polymer it is unstable in organic solvents and some small weight loss of the polymer is observed in the given solvent. In the case of absorbents with higher weight % of MA and CA (EVAM2 and EVAM3), the prepared polymer displays higher cross-linked polymer networks resulting in a decrease in the effective pore volume of the polymer and thus giving lower absorption capacities (evident from SEM image). From the SEM image, it is also observed that the concentration of MA and CA in EVAM1 results in an expandable polymer network which is appropriate for better absorption of organic solvents and oils and therefore it has shown the best absorption performance in contrast to those which are prepared with higher amounts of CA and MA (EVAM2 and EVAM3).

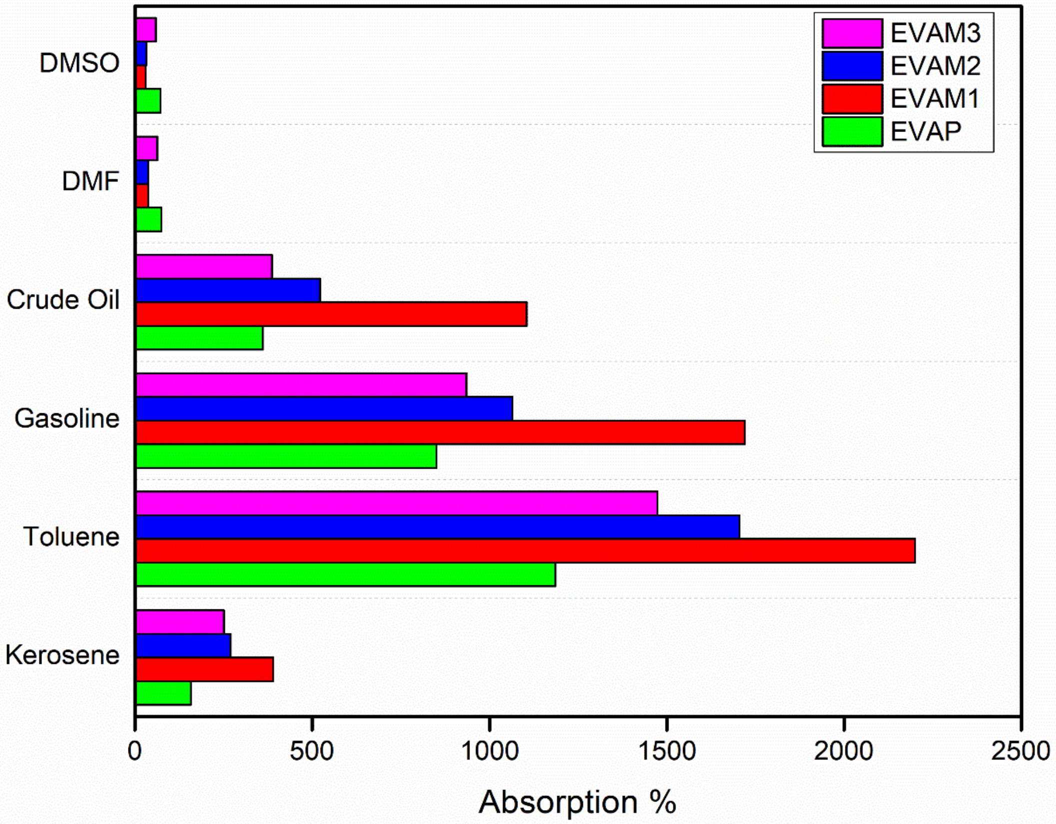


Fig. 2.6 Absorption capacities of the synthesized EVA based absorbents

2.4.8 Reusability of the synthesized absorbents

The retention time for the various swollen sorbents was examined in toluene by evaluating the weight loss at 50^{0}C. The sorbents recovered their original dry weight within 1 hour after releasing the absorbed solvent from its matrix (fig 2.7). The sorbent was again immersed in toluene to study its absorbing efficiency. This absorption-desorption process was continued for 10 cycles. The absorption capacity of the sorbents remained almost unaltered even after 10 cycles (fig. 2.8). Thus, the sorbent can be regenerated and reused after eliminating oils and organic solvents from the environment. Zhang et al. [15] also observed that their foam composite had excellent reusability characteristics of more than 5 absorption-desorption cycles. Son T. Nguyen et al. [18] observed that the absorbent prepared from cellulose showed a high absorption capacity of 18.4 g/g in cycle 1. However, the absorption efficiency reduced to 0.96, 0.68, 0.59, and 0.63 g/g in cycles 2, 3, 4, and 5 respectively. Some other absorbents with carbon nanotubes (CNT) [16]showed excellent reusability and can be applied for 150 cycles while maintaining similar absorption capacity.

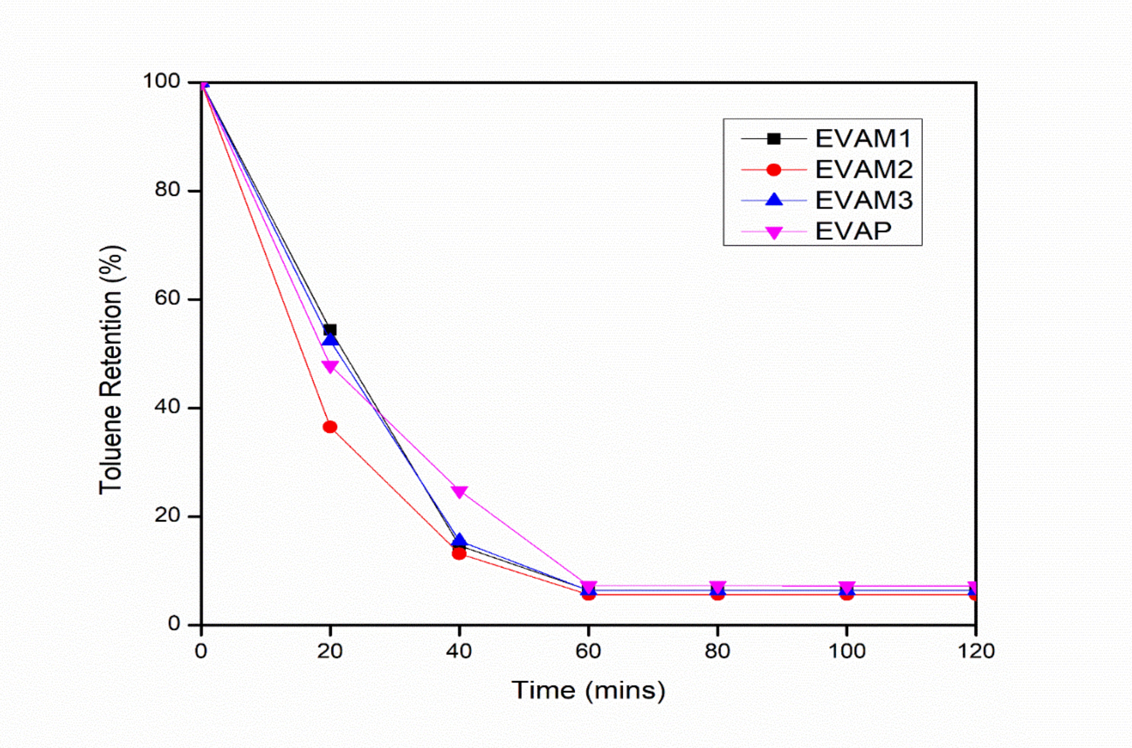


Fig. 2.7 Toluene retention of the synthesized absorbents

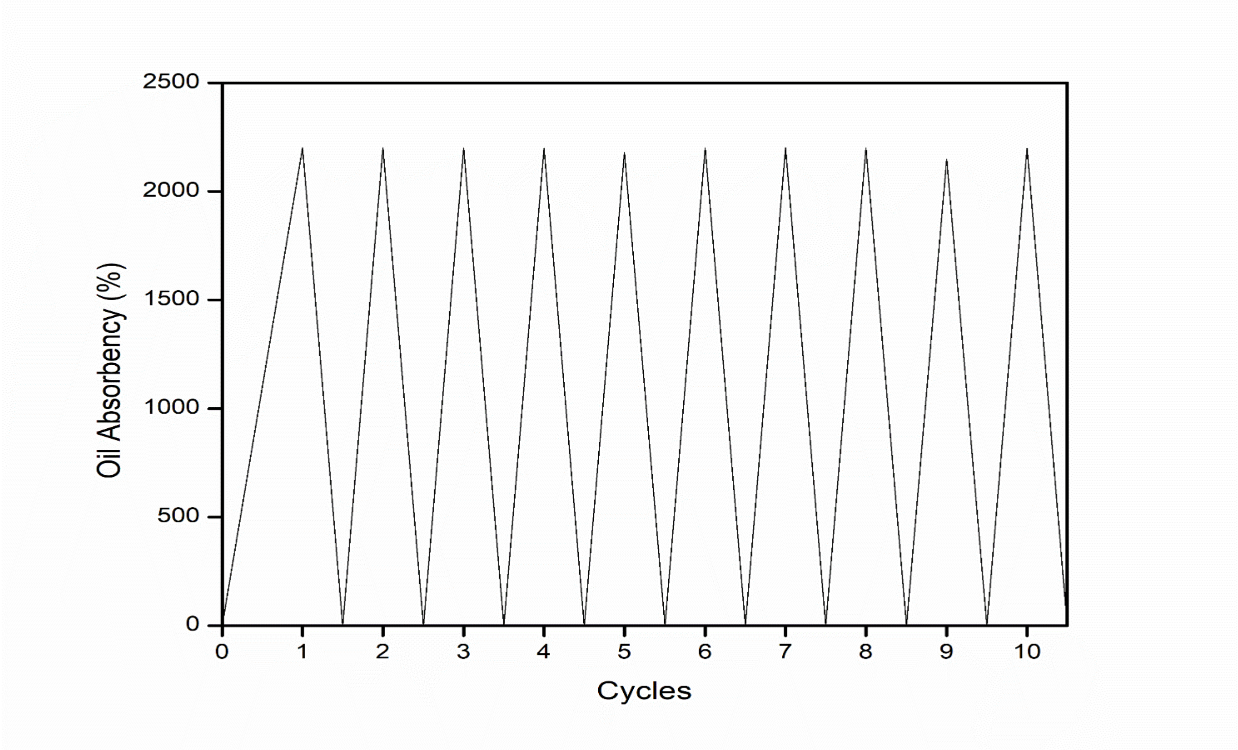
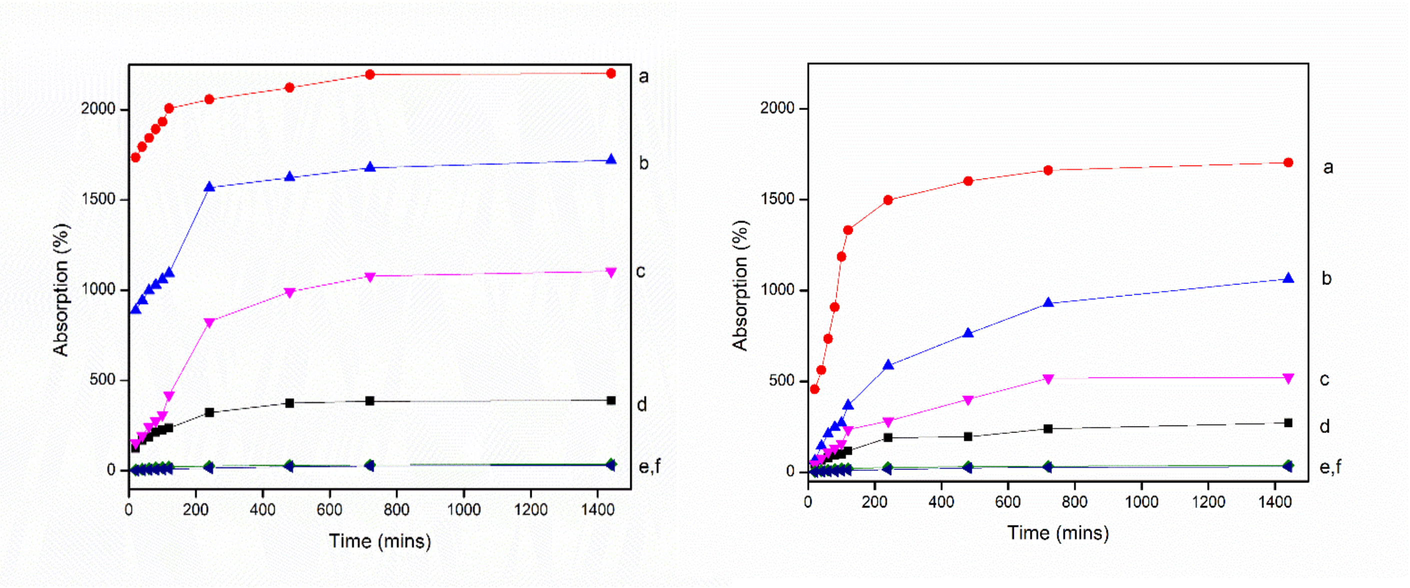


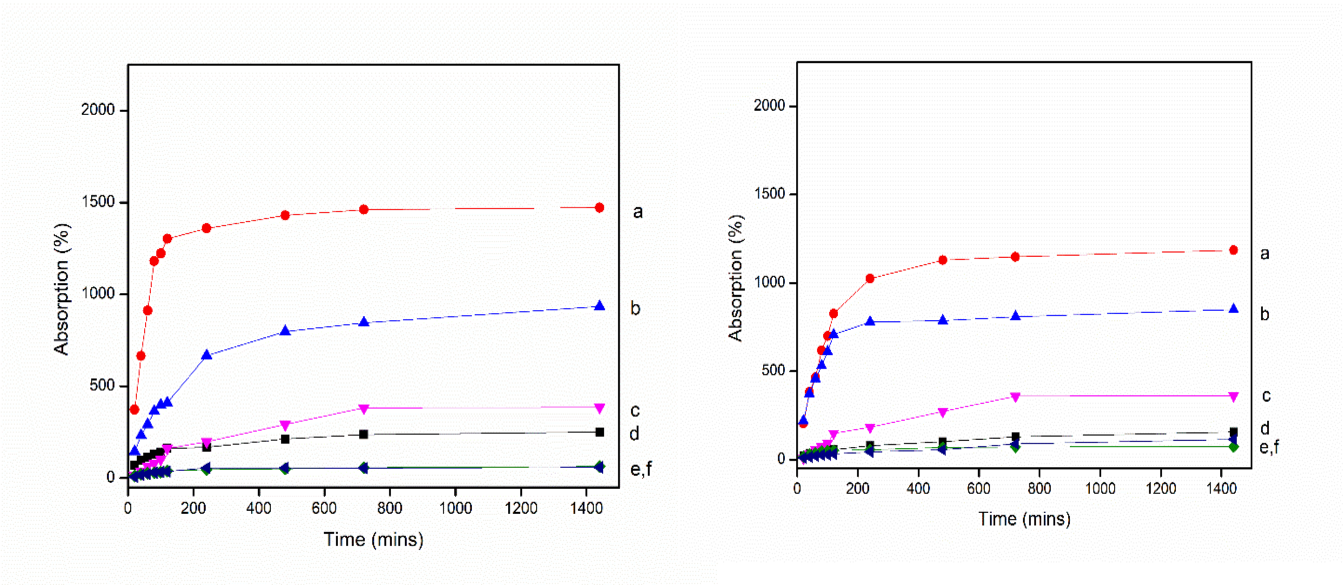
Fig. 2.8 Reusability of the synthesized absorbent for various absorption-desorption cycles

2.4.9 Swelling Kinetics

For practical applications, the swelling rate of the absorbent is another important parameter in addition to higher swelling capacity. To obtain the kinetic curves the absorption percentage



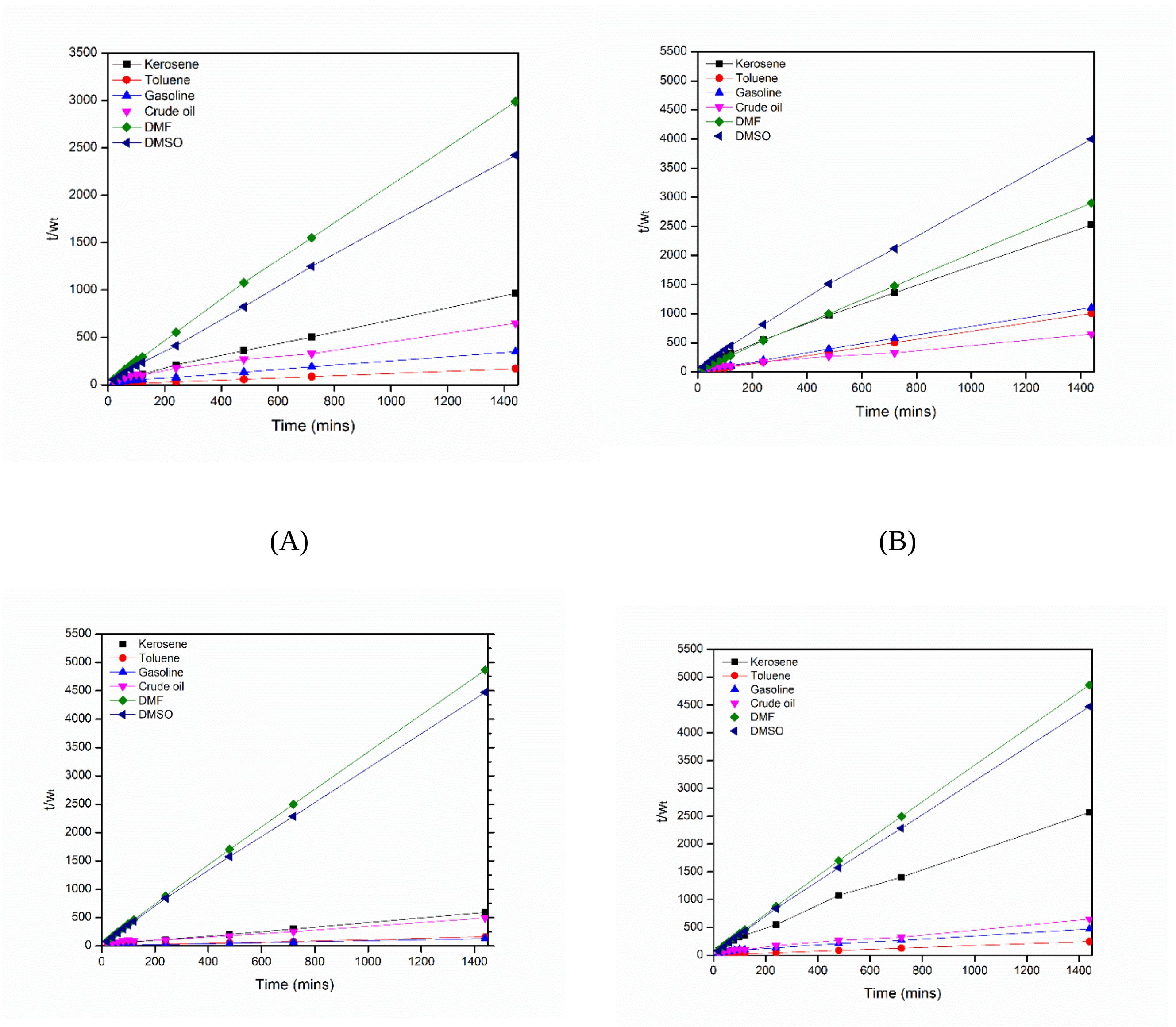
(A) (B)



(C) (D)

Fig. 2.9 Absorption kinetics in a) Toluene b) Gasoline c) Crude oil d) Kerosene e) DMF f) DMSO for (A) EVAM1 (B) EVAM2 (C) EVAM3 (D) EVAP

was plotted as a function of time for oils and various organic solvents. The absorption initially increased at a rapid rate until it reached equilibrium in about 12 hours. The swelling kinetics for EVAM1, EVAM2, EVAM3, and EVAP resemble each other. The rate constant of the absorption process was determined by plots of ln $W_\infty/(W_\infty - W_t)$ vs t (from equation 3) and t/W_t vs t (from equation 5). It was observed that the experimental kinetic data gave linearized curves as per the pseudo-second-order rate equations (fig. 2.9) with correlation coefficients R^2 of 0.99. The pseudo- second-order parameters for all the absorbents with different oils and solvents are summarized in Table 2.3.



(A)

(B)

(C)

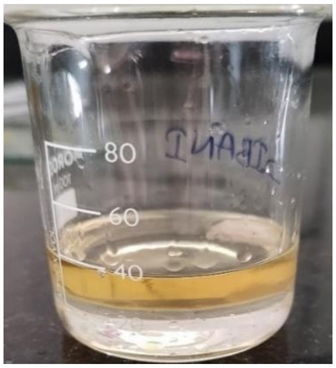
(D)

Fig. 2.10 Pseudo-second order absorption kinetics for (A) EVAM1 (B) EVAM2 (C) EVAM3 (D) EVAP

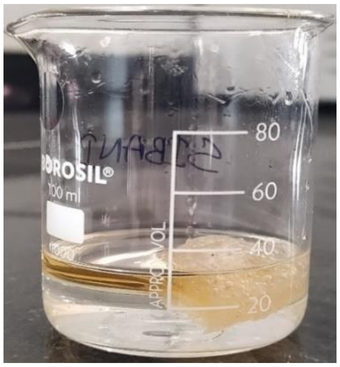
Table 2.3 Pseudo-second-order parameters for EVAP, EVAM1, EVAM2 and EVAM3

Oil/Organic solvent	Rate constant ($K_{2)}$				Correlation coefficients (R^2)			
	EVAP	EVAM1	EVAM2	EVAM3	EVAP	EVAM1	EVAM2	EVAM3
Toluene	3.15x10^{-4}	9.82 x10^{-4}	1.4x10^{-4}	14.1 x10^{-4}	0.99166	0.99876	0.99955	0.99939
Gasoline	29.6 x10^{-4}	34.7 x10^{-4}	2x10^{-4}	3.92 x10^{-4}	0.99924	0.99988	0.997	0.99805
Crude Oil	11 x10^{-4}	2.67 x10^{-4}	3.2x10^{-4}	3.15 x10^{-4}	0.99959	0.99074	0.99628	0.99166
Kerosene	8.23 x10^{-4}	9.74 x10^{-4}	5.5x10^{-4}	9.16 x10^{-4}	0.99714	0.99926	0.99764	0.99825
DMF	23.7 x10^{-4}	22.7 x10^{-4}	22.7x10^{-4}	25.5 x10^{-4}	0.99984	0.99958	0.99981	0.99977
DMSO	11.3 x10^{-4}	26.8 x10^{-4}	26.8x10^{-4}	18.7 x10^{-4}	0.99805	0.99975	0.99989	0.99937

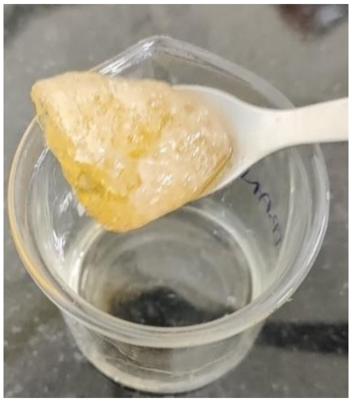
2.4.10 Separation of Oil-Water mixture



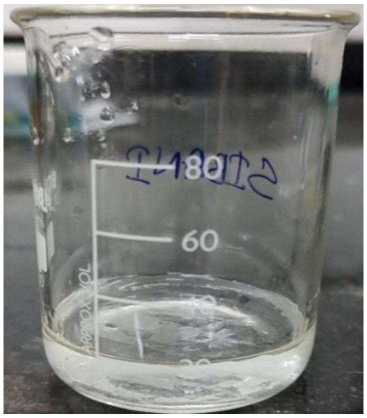
(A)



(B)



(C)



(D)

Fig. 2.11 Gasoline absorption from water surface by EVAM1; (A) EVAM1 sample immersed in the oil-water mixture (B) Gasoline absorption by EVAM1 sample after 15 mins (C) EVAM1 sample after absorption of gasoline (D) Separated water from the oil-water mixture.

The rate at which absorption of oils occurs from the water surface and stability in water is another significant parameter that determines the efficiency of sorbents in a real-time oil spill environment. The study on the separation of oil from the oil-water mixture by the synthesized absorbent is represented in Fig. 2.11. The pictures depict the absorption of gasoline from the surface of the oil-water mixture with the use of EVAM1 absorbent which showed the best absorption in this study. The sorbent absorbed most of the gasoline within 30 mins leaving behind water in the beaker. This study demonstrates its effectiveness in practical oil spills and its stable oil absorption efficiency even in the presence of water.

2.5 Conclusion

In this study, elastic and hydrophobic reusable crosslinked Poly (ethylene-co-vinyl acetate) (EVA) copolymer modified with cetyl alcohol-based sorbent has been successfully prepared. The modified EVA sorbents are excellent absorbents of oil and organic solvents. Maximum efficiency was found in toluene with an absorption capacity of 22g per 1 gm of the sorbent. High absorption capacity was also seen in various oils and organic solvents. The absorbent shows good hydrophobic nature with contact angle of 123^0. The reusability of the absorbent was studied and it was found that the absorbent could be recycled for more than 10 absorption desorption cycles. Since EVA is an important widely used commercial synthetic material, the synthesis of high swelling capacity and reusable absorbent proposes its application in a new field of oil absorption. In addition to its high absorption capacity, its reusable nature makes it a potential candidate for use in various practical industrial fields such as water treatment and environmental cleanups.

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CHAPTER 3

DEVELOPMENT OF POROUS CROSSLINKED ABSORBENTS AND STUDIES ON THEIR OIL REMOVAL EFFICIENCY

3.1 Introduction

Poly (ethylene-co-vinyl acetate) or EVA is a thermoplastic copolymer of ethylene and vinyl acetate. Depending on the ethylene and vinyl acetate (VA) content this polymer exhibits different properties like melting point, crystallinity, stiffness and polarity. A wide number of literatures is available on the use of EVA as a drug delivery substance. These include drug delivery in cervical cancer, oral delivery of antifungal and anti-microbial [1], controlled release of dopamine [2], delivery of levodopa for a continuous extended period [3] among various other chemicals used in pharmaceutical Science. The most common industrial processing technique which is used for the synthesis of various EVA-based products is the hot-melt extrusion process which is a combination of melting, blending, and shaping and also a solvent free process that is compatible with various polymeric applications [4,5].

EVA has been widely used as an encapsulating material because of its superior properties like high transmission value, good toughness at low temperature, UV resistance, and high-volume resistivity [6]. Klampaftis et al. [7] have reported that luminescent material added to the EVA layer as encapsulating material resulted in improving the efficiency of silicon solar cell. Yuwaween et al. [8] modified EVA encapsulating film using esterified bacterial cellulose nanofibers and observed the increase of mechanical, as well as barrier properties of EVA encapsulating film. Even various studies have also been conducted to investigate the causes and effects of EVA encapsulation degrading behavior in U.V radiations [9]

EVA has also been used to develop microcellular foams blended with polybutadiene rubber (BR) for footwear applications having higher tensile strength, wear and tear properties with low hardness [10]. Bahattab et al. [11]have also reported the synthesis of crosslinked EVA/LDPE/metal hydroxide composites for wire and cable application because of higher mechanical and other physical properties with easier processing. Bidsorkhi et al. [12]prepared EVA nanocomposites where halloysite nanotubes (HNT) are dispersed in the EVA matrix and found that as the HNT concentration increases the tensile strength of the EVA nanocomposites also gets increased.

Here in this work, the present author has investigated the potential of EVA composites in environmental applications like water treatment and oil spill removal and studied its absorbing capacity in various oils and organic solvents in detail. In my previous studies, it has been noticed considerable oil/organic solvent absorption efficiency of EVA [13].

Removal of oil and organic solvents from wastewater has gained immense attention in the recent times owing to its non-biodegradable properties and detrimental effect on human health, as well as aquatic flora and fauna [14]. The source of this wastewater is basically from hydrocarbon drilling, textile, paper, and pulp industries, etc. where water is produced as an effluent. Although three approaches namely physical, chemical and biological have been widely used in the removal of these contaminants from wastewater, owing to certain technical as well as economic drawbacks these approaches have become stagnant, and the use of polymeric composites as oil absorbents has gained wide popularity during recent times. Some of the most promising polymeric composites which are being widely used all over the world as oil absorbents are based on polyurethane [15], Poly (alkoxysilane)s [16], polypropylene [17], polymethacrylate [18], and polystyrene (Lin et al., 2012).

In this work, the present author has attempted to increase the porosity of C-EVA by adding sodium chloride (NaCl) into the polymer network as porogen and followed by leaching out of NaCl from the polymer matrix by water extraction. This will influence the porosity of polymer matrix. Although the use of NaCl as porogens to increase the porosity of scaffolds in tissue engineering has been widely studied but to the best of our knowledge, there is no report on studies relating to the use of NaCl porogens in oil absorbing polymers to increase its oil-absorbing efficiencies in various oils and organic solvents. Tran et al. [20] developed an effective facile method to improve the control on the NaCl size distribution (13.78±1.18 µm) from the traditional method having size (13.89±12:49 µm) and fabricated scaffolds with improved interconnectivity and microchannels. Kang et al. [21]studied the effect of NaCl particles in AZ91 alloy foams and found that the addition of NaCl resulted in an increase in pore structure providing excellent compressive strength to A91 foams. Yu et al. [22]studied the effect of variant pore sizes and porosity created by the different particle sizes of NaCl porogens on the mechanical properties and microstructure of poly-Ɛ-Caprolactone-hydroxyapatite composites and concluded that the use of varied particle size of porogens in HA-PCL scaffolds results in altered porous features and mechanical properties. Xia et al. [23]had studied the effect of NaCl porogens on the pore structure of silk fibroin (SF)/Hydroapatite (HA) composites and results from this study indicated that the increase in NaCl content, particle size distribution, and particle size of NaCl porogens have significant improvement in pore connectivity and mechanical properties of the synthesized composite.

3.2 Materials and Methods

Poly (ethylene-co-vinyl acetate) (18% vinyl acetate content, melt index 15.08 g/10 min, and molecular weight 142849 Da) used in this work was supplied by Max Specialty Films Limited. For cross-linking of poly (ethylene-co-Vinyl acetate), benzoyl peroxide (BP) obtained from G.S chemical testing lab and allied industries, Maleic Anhydride (MA) obtained from Merck and Cetyl alcohol (CA) supplied by Loba Chemie Pvt Ltd was used. Sodium chloride (NaCl) 99% pure was obtained from Merck. Various solvents (toluene, dichloromethane, chloroform, dimethyl formamide, dimethyl sulphoxide) used in the absorption study were supplied by Merck. Kerosene and Gasoline were locally collected whereas crude oil was collected from GGS, ONGC.

3.2.1 Preparation of crosslinked EVA polymers

40 g of EVA, 1.2 g of MA, 2 g of BP, 2.4 g of CA and different content of NaCl (2.5-3 µm) (5, 10, 15%) were measured in an electronic balance. Sodium chloride (99% pure) was finely grounded in a mortar and pestle. Four different samples (EVAM, EVAMN5, EVAMN10, and EVAMN15) were then prepared using 0, 5, 10, and 15 % NaCl respectively by melt mixing in a Brabender plastic order. This blending process was carried out at 50 rpm for 10 mins at a temperature of 120^0C. The prepared samples were then cured for 24 hours at 100^0C in a hot air oven. Finally, the samples were stored in a desiccator to protect them from moisture.

3.2.2 Leaching of NaCl from the prepared polymer

The process of leaching NaCl from the polymers was carried out at a temperature of 50^0C. About 80 ml of distilled water was taken in a beaker and the samples were then stirred in the beaker using a magnetic stirrer at 250 rpm for 4 hours. The samples were then dried in a hot air oven at a temperature of 70^0C for about an hour to eliminate all the moisture from their surface and again transferred to the desiccator until further experimental procedures.

3.2.3 Porosity measurement

To measure the porosity of the leached polymer samples, the liquid displacement technique was used. In this process a known volume of water (V_1) was taken in a measuring cylinder and the sample was immersed in water for 24 hours. The volume rise of water was observed and the total volume of the water along with the sample in the cylinder was measured (V_2). The volume of the liquid in the cylinder after withdrawing the sample from the cylinder was taken as V_3. Three test results were obtained for each sample and average porosity was evaluated from them. The porosity of the samples can be evaluated from the equation,

$$\text{Porosity} = \frac{V1 - V3}{V2 - V3} \text{x}100\ \%$$

3.2.4 Absorption studies in oils/organic solvents

ASTMF726-99-Standard Test Method was used to study the absorption behavior of the polymer samples. In this method the prepared polymeric samples were immersed in various organic solvents viz. toluene, dichloromethane (DCM), chloroform, dimethyl formamide (DMF), dimethylsulphoxide (DMSO) and oils like kerosene, gasoline and crude oil taken in different beakers. The dry weight of the samples (W_i) was measured prior to immersing the samples in the beakers. After an interval of 2 hours, the swelled samples were taken out from the beaker, held undisturbed for 10 secs to drain off any liquid which had adhered on its surface and then weighed (W_t) in a precision electronic balance. This process was repeated after 4, 8, 12 and 24 hours. The absorption capacity of the samples was measured using equation (1)

$$\text{Oil absorption (g/g)} = \frac{Wt - Wi}{Wi} \qquad (1)$$

Where W_t is the weight in grams of the immersed samples at a measured time interval (t).

3.2.5 Study on Recyclability

Recyclability of the polymer was tested by the absorption-desorption process. The sample with the best absorption performance from the previous absorption study was evaluated for its recyclability. EVA polymer was immersed in Toluene and the weight of the swelled sample was taken after 24 hours as it reaches its maximum absorption. The sample was then heated at 50^0C for 1 hour to allow the absorbed toluene to escape the polymer lattice. This absorption-desorption process was repeated more than 30 times.

3.2.6 Kinetic Study

For the kinetic study, the absorption capacities of the polymer samples were plotted as a function of time [24,25]. The samples were immersed in different oils and organic solvents and allowed to swell. The swelled samples were then weighed (W_t) at regular intervals ie. 20, 40, 60, 80,……mins. Equation (2) represents the first order absorption kinetics:

$$\frac{dW_t}{dt} = K(W\infty - W_t) \quad (2)$$

where W_t is the weight of the sample after absorption at time t, and $W\infty$ is the weight of the sample after absorption reaches equilibrium.

Integrating Eq. (2), we get,

$$\ln W\infty / (W\infty - W_t) = Kt. \quad (3)$$

If the graph obtained by plotting ln $W\infty/(W\infty - W_t)$ vs t represents a straight line the absorption follows first-order kinetics.

Equation (4) represents the second order absorption kinetics:

$$\frac{dW_t}{dt} = K(W\infty - W_t)^2 \quad (4)$$

Integrating Eq. (4), we get,

$$\frac{t}{W_t} = \frac{1}{KW\infty^2} + \frac{1}{W\infty}t \quad (5)$$

If the graph obtained by plotting t/W_t vs t is a straight line, the absorption follows second-order kinetics.

3.2.6 Characterization

Fourier transform infrared spectroscopy (FTIR) instrument (PerkinElmer, Frontier MIR-FIR) with a scanning range of 400-4000 cm^{-1} was used for the IR study of EVAM, EVAMN5, EVAMN10, and EVAMN15 samples. X-ray diffractometer (Bruker Axs, Germany, scanning rate-10 min^{-1}) with angle varying from 70 to 500 was used to investigate the X-ray diffraction (XRD) pattern of the polymer samples. Thermogravimetric Analysis (TGA) instrument (TGA-50, Shimadzu, Japan) was used to conduct the thermal study of the prepared polymers. The hydrophobicity of the samples was determined in a Contact angle goniometer (Kyowa, DMs401) setup. A scanning electron microscope (SEM) (JEOL, JSM Model 6390 LV) elucidated the surface morphology of the porous polymer framework. The hardness of the prepared polymers was measured using ASTMD-2240 by means of a durameter of RR12 model measured in units of shore D hardness. The pore size was evaluated from the SEM micrographs using g ImageJ

(NIH) software. The results obtained are expressed as the average of three trials with standard deviation.

3.3. Results and Discussion

3.3.1 FTIR study

From the FTIR study (Fig. 3.1) it is clearly visible that the stretched deformation of C-H bond in CH_3 and CH_2 appears clearly at a wavelength of 2917cm^{-1} and 2850 cm^{-1} [26]. The absorption peak at 1642 cm^{-1} represents the C=C characteristic peak. A typical absorption peak of methylene group due to CH_3 deformation is observed at 1377 cm^{-1} [27]. A band at 1023 cm^{-1} represents the C-O-C symmetric group of acetate [26]. The presence of vinyl acetate is also confirmed by the presence of characteristic band of C-H at 950 cm^{-1} [27]. The characteristic C=O bands of MA at 1857 and 1778 cm^{-1} disappeared in the FTIR curves due to the ring-opening reaction of maleic anhydride with the -OH group of cetyl alcohol which clearly confirms the formation of the polymer.

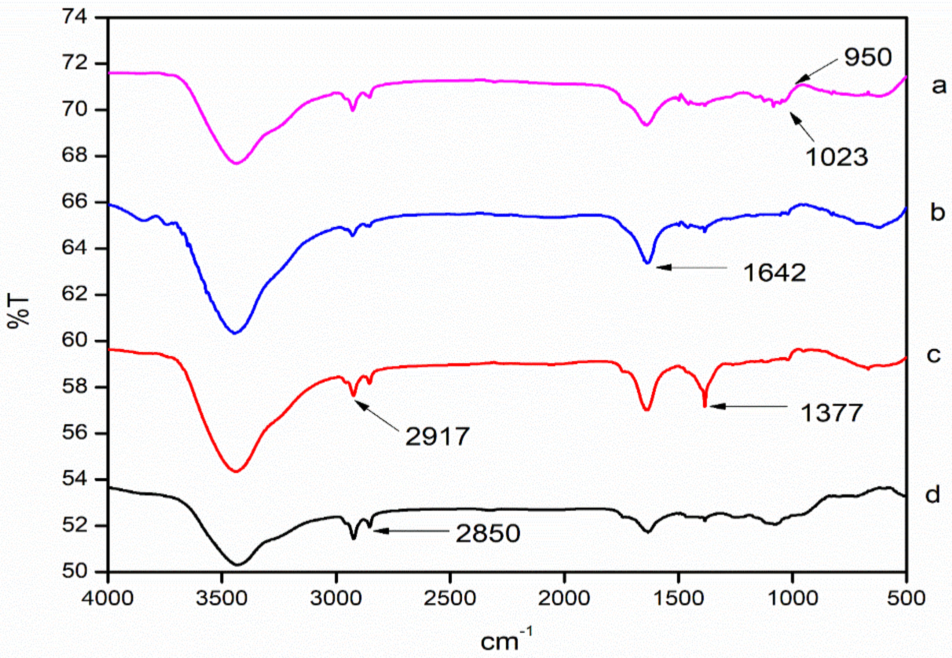


Fig. 3.1 (A): FT-IR spectra of a) EVAM b) EVAMN5 c) EVAMN10 d) EVAMN15

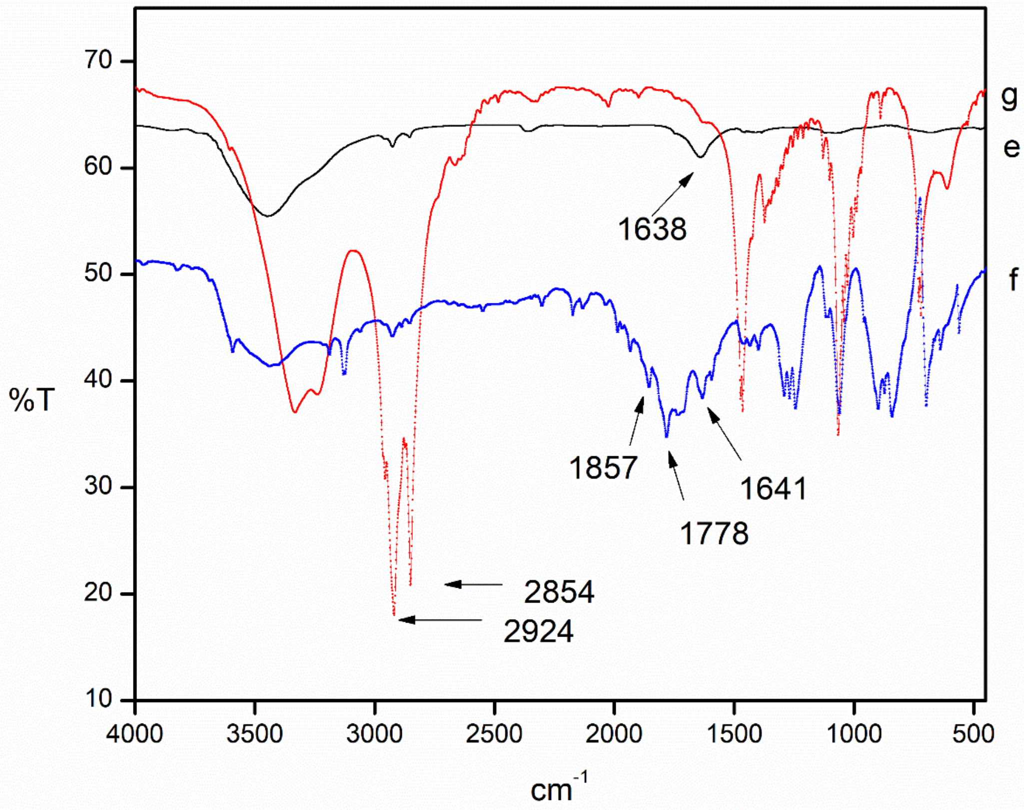
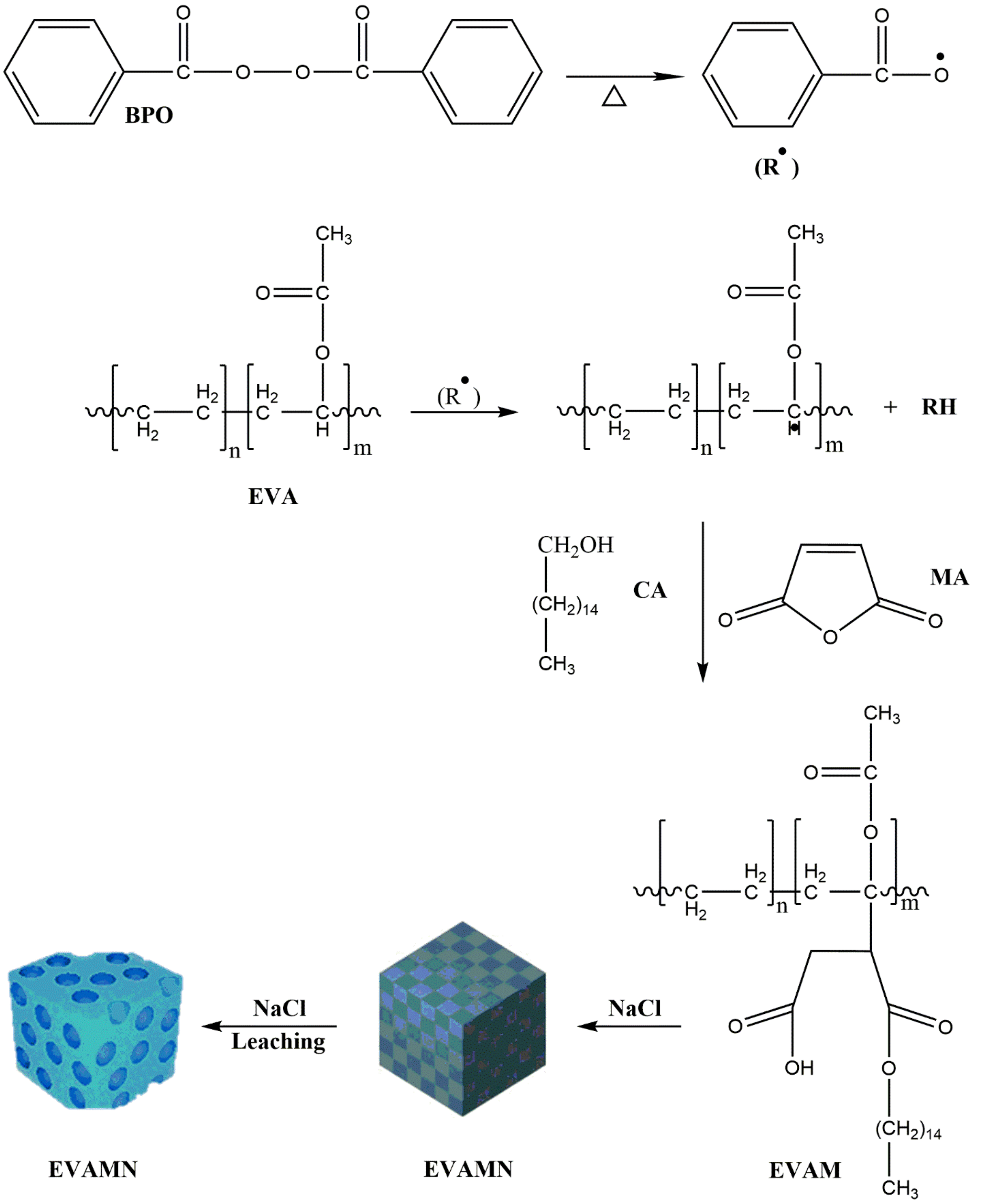


Fig. 3.1 (B) FT-IR spectra of e) EVA f) Maleic anhydride (MA) g) Cetyl alcohol (CA)



Scheme 2. Plausible mechanism for grafting of MA and CA on EVA and pore formation after NaCl leaching

3.3.2 X-Ray diffraction

The XRD pattern of EVAM, EVAMN5, EVAMN10, and EVAN15 are depicted in the Fig. 3.2. XRD peaks at 21.06^0 2θ (110 plane) and 23.56^0 2θ (200 plane) are visible for EVAM which corresponds to the crystalline and amorphous regions of EVA respectively. This indicates that the crystalline behavior of EVA remains unaltered during the crosslinking process. However, with an increase in NaCl porogens, the diffraction peaks gradually disappear. This is mainly due to the occurrence of pores after the leaching out of NaCl.

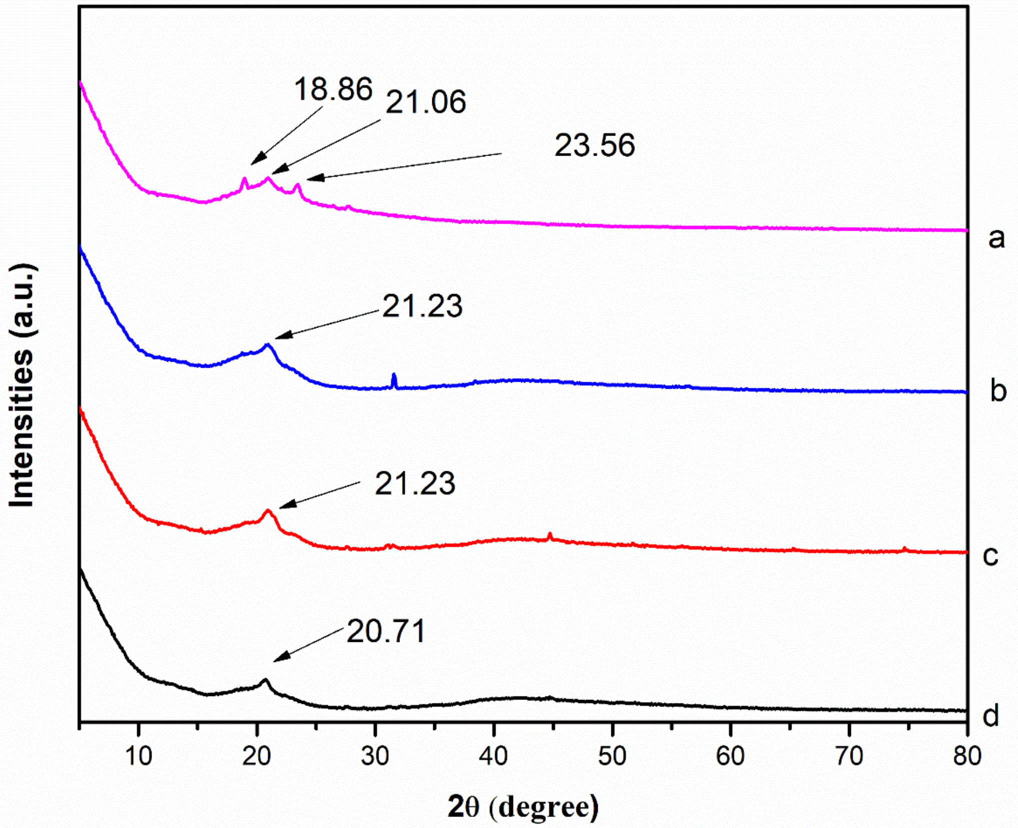
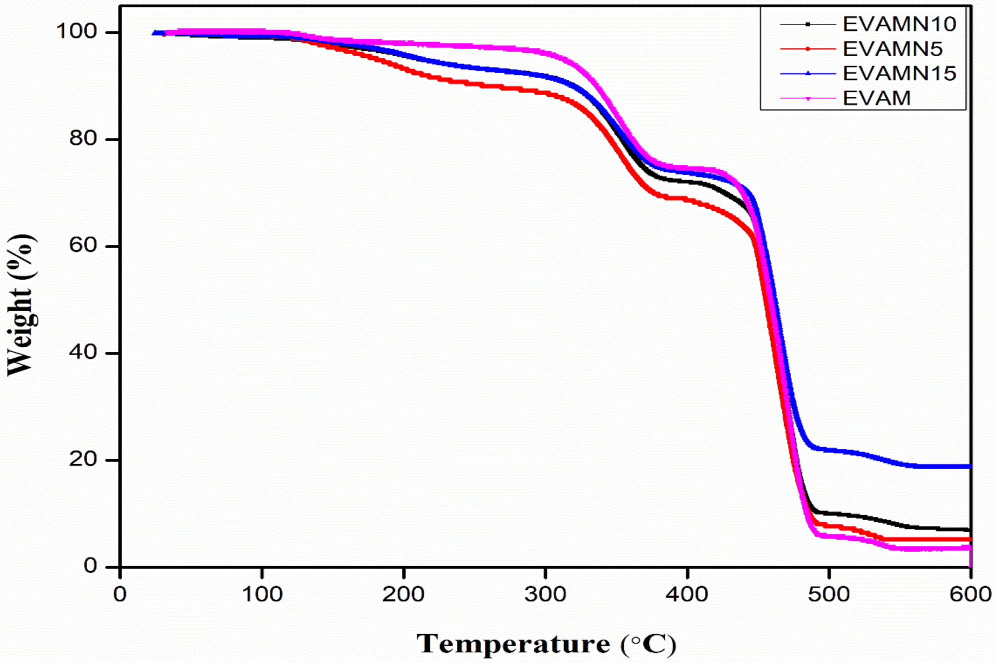


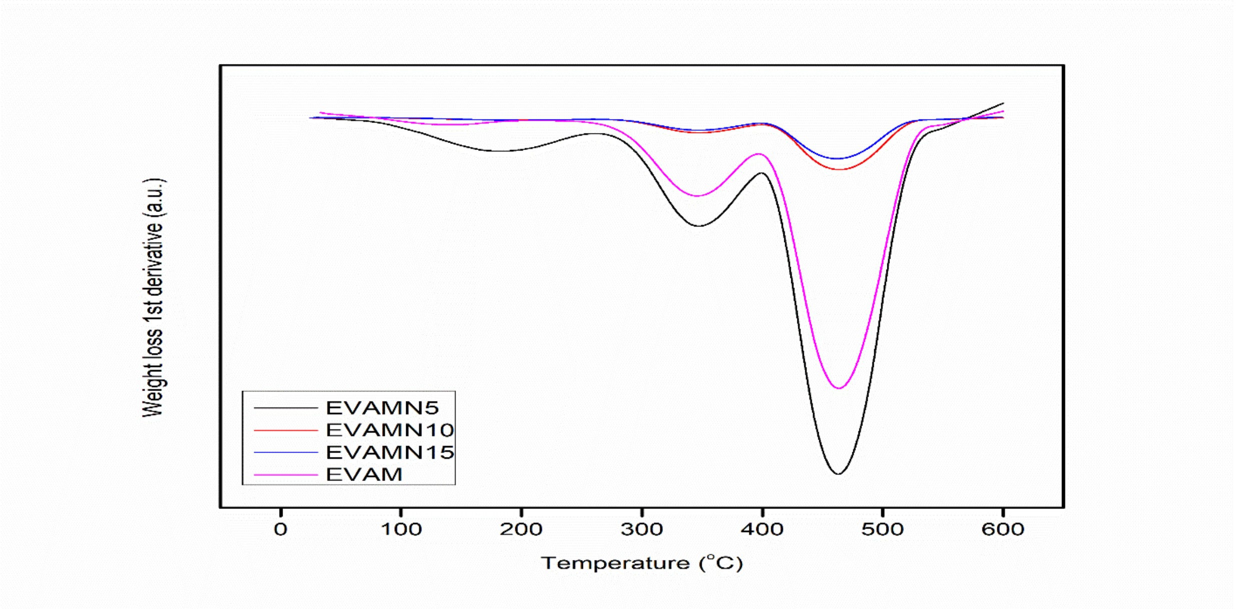
Fig. 3.2 XRD spectra of a) EVAM b) EVAMN5 c) EVAMN10 d) EVAMN15

3.3.3 Thermogravimetry (TG)

The thermal behavior of the polymer was studied by the TGA measurement and the results from the study are shown in fig. 3.3. It is evident from this study that the synthesized polymer undergoes two-step degradation. The initial weight loss which is completed at about 400^0C is mainly due to the autocatalytic deacetylation in the vinyl acetate fraction [28]. The second weight loss which is observed between $404\text{-}491^0$C corresponds to the completion of the chain scission of the residual polyethylene main chain. The thermal stability of all the crosslinked EVA is similar. The value for $T_{0.05}$ for all the composites was found to be above 200^0C, however, $T_{0.05}$ in the case of EVAMN5 was observed at around 180^0C (Fig. 3.3 b) which may be due to the elimination of moisture from the composite. Temperature exhibiting 50% mass loss ($T_{0.5}$) for all the polymers remains almost similar as evident from the TGA curves. It is observed that considerable residual weight is left out after 600^0C. EVAMN15 having a higher percentage of NaCl shows the highest residual weight (19%). This is due to incomplete leaching of NaCl from the crosslinked polymer [29].



(a)



(b)

Fig. 3.3 (a)TGA thermogram of EVAM, EVAMN5, EVAMN10 and EVAMN15

(b) DTG curves of EVAM, EVAMN5, EVAMN10 and EVAMN15

The initial degradation temperature (T_i), maximum degradation temperature (T_m), different weight loss temperature (T_D), and residual weight at 600^0C for the polymers are tabulated in Table 3.1

Table 3.1 Thermal analysis of EVAM, EVAMN5, EVAMN10, and EVAMN15.

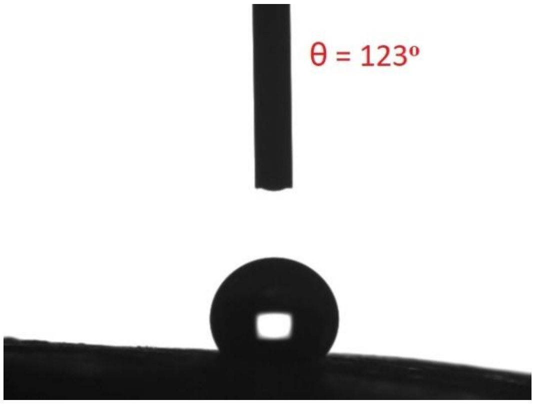
Sample	**T_i**	**$T_m{}^a$**	**$T_m{}^b$**	**$T_{0.05}$**	**$T_{0.5}$**	**T_D(^{0}C) at different weight loss (%)**				**RW % at 600^0C**
						20%	**40%**	**60%**	**80%**	
EVAM	332	347	466	309	458	364	456	465	473	3.35
EVAMN5	330	348	464	180	456	344	450	464	477	5.07
EVAMN10	328	348	464	210	458	354	456	465	473	6.79
EVAM15	312	332	458	210	456	320	456	465	473	19

[a]maximum pyrolysis 1st step

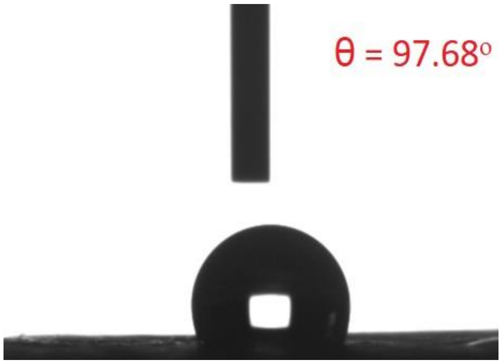
[b]maximum pyrolysis 2nd step

3.3.4 Contact angle measurement

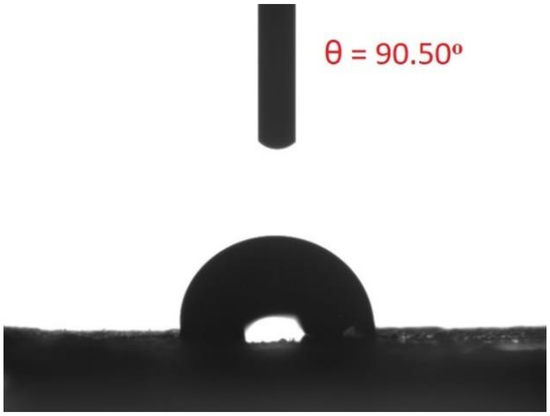
The effect of NaCl concentration on the wetting characteristics of the polymers was determined by measuring the contact angles which are presented in Table 3.2. Although the synthesized polymers show hydrophobic nature, however it was observed from the contact angle measurement that as the NaCl porogen concentration was increased there was a decline in the contact angle. This could be attributed to the fact that with the addition of NaCl, larger pores are formed on the polymer surface which allows liquid drops to diffuse through them, thus elevating the wetting characteristics of the polymer [30]. EVAM15 shows a higher contact angle which may be due to agglomerations at a higher NaCl concentration. But however, after soxhlet extraction from the sample, the contact angle of EVAMN15 was found to be 90.38^0.



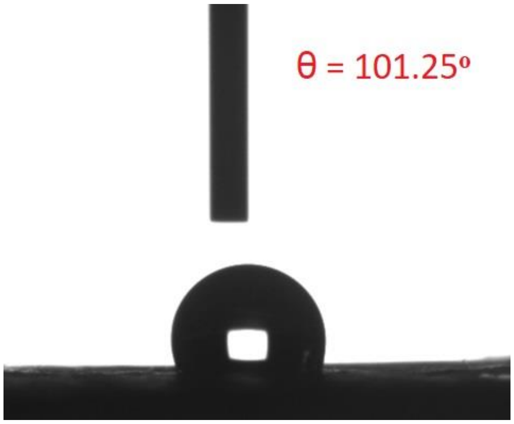
a)



b)



c)



d)

e)

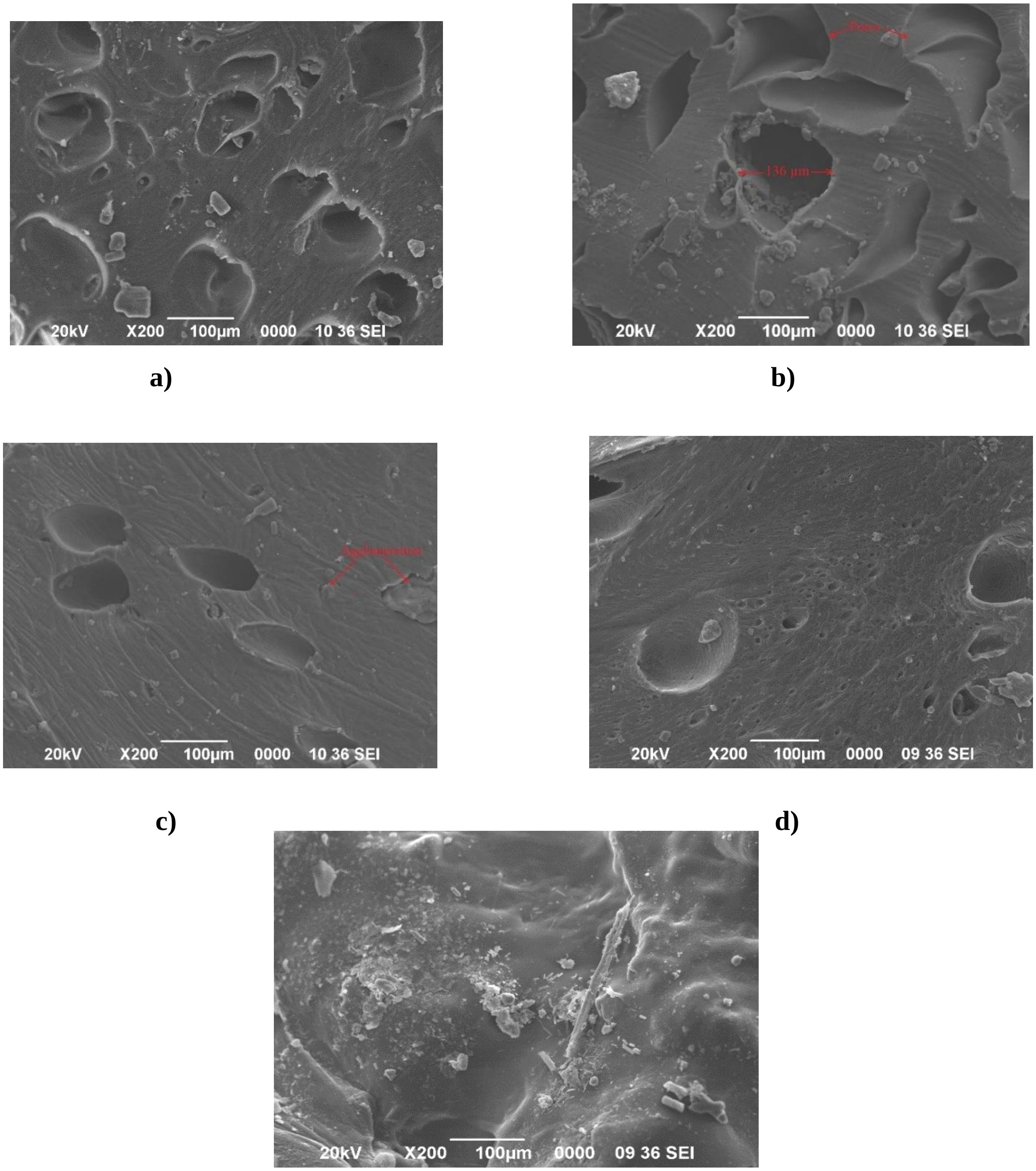
Fig. 3.4 Contact angle measurements of a) EVAM b) EVAMN5 c) EVAMN10 d) EVAMN15 before soxhlet extraction e) EVAMN15 after soxhlet extraction

Table 3.2 Contact angles of the synthesized polymers

Absorbent	**Contact angle (º)**
EVAM	123^0
EVAMN5	97.68^0
EVAMN10	90.50^0
EVAMN15 (before soxhlet extraction)	101.25^0
EVAMN15 (after soxhlet extraction)	90.38^0

3.3.5 Scanning Election microscopy (SEM) Study

The fractured surface of the polymer blends was studied under SEM to evaluate its pore size, shape, and pore distribution. The surface morphology of EVAM, EVAMN5, EVAMN10, and EVAMN15 is shown in fig. 3.5. In the SEM images, significant pores are visible which are formed as the NaCl particles are pulled out from the polymer matrix by leaching. This indicates a weak interfacial affinity between NaCl and the polymer network. The pore size increases from 107 µm in EVAMN5 to 136 µm in EVAMN10 as the porogen concentration increases. However, it has been evident from the SEM image (c) that with the increase in NaCl content (EVAMN15) porosity of the polymer decreases as the NaCl particles remain entrapped in the polymer matrix even after leaching [31].



a) b)

c) d)

e)

Fig. 3.5 SEM micrographs of a) EVAMN5 b) EVAMN10 c) EVAMN15 d) EVAM e) EVAMN10 after reusability study

3.3.6 Porosity measurement

The porosity of the synthesized samples was obtained by the liquid displacement method and tabulated in Table 3.3. The results clearly show that as the porogen concentration increases from 5% to 10% there is a simultaneous increase in the porosity of the polymer samples. But, with further increase in concentration (EVAMN15), the porosity decreases due to similar reasons already stated in the SEM morphology study**.** However, after soxhlet extraction from the sample, the porosity of EVAMN15 further increases as shown in Table 3.3.

Table 3.3: Pore diameter and measured porosity of the polymer samples

Sample code	Pore diameter	Porosity (%)
EVAM	88±16 µm	27.27±1.8
EVAMN5	107±10 µm	33.33±1.4
EVAMN10	136±12 µm	42.85±1.2
EVAMN15 (before Soxhlet extraction)	82±10 µm	11.11±1.3
EVAMN15 (after Soxhlet extraction)	82±10 µm	32.47±1.6

3.3.7 Absorption studies in oils/organic solvents

The polymers show excellent oil absorption capacity and equilibrium is obtained after 24 hours of exposure in various oils and organic solvents. Molecules of toluene, chloroform, and DCM being smaller get penetrated in the pores readily and thus show excellent affinity towards the polymers. On the other hand, due to the presence of long aliphatic chain (from cetyl alcohol), these polymers also allow long chain oils like gasoline, kerosene and crude oil to be adsorbed on its surface thus showing good oil absorption capacity. However, solvents like DMF and DMSO show very weak affinity towards the polymers because of their polar nature. The absorption capacity of the polymers in various oils and organic solvents is shown in fig 3.6. It is evident from the absorption study that EVAMN10 shows the maximum absorption in toluene (27.39 g/g) followed by gasoline (20.26 g/g) and chloroform (16.15 g/g). It could also be observed that EVAMN10 shows excellent absorption capacity in various oils and organic solvents in comparison to the other synthesized polymers. This is mainly because as the NaCl content increases larger pores and porosity is obtained after leaching which is evident from the SEM micrographs. However, EVAMN15 with 15% NaCl content rather shows decreased absorption capacity. This may be attributed to the fact that as the porogen (NaCl) content increases, during the adsorption process the ions get closely packed onto the inner wall of the pores which results in reducing the total pore volume [32]. Also because of the high content of NaCl, the NaCl particles gets agglomerated and gets entrapped in the pore spaces which results in a decrease in the porosity of the polymers [31].

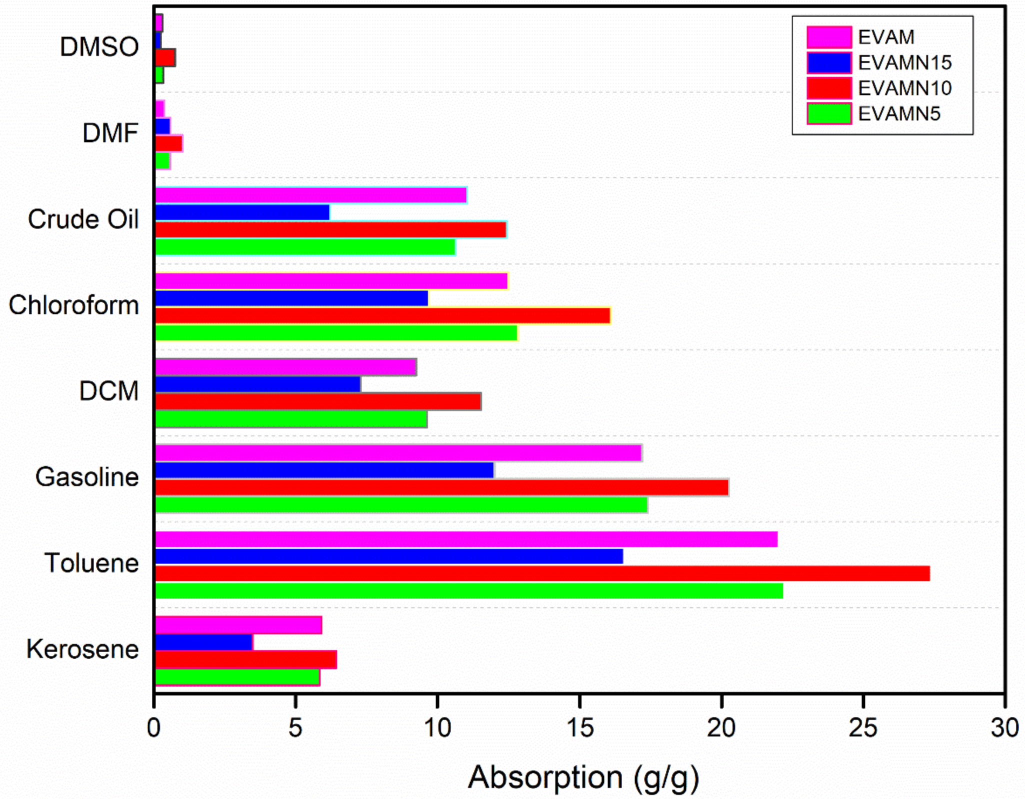


Fig. 3.6 Absorption capacities of the synthesized polymers

3.3.8 Effect of curing time on absorption

To evaluate the effect of curing time on the absorption capacity, the polymers were post cured for 1, 4, 6, 12 and 24 hours after synthesis. Fig. 3.7 shows the relationship between time of curing and absorption capacity of EVAM in toluene and gasoline. It was found that as the curing time is increased the absorption capacity also increases. EVAM showed the best absorption at 24 hours curing. Allowing higher time for curing results in more amount of crosslinking in the polymeric chain which increases its stability. On the other hand with shorter time for curing, the polymers do not crosslink sufficiently and remains stable for about 6 hours when submerged in various oils and organic solvents. But eventually loss in weight occurs and thus decreasing its absorption capacity (fig. 3.8). Similar findings were also observed in case of EVAMN5, EVAMN10 and EVAMN15

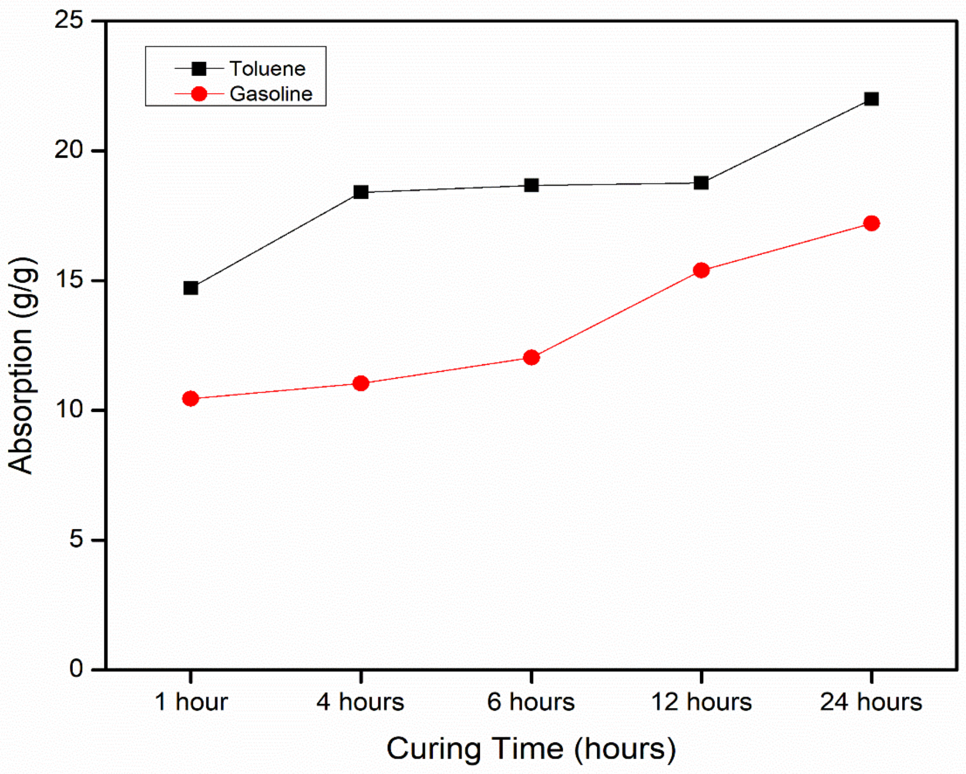


Fig. 3.7 Curing Time vs absorption curves of EVAM in toluene and gasoline.

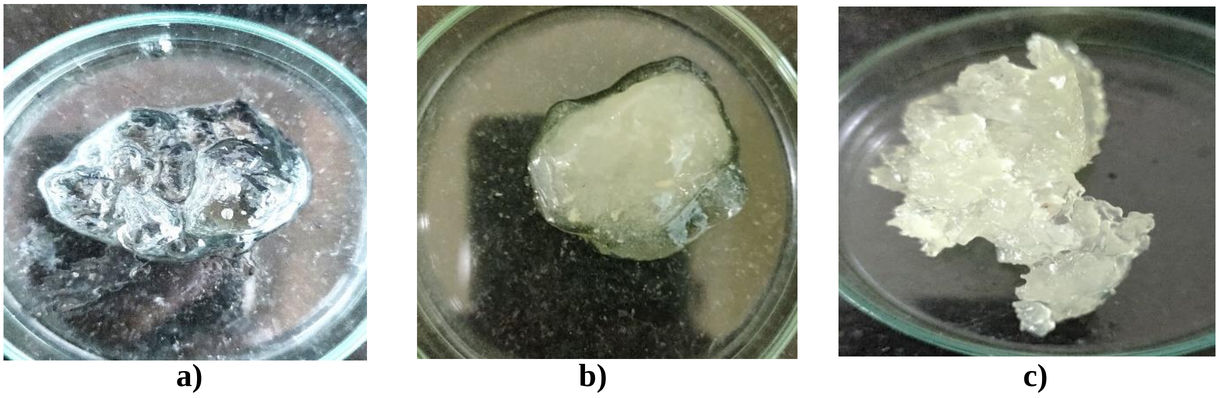

a) b) c)

Fig. 3.8 Images of EVAM samples after 24 hours absorption a) curing 1 hour, b) curing 4 hours and c) curing 24 hours

3.3.9 Hardness Test

The hardness characteristics of the crosslinked polymers was measured using a durameter. It was observed that hardness was maximum in EVAM (16 shore D) due to their cross-linked structure. However, it decreases in EVAMN5 (13 shore D) and EVAMN10 (12 shore D) as porosity increases after porogen (NaCl) leaching. Hardness in case of EVAMN15 (14 shore D) has increased slightly due to agglomeration of NaCl particles and decrease in pore volume.

3.3.10 Recyclability

Fig. 3.9 represents the reusability nature of the polymers. It was observed that the absorption capacity of the polymer remains unchanged even after 15 absorption-desorption cycles. However, the absorption efficiency gradually declines from the 15th cycle and it reduces by 24% at the end of the 30th cycle which may be the result of a decrease in porosity due to continuous absorption and thermal desorption process as revealed from the SEM image (Fig. 3.5 e). Thus, it can be very well concluded that polymer have excellent reusability and can be recycled for more than 30 absorption-desorption cycles.

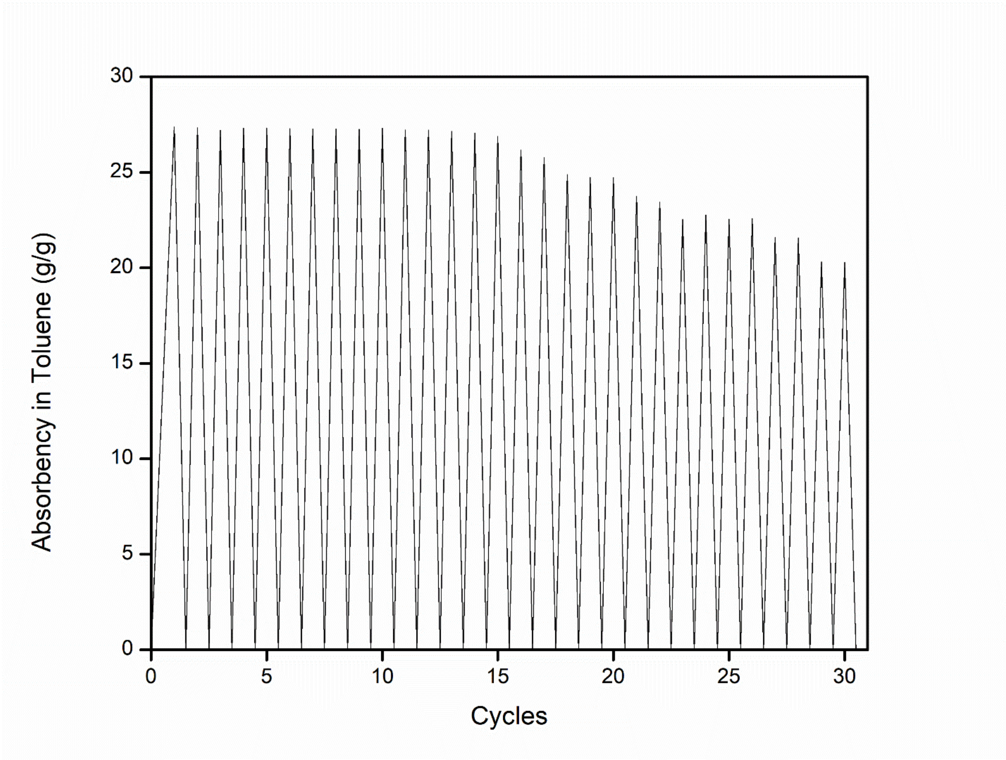
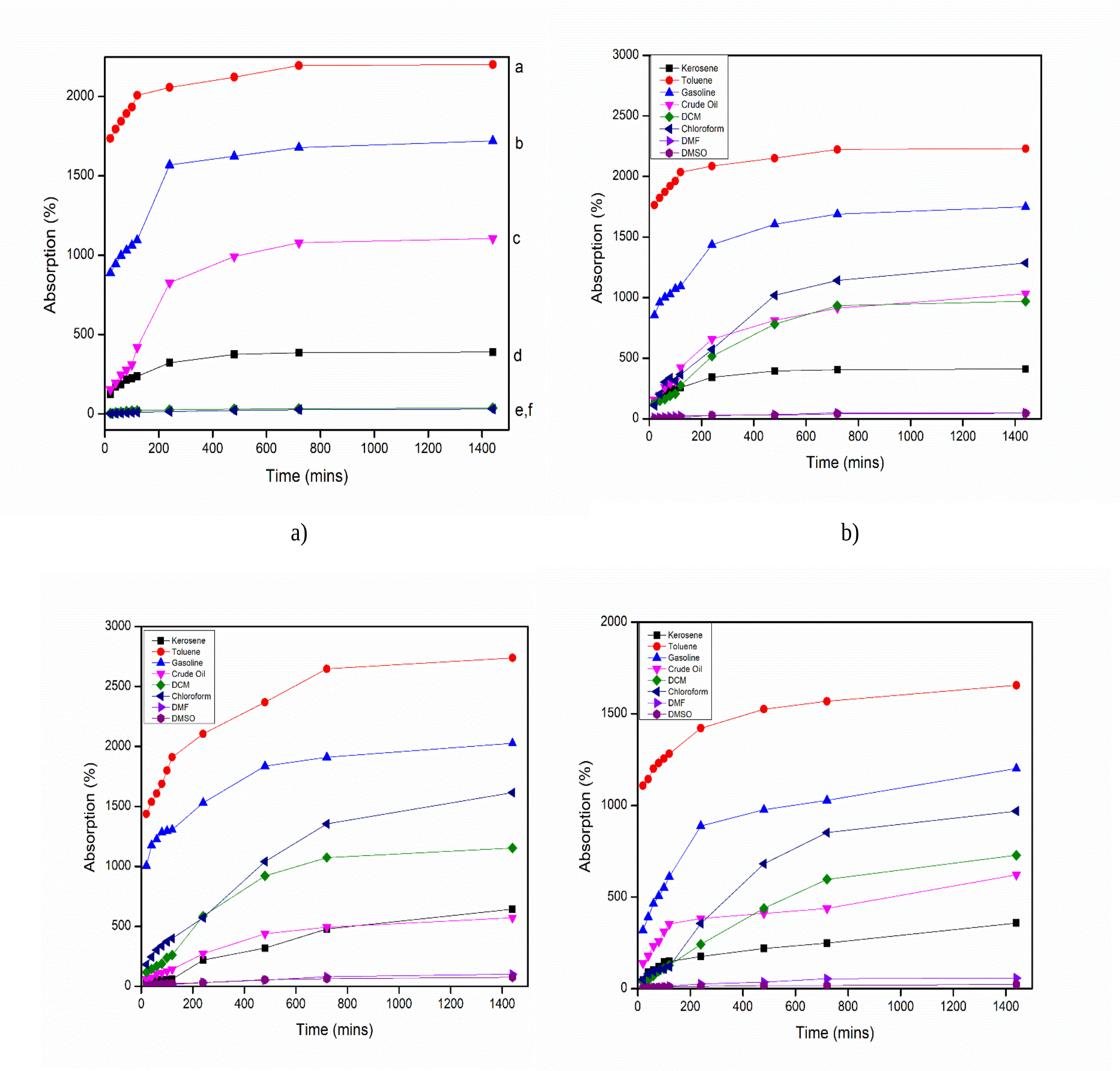


Fig. 3.9 Reusability of EVAMN10 for various absorption-desorption cycles

3.3.11 Absorption Kinetics

To elucidate the reaction routes and mechanism the adsorption kinetics was studied on the absorption of oils and organic solvents by the prepared crosslinked polymers. The study was conducted by plotting the absorption percentage in various oils and organic solvents as a function of time. It was observed from the kinetic curves (fig. 3.10) that there is a steep rise in the absorption initially but the rate gradually decreases and reaches equilibrium after 12 hours. This absorption rate remains almost constant till 24 hours. The absorption rate constant was determined by plotting the experimental data in to the pseudo first order and second order equations. The experimental data fits almost perfectly in the first order kinetic equation with correlation factor (R^2) ~0.99 (fig. 3.11) whereas it does not fit in the second order kinetics. These findings clearly suggests that the rate of reaction and the absorption process is governed by the pseudo second order kinetic equation.



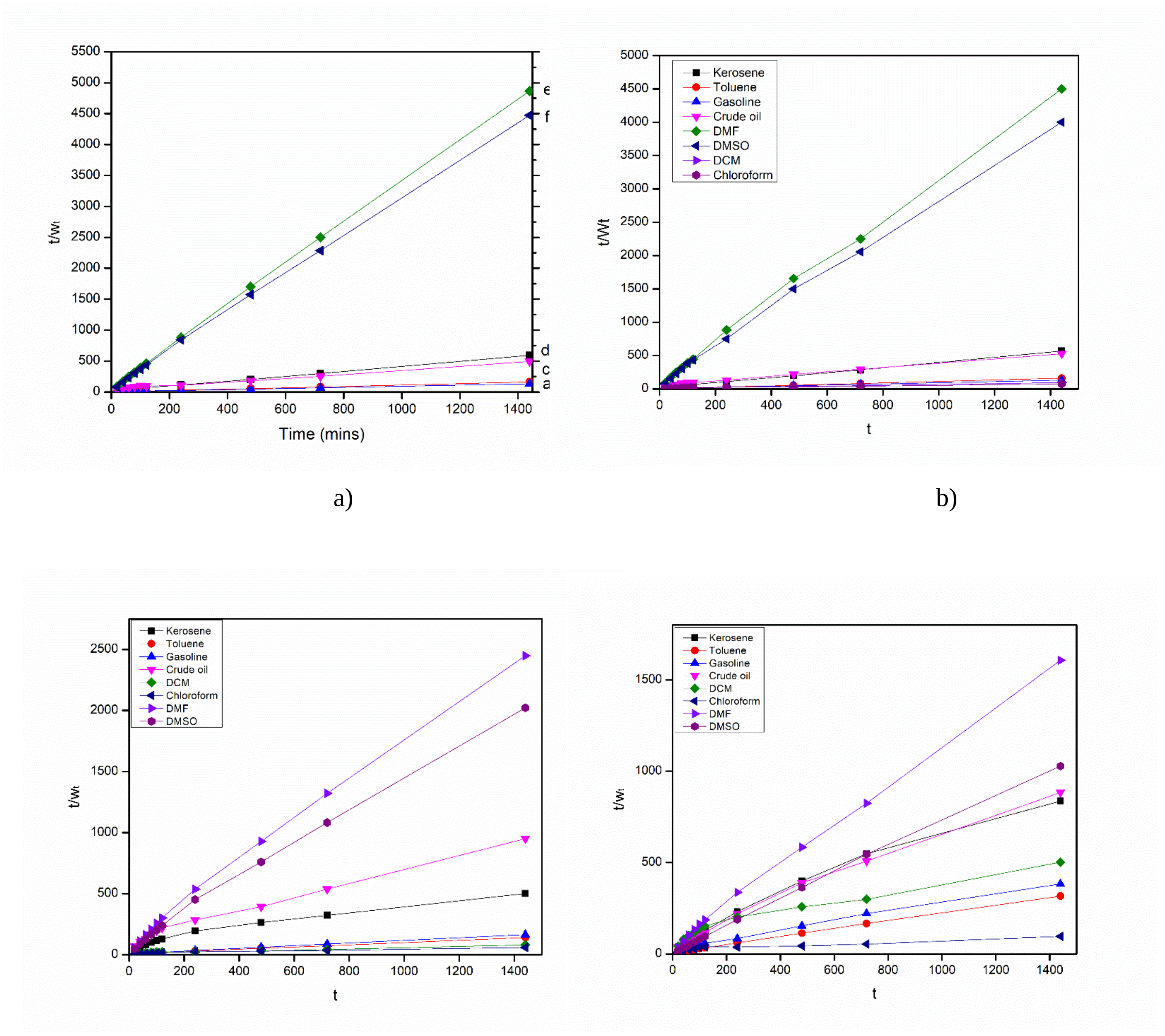
a)

b)

c)

d)

Fig. 3.10 Absorption kinetics for a) EVAM b) EVAMN5 c) EVAMN10 d) EVAMN15



a) b)

c) d)

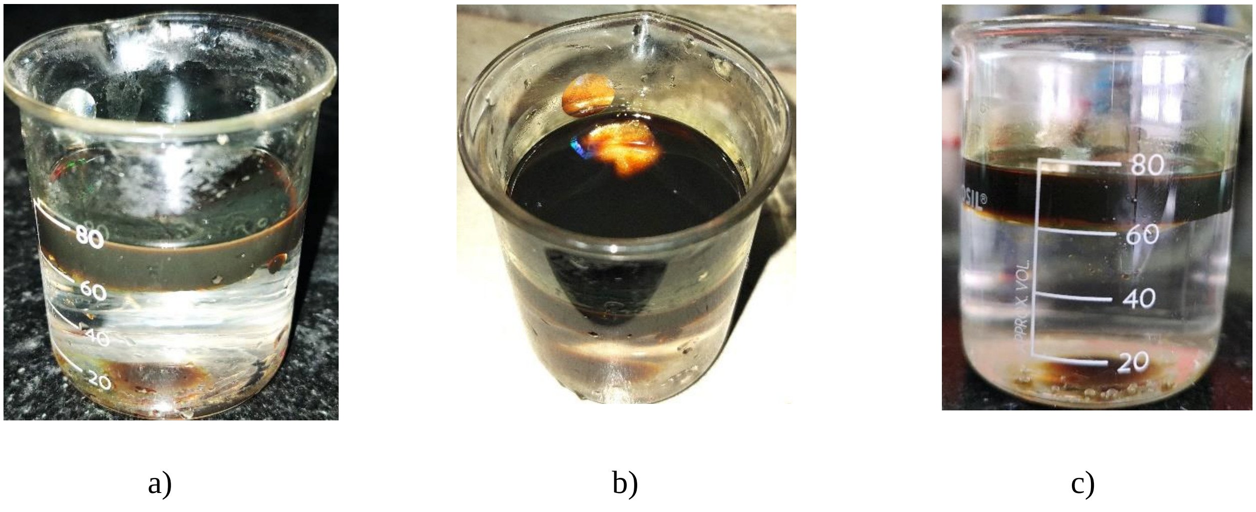
Fig. 3.11 Pseudo-second-order absorption kinetics for a) EVAM b) EVAMN5 c) EVAMN10 d) EVAMN15

Table 3.4 Pseudo-second-order parameters for EVAMN10

Oil/Organic solvent	Rate constant (K_2)	Correlation coefficients (R^2)
Toluene	0.00196	0.99773
Gasoline	0.00231	0.99805
Crude Oil	0.00310	0.98774
Kerosene	0.00130	0.99048
DCM	0.00017	0.98150
Chloroform	0.00013	0.98817
DMF	0.03411	0.99707
DMSO	0.03411	0.99707

3.3.12 Crude oil/water separation experiment

The selective removal of oil from oil-water mixture as well as stability in oils and organic solvents determines another parameter of efficiency of the polymers used in absorption application. Fig. 3.12 demonstrates the experiment conducted to determine such selective removal ability of our polymer EVAMN10 showing best absorption results in our study. The polymer absorbed most of the crude oil from the water surface within 24 hours. This experiment very well demonstrates the efficiency of the grafted polymer in cleaning natural oil spills and water treatment operations.



a) b) c)

d) e) f)

Fig. 3.12 Sequence of events during selective removal of crude oil from oil-water mixture

4. Conclusion

Poly (ethylene co vinyl acetate) (EVA) was successfully crosslinked using maleic anhydride and cetyl alcohol to prepare a polymer composite with increased strength and stability. The NaCl leaching technique was successfully utilized to increase the pore content and porosity of the polymer. SEM images confirmed the formation of large pores on the polymer morphology. It was observed that with the increase of NaCl content from 5% to 10% although a porous framework was obtained however the thermal properties, wetting characteristics and hardness of the polymer declined. But, with further increase in the porogen content these properties show an increasing trend but the porosity of the polymer decreases. The oil absorption test reveals that the polymer has excellent absorption capacity in various oils and organic solvents with absorption capacity in toluene as high as 27.39 g/g. Thus, it can be concluded that this EVA polymer has immense potential to be used in advanced fields of environmental operations like natural oil spill cleanup and waste water treatment.

5. References

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CHAPTER 4

DEVELOPMENT OF NANO ABSORBENT USING POLY (ETHYLENE-CO-VINYL ACETATE)

4.1. Introduction

The land and marine pollution studies and their impact assessment has gained enormous attention in the recent times. Oils spilled in both these environments has caused an adverse effect on the ecosystem. Oils floating on the water surface prevent light to reach the marine flora and fauna and effects their entire physiology. The detrimental influence of severe toxic oily waste water as well as the scarceness of water in many regions and countries around the globe has compelled researchers and scientists to develop novel and efficient techniques and approaches to make water free from oils and other solvents for reuse in various industrial applications. Frequent oil spills and enormous oily waste water released from the petrochemical, textile, food processing and other industries has been posing as s substantial threat to the environment [1]. The application of conventional techniques for waste water treatment like gravity separation, skimming, coagulation and flocculation has been inefficient in removing these contaminants since the oil particles remains uniformly dispersed in water due to surface active stabilization. Therefore, investigation on the synthesis and study of innovative novel material for eradicating oils and organic solvents with scalable synthesis and high recyclability has gained wide popularity in the recent times.

Studies on elimination of harmful oils and organic solvents from waste water with novel polymeric absorbent has gained immense attention during the last decade due to their high absorption capacity. Although various absorbent based on natural materials like cotton [2], sugarcane [3] , wool fibres [4], active carbon [5] etc. has been investigated as an oil and also solvent absorbent but however owing to their low absorption capacity and poor reusability, these materials were not widely used as an absorbent. Polymeric absorbents which has been widely investigated and found to have excellent oil and organic solvent removal capacity are mainly based on polyurethane [6], polypropylene [7], polystyrene [8], polyvinyl alcohol [9] and polymethacrylate [10,11].

Poly (ethylene-co-vinyl acetate) or EVA is a thermoplastic copolymer of ethylene and vinyl acetate. The various properties exhibited by EVA like polarity, crystallinity, melting point and mechanical properties depend on its ethylene and vinyl acetate (VA) content. EVA has been widely used as an encapsulation material having superior properties in wire coating [12], drug delivery [13] [14]and footwear applications due to its higher tensile strength, wear and tear properties with low hardness [15].

The application of nanoclay in removing harmful contaminants from wastewater has been widely investigated in recent times due to their abundance, minimum toxicity, and superior absorption capacity [16]. In one of the recent studies, Ramanayaka et al. attempted to study the potential of halloysite nanoclay in eradicating oxytetraycline antibiotic from water and found that oxytetraycline removal is pH dependent and best removal efficiency of 68% was observed at pH 3 [17]. Rafati et al. [18] studied the modification of nanoclay with β-cyclodextrin and polyvinylpyrrolidone and investigated the optimum conditions for eliminating naproxen from contaminated water. It was found from this study that 90% of naproxen could be removed at a optimum pH of 6. The discharge of water contaminated with dyes into the fresh water bodies is another cause of marine pollution. El Haouti et al. attempted to study the absorption character of Na-montmorillonite nanoclay on toluidine blue (TB) and crystal violet (CV). They noticed that with the increase in absorbent content from 0.1 - 0.2 g L−1, the removal efficiency increases considerably [19]. Salam et al. investigated the probable efficiency of modified nanoclay in removing orange G dye from water and found that nanoclay modified with octadecylamine has shown excellent absorption efficiency removing about 98% of the dye from the water system [20]. In some recent works, researchers have developed polymeric absorbents modified with nanocomposites for absorbing oils and also organic solvents from the surface of waste water. Kahraman et al. prepared nanocomposites by incorporating nanoclay into PAN fibres and found that the nanocomposite could absorb organic solvent upto 200 times its own weight [21]. Nikkhah et al. prepared polyurethane foam modified and improved by nanoclay and observed that addition of 3 wt.% of closite 20A improved the absorption capacity upto 16% and selective removal of oil water system by 56% [22]. In another recent study Wu et al. coated hydrophobic polyurethane foam using clay nanotubes modified and improved with polysiloxane. The modified polyurethane foam revealed excellent absorption capacity 104 and 74 g/g in chloroform and dichloroethane respectively with water contact angle higher than 150^0 [23]

In this study, we have attempted to develop a nano absorbent by incorporating nanoclay in the polymeric network of EVA and study its oil and solvent absorbent ability in detail. In our earlier studies we have successfully investigated the oil absorbing efficiency of pristine poly(ethylene-co-vinyl acetate) or EVA. Although EVA has shown good potential in majority of oils and also various organic solvents, however it has to be modified to enhance its strength and improve its stability after absorbing various oils and solvents [24]. EVA has been found to have good compatibility with nanoclay forming nanocomposites due to its high polarity and fluidity at higher temperature which results in formation of highly intercalated and exfoliated nanocomposite structure [25]. Although EVA has been modified by nanoclay for different applications, however to our best knowledge there is no literature on the investigation of EVA nanocomposite in removing oils and solvents from wastewater.

4.2 Materials and Methods

Poly (ethylene-co-vinyl acetate) (EVA) (vinyl acetate content 18%, molecular weight 142,849 Da and 15.08 g/10 min melt index) was supplied by Max Specialty Films Limited. Benzoyl peroxide (BP) was obtained from G.S chemical testing lab and allied industries and sodium chloride (NaCl) 99% pure was obtained from Merck. OMMT (organically modified montmorillonite with octadecylamine and aminopropyltriethoxysilane) was used directly as obtained from Sigma-Aldrich, USA. Various solvents used in the study like toluene, dichloromethane, chloroform, dimethyl formamide and dimethyl sulphoxide were obtained from Merck, oils like kerosene, and gasoline were collected locally whereas crude oil was obtained from GGS, ONGC.

4.2.1 Preparation of nanocomposites using poly(ethylene-co-vinyl acetate)

40 g of poly (ethylene-co-vinyl acetate**)**, and 2 g of benzoyl peroxide were initially transferred for melt blending in the brabender plasticoder. This initial mixing was conducted at 50 rpm screw speed for about 3 mins which was followed by adding different proportions of OMMT (3, 5 wt.%) into the mixing chamber. The final blending of the components was conducted at 70 rpm for 5 mins at a temperature of 120^0C. Nanocomposites with 3% nanofiller (BEN3) and 5% nanofiller (BEN5) were thus prepared. Finally, the samples were stored in a desiccator to protect them from moisture.

4.2.2 Preparation of highly porous nanocomposites using Poly (ethylene-co-vinyl acetate)

Porous EVA nanocomposites were prepared in a similar method as discussed in the earlier section. In this process, 10% NaCl was added as porogens in the initial mixture along with EVA and BP before the addition of OMMT in the final stage. Porous nanocomposites with 3 wt.% of nanofiller (BENN3) and 5 wt.% of nanofiller (BENN5) nano loading were synthesized in this process. This was followed by leaching of NaCl from the nanocomposites at a temperature of 50^0C. The nanocomposites were stirred by the aid of a magnetic stirrer in a beaker containing about 70 ml of distilled water at 250 rpm for 5 hours. The samples were then placed in the hot air oven for about an hour in order to remove all the moisture from their surface and finally shifted to the desiccator for subsequent experimental study.

4.2.3 Absorption studies in oils/organic solvents

ASTMF726-99-Standard Test Method was used to study the absorption behavior of the nanocomposite samples. In this method, preweighed nanocomposite samples were dropped in a beaker containing 60 ml of oil or organic solvent. Prior to exposing the samples for absorption, dry weight was taken and marked as W_i. The samples were then allowed to absorb oil/solvents from the beaker and their swelled weights (W_t) were taken after regular time intervals (2, 4, 8, 12, and 24 hours) using a precision electronic balance. The absorption capacity of the samples was measured using equation (1)

$$\text{Oil absorption (g/g)} = \frac{Wt-Wi}{Wi} \qquad (1)$$

Where W_t is the weight in grams of the immersed samples at a definite interval of time (t).

4.2.4 Study on Recyclability

Reusability is one of the critical parameters which determines the efficiency of an absorbent. Various cycles of absorption and desorption were conducted to evaluate the reusability of the nanoabsorbent. Herein, the absorbent was immersed in toluene and its weight was taken after 24 hours as the sorbent gets saturated with the oil or solvent. In the desorption process, the absorbed toluene was allowed to escape from the polymer lattice by heating in a hot air oven at 50^0C for an hour.

4.2.5 Separating oils from oil-water mixture

To determine the selective oil separating efficiency of the nano composites from oil and water mixtures, 25 ml of water was supplemented with 40 ml of toluene to form an oil/water suspension. Water was colored with a blue dye for accurate observations. 0.35 g sample of the composite was immersed completely in the oil/water mixture and the removal efficiency was determined with respect to time.

4.2.6 Kinetic Study

To study the kinetics, the absorption capacities of the polymer samples were plotted against time [26,27]. The samples were put in beakers containing different oils and various organic solvents and allowed to swell. The swelled samples were then weighed (W_t) at regular intervals i.e. 20, 40, 60, 80,……mins. Equation (2) represents the first order absorption kinetics:

$$\frac{dW_t}{dt} = K(W\infty - W_t) \qquad (2)$$

where W_t represents weight of the sample after absorption in time t, and $W\infty$ represents weight of the sample after the absorption process reaches equilibrium.

After integration of eq. (2), eq. (3) is obtained,

$$\ln W\infty/(W\infty - W_t) = Kt. \qquad (3)$$

If a straight line graph is obtained by a plot between $\ln W\infty/(W\infty - W_t)$ vs t, we can infer that first-order kinetics is followed by the absorption process.

Equation 4 corresponds to the second-order kinetics:

$$\frac{dW_t}{dt} = K(W\infty - W_t)^2 \qquad (4)$$

After integration of eq. (4), eq. (5) is obtained,

$$\frac{t}{W_t} = \frac{1}{KW\infty^2} + \frac{1}{W\infty}t \qquad (5)$$

If a straight-line graph is obtained by a plot between t/W_t vs t, we can infer that second-order kinetics is followed by the absorption process.

4.2.7 Characterization

4.2.7.1 FTIR studies

FTIR spectra for BEN3, BEN5, BENN3 and BENN5 were recorded in FTIR spectrophotometer of PerkinElmer, Frontier MIR-FIR with KBr pellet within the wave number range of (400–4000 cm^{-1}).

4.2.7.2 XRD studies

Wide angle diffraction (XRD) patterns were acquired from an X-ray diffractometer (Bruker Axs, Germany, D8 FOCUS) operated under copper K_α radiation with 1^0 min^{-1} rate of scanning and an angle ranging between 7^0 to 50^0.

4.2.7.3 Thermal property

The thermal behavior of the nanocomposites was acquired using TGA-50 (Shimadzu, Japan) TG analyzer with a constant rate of heating (10^0 C min^{-1} to 600^0 C) using a nitrogen environment while maintaining a constant flow rate (30 ml min^{-1}).

4.2.7.4 Contact angle measurement (θ)

The contact angle was obtained by a goniometer (Kyowa interface measurement, DMs401) arrangement to determine the wetting characteristics. The standard FAMAS software® was used to collect the data.

4.2.7.5 Scanning electron microscopy (SEM)

The morphology and surface of the nanocomposite surface was precisely investigated by a scanning electron microscope (SEM). JEOL, 6390 LV, JSM Model was used with an accelerated voltage of 15 kV. In this study, the fracture composite surface was sputtered with platinum on a brass holder.

4.2.7.6 TEM studies

To evaluate the dispersion of nanoclay within the composite TEM study was conducted on a JEOL JEM-2010 device with a scanning CCD camera installed and using 200 kV accelerated voltage. ImageJ software was used to determine the d-spacing between the layers from the TEM micrographs. The results obtained are expressed as the average of three trials with standard deviation.

4.2.7.7 Hardness Testing

A durameter of RR12 model measuring in units of shore D hardness was used to evaluate the hardness of the nanocomposites.

4.3. Results and Discussion

4.3.1 FTIR analysis

FTIR spectra of BEN3, BEN5, BENN3 and BENN 5 are described in Fig. 4.1. The distinctive characteristic absorption peaks of OMMT are observed at 3448 cm^{-1} representing -N-H stretching. The absorption peak observed at 2924 and 2846 cm^{-1} represents the C-H stretching in OMMT. The distinctive characteristic absorption peak of EVA is observed at 2915-2918 and 2848-2851 cm^{-1} which indicates the C-H bond deformation of methane group, methylene group and methyl group of poly(ethylene-co-vinyl acetate). The presence of vinyl acetate is also confirmed by the presence of the corresponding band of C-H at 950 cm^{-1}. From the IR spectrum, it is clearly visible that the -NH stretching band appearing at 3448 cm^{-1} decreases to a lower wave number in the nanocomposites indicating a better interaction of OMMT with the polymer matrix through H-binding as shown in Scheme 1. Further, the typical peak at 1045 cm^{-1} detected in OMMT disappeared in the nanocomposites which signifies an adequate interaction of EVA with the delaminated structure.

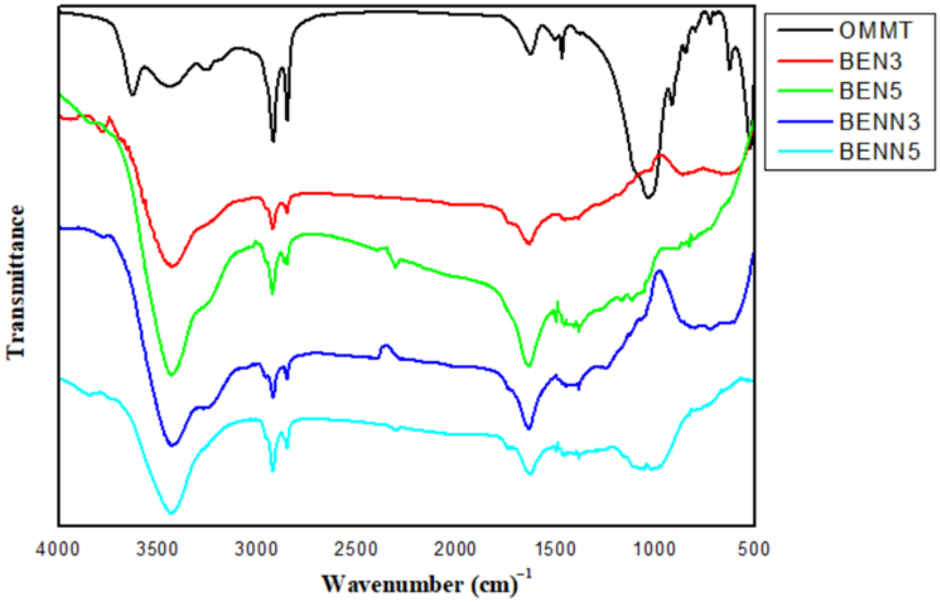
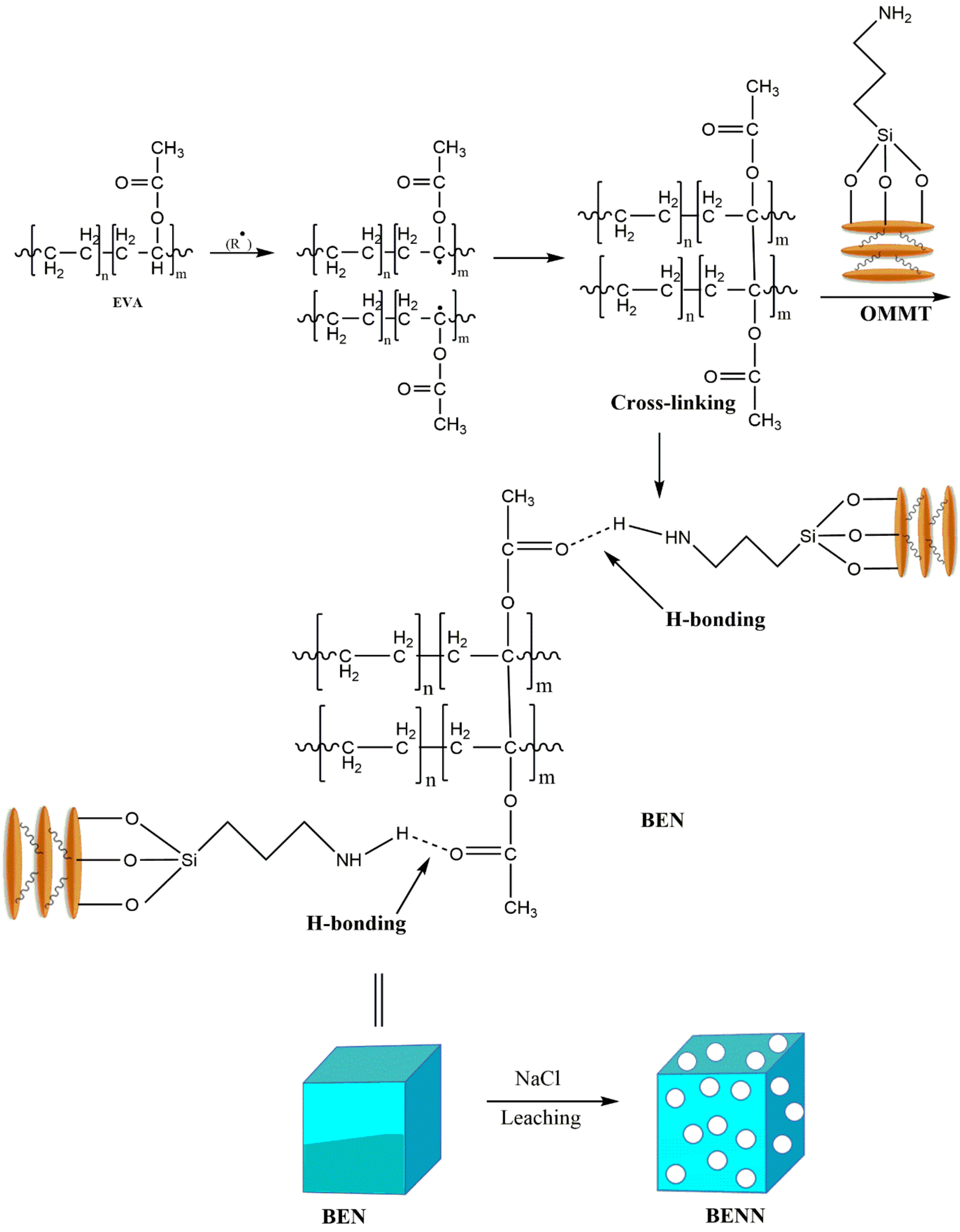


Fig. 4.1 FT-IR spectra of the prepared nanocomposites



Scheme 3. Plausible mechanism of interaction of EVA with OMMT and pore formation after NaCl leaching

4.3.2 X-Ray diffraction

The XRD patterns of BEN3, BEN5, BENN3, and BENN5 are shown in Fig. 4.2. The characteristic peak observed at around $2\theta=20.8^0$ corresponds to the crystalline region of EVA which gets reduced as the clay loading increases. The OMMT shows characteristic absorption peaks at 7.9^0, 19.7^0 and 24.4^0 However, the XRD spectra of the nanocomposites exhibit a broad diffraction peak at around 22.4^0 which indicates the amorphous nature of the composites. However, there is no typical diffraction peak of the OMMT present in the nanocomposites implying that the OMMT was notably exfoliated in the polymer matrix. Moreover, the characteristic peak of the nanocomposite has increased as the OMMT content increases. This is mainly due to the interaction of OMMT with the polymer matrix as shown in **Scheme 3**. However, after leaching out of NaCl from the polymer matrix (BENN3 and BENN5), the characteristic peak of the nanocomposite was reduced due to the formation of pores in the polymer matrix.

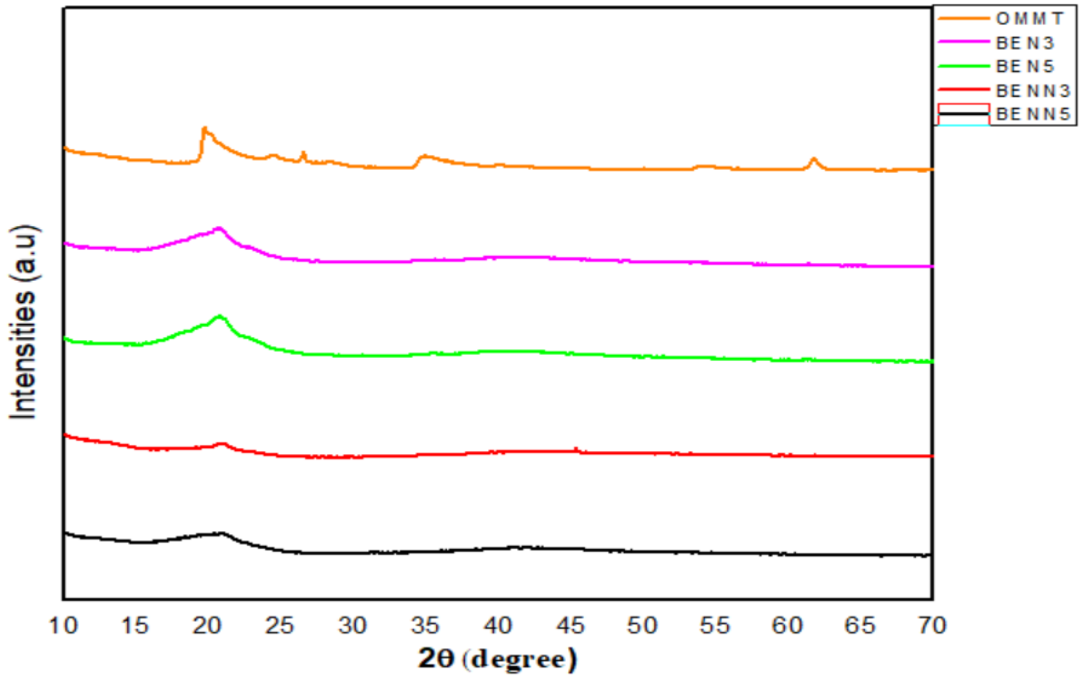


Fig. 4.2 XRD spectra of OMMT, BEN3, BEN5, BENN3 and BENN5

4.3.3 Thermogravimetry (TG)

The TG measurement in Fig. 4.3. delineates the thermal behavior of the prepared nanocomposites. The TG analysis indicates a two-step weight loss event. The initial weight loss observed at 260-362^{0}C may be due to the decomposition of aminopropyltriethoxysilane (APTES) attached with clay. The second weight loss which is observed between 362-500^{0}C may be attributed to the decomposition of octadecylamine and completion of the chain scission of the residual polyethylene main chain. It is observed that the prepared nanocomposites have similar thermal stability and they remain stable up to 600^{0}C. The TG curves also reveal considerable residual weight after degradation. BENN3 shows the maximum residual weight (12%) which is mainly due to the filler content and unburnt carbon.

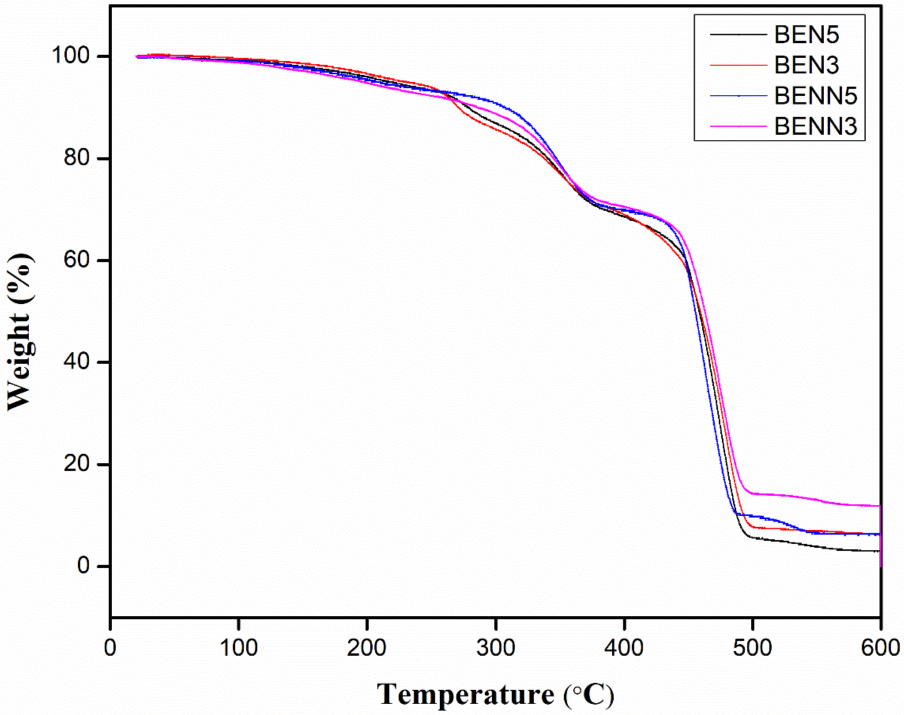


Fig. 4.3 Thermogravimetric thermogram of BEN3, BEN5, BENN3 and BENN5

The initial temperature of degradation (T_i), maximum temperature of degradation (T_m), different temperatures of weight loss (T_D) together with the residual weight at 600^{0}C of the composites are tabulated in Table 4.1.

Table 4.1 Thermal analysis of BEN3, BEN5, BENN3, and BENN5.

Sample	T_i	T_m^a	T_m^b	T_D (^{0}C) at significant weight loss (%)				RW% (600^0C)
				20%	40%	60%	80%	
BENN3	265	355	490	349	353	470	487	12
BENN5	265	355	487	344	353	471	477	6.5
BEN3	262	356	489	340	352	462	485	6.5
BEN5	263	357	483	340	352	465	478	2.6

[a] maximum pyrolysis 1st step

[b] maximum pyrolysis 2nd step

4.3.4 Contact angle measurement

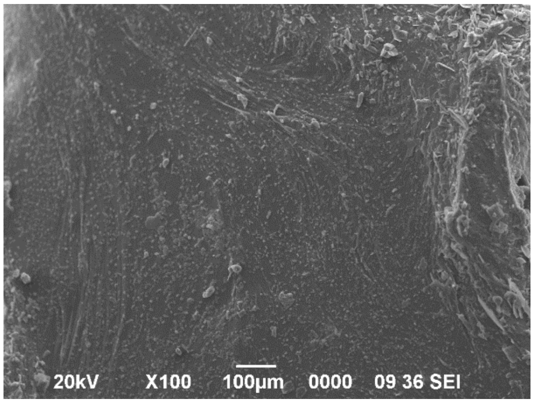
The wetting characteristics of the nanocomposites was studied in terms of the contact angle. From Fig. 4.4, it is evident that the hydrophobic nature of BEN3 (3% nanofiller) and BEN5 (5% nanofiller) is almost similar. However, with the development of pores on the surface of BENN3 and BENN5 on addition of 10% NaCl, although the composites show a hydrophobic nature but contact angle could not be measured since large pores formed on the polymer surface allows liquid drops to diffuse through them, thus elevating the wetting characteristics of the composites [28].

b) b)

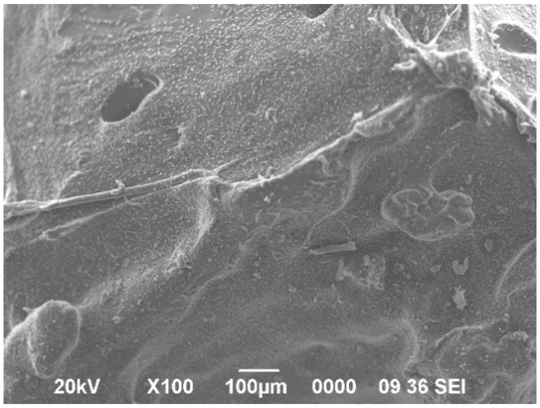
Fig. 4.4 Contact angles of BEN3 and BEN5

4.3.5 Scanning Election microscopy (SEM) Study

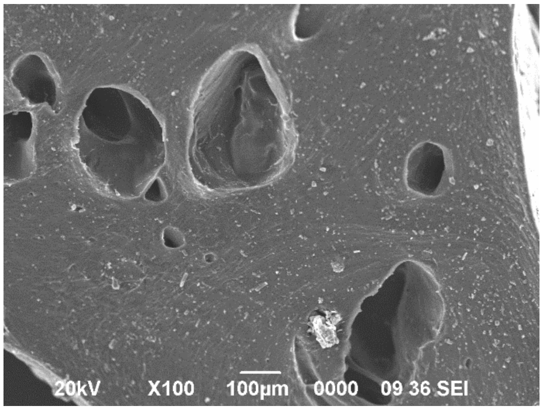
The surface morphology of BEN3, BEN5, BENN3, and BENN5 are shown in fig. 4.5. BEN3 reveals a uniform surface while BEN5 shows a rough surface (Fig. 4.5a and 4.5b). This may be due to better interaction with the addition of nanofiller. Moreover, as the percentage of nanoclay increases, agglomeration of OMMT occurs which may play a substantial role in appearance of a rough surface as the nano loading increases. In the SEM images of BENN3 and BENN5, considerable pore spaces are seen to be developed on the morphology of the nanocomposites due to the leaching of NaCl from the polymer matrix (Fig. 4.5c and 4.5d). Due to the porous structure of BENN3 and BENN5 more surface area is available for wetting of solvents and oils.



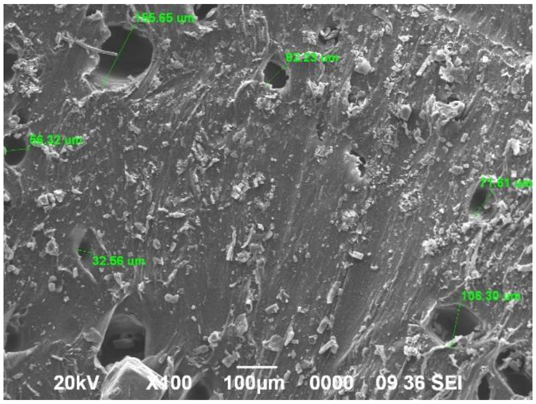
a)



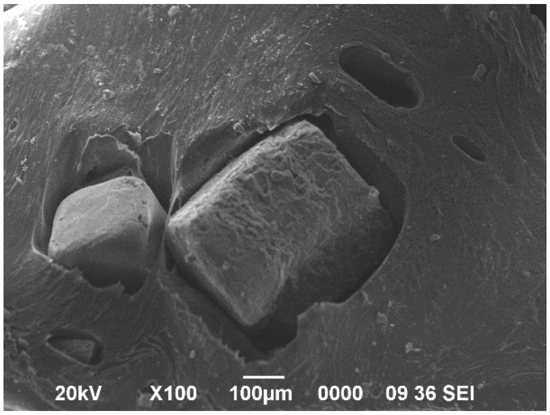
b)



c)



d)

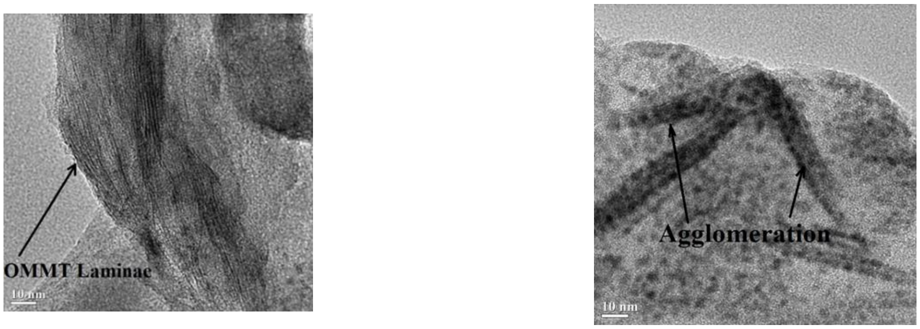


(e)

Fig. 4.5 SEM micrographs of (a) BEN3 (b) BEN5 (c) BENN3 (d) BENN5 after leaching (e) BENN5 before leaching

4.3.6 Transmission Electron Microscopy (TEM) study

TEM micrographs of BEN3 and BEN5 with 3% and 5% nano loading are shown in Fig. 4.6. It is evident that BEN3 (Fig. 4.6 a) displays a better dispersion and delamination of OMMT. The interaction like H-bonding between amine groups of OMMT with the C=O of the polymer matrix helps in the uniform dispersion and exfoliation of OMMT in the polymer networks. The d-spacing as interpreted from the ImageJ software was found to be about 2.036 nm. With the increase in nano filler in case of BEN5 (Fig. 4.6 b), agglomerations are observed due to the elevation of surface interaction among them.



a) b)

Fig. 4.6 TEM micrographs of a) BEN3 b) BEN5

4.3.7 Absorption studies in oils/organic solvents

The nanocomposites displayed excellent absorption capacity in various oils as well as organic solvents. Although unmodified EVA shows good absorption as seen from our previous studies, but it disintegrates after absorbing the oils and solvents. But with the addition of organically modified clay (OMMT), significant increase in strength as well as interchain spacing has been observed. The absorption efficiency of the nanocomposite was calculated using equation 1. The composite surface allows smaller molecules of toluene, chloroform and DCM to readily invade its pore spaces and thus reveal a good absorption capacity. Hence, porous BENN5 exhibits excellent absorption of 40 g/g with DCM, 17 g/g with toluene and 16 g/g with chloroform. Moreover, it seems that the octadecylamine (ODA) present in the clay provides the hydrophobic separation in the clay layer spacing and provides the hydrophobic force which allows absorption of various oils and solvents and formation of secondary aggregates of clay units. It could also be observed that polar solvents like DMF and DMSO show poor absorption in the composite owing to the nonpolar nature of the nanosorbent. The application of the NaCl leaching technique improves the pore size of the nanosorbents which is clearly observed from the SEM micrographs. Due to this increase in pore size, the absorption on to the absorbent surface further escalates as the oil molecules get readily entrapped into these larger pore spaces. The absorbing capacity of the polymers in various oils and different organic solvents is shown in fig. 4.7.

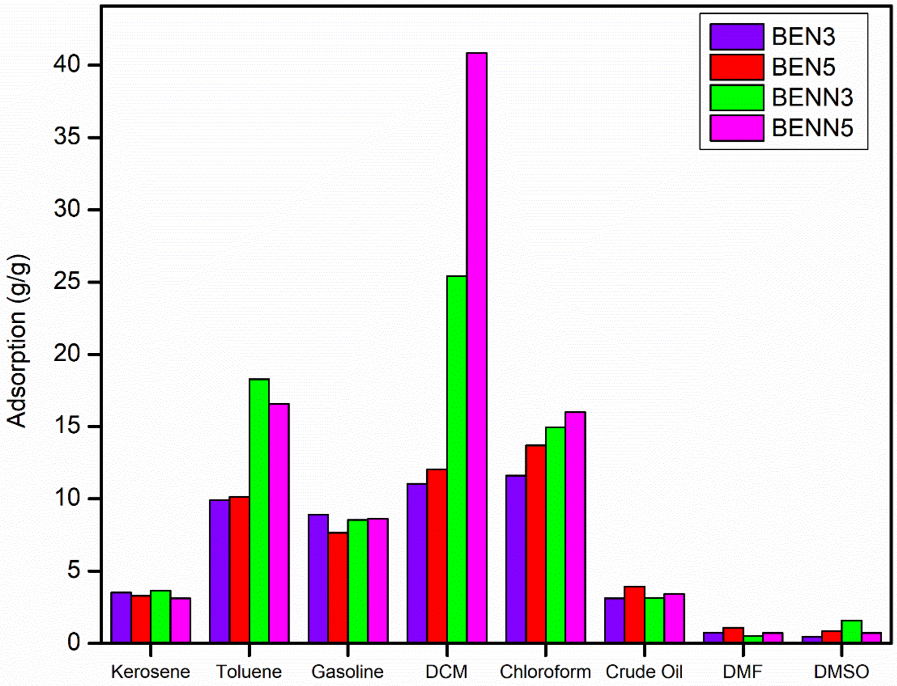


Fig. 4.7 Absorption capacities of the synthesized nanosorbents

4.3.8 Hardness Test

The hardness parameters of the nanocomposites were measured using a durameter. BEN3 (18 shore D) and BEN5 (22 shore D) showed maximum hardness characteristics which may be attributed to the dispersion of silicate layers in the nanocomposite. However, it decreases in BENN3 (15 shore D) and BENN5(16 shore D) due to the development of large diameter pores on the surface of the composites, thus forming a highly porous structure.

4.3.9 Recyclability

Fig. 4.8 represents the reusability nature of the nanocomposites. Reusability study was conducted on BENN5 for 30 absorption-desorption cycles. It was observed that the absorption capacity of the nanocomposites displays similar trend for the first 20 absorption-desorption cycles. However, from the 20th cycle it gradually declines and by the end of 30th cycle, the absorption efficiency reduces by 20% of its initial absorption capacity. Thus, it can be very well concluded that the addition of OMMT into the polymeric network has induced excellent recycling property into the nanocomposites.

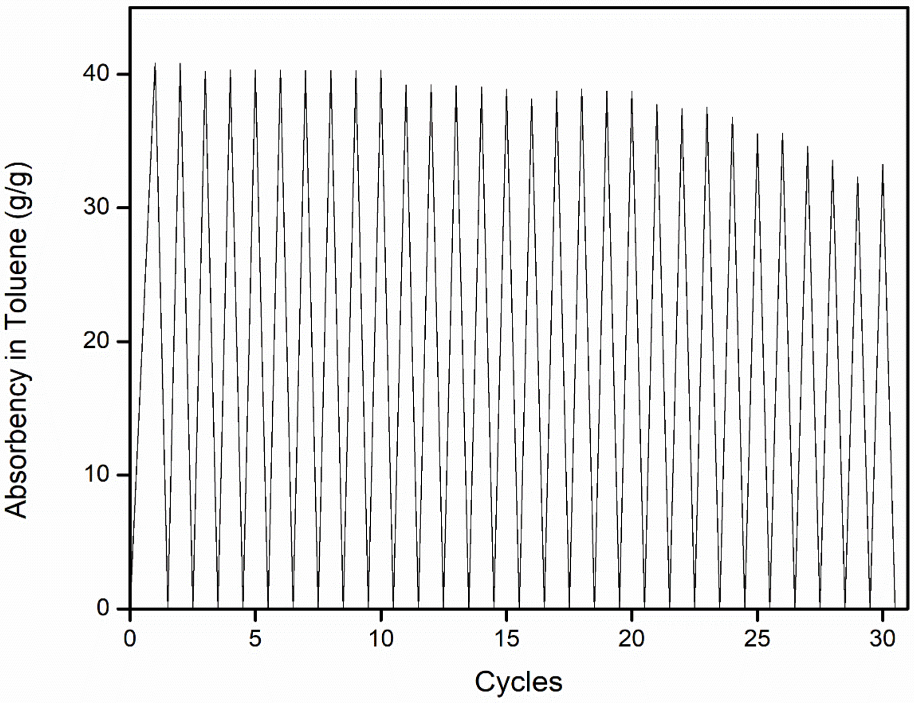
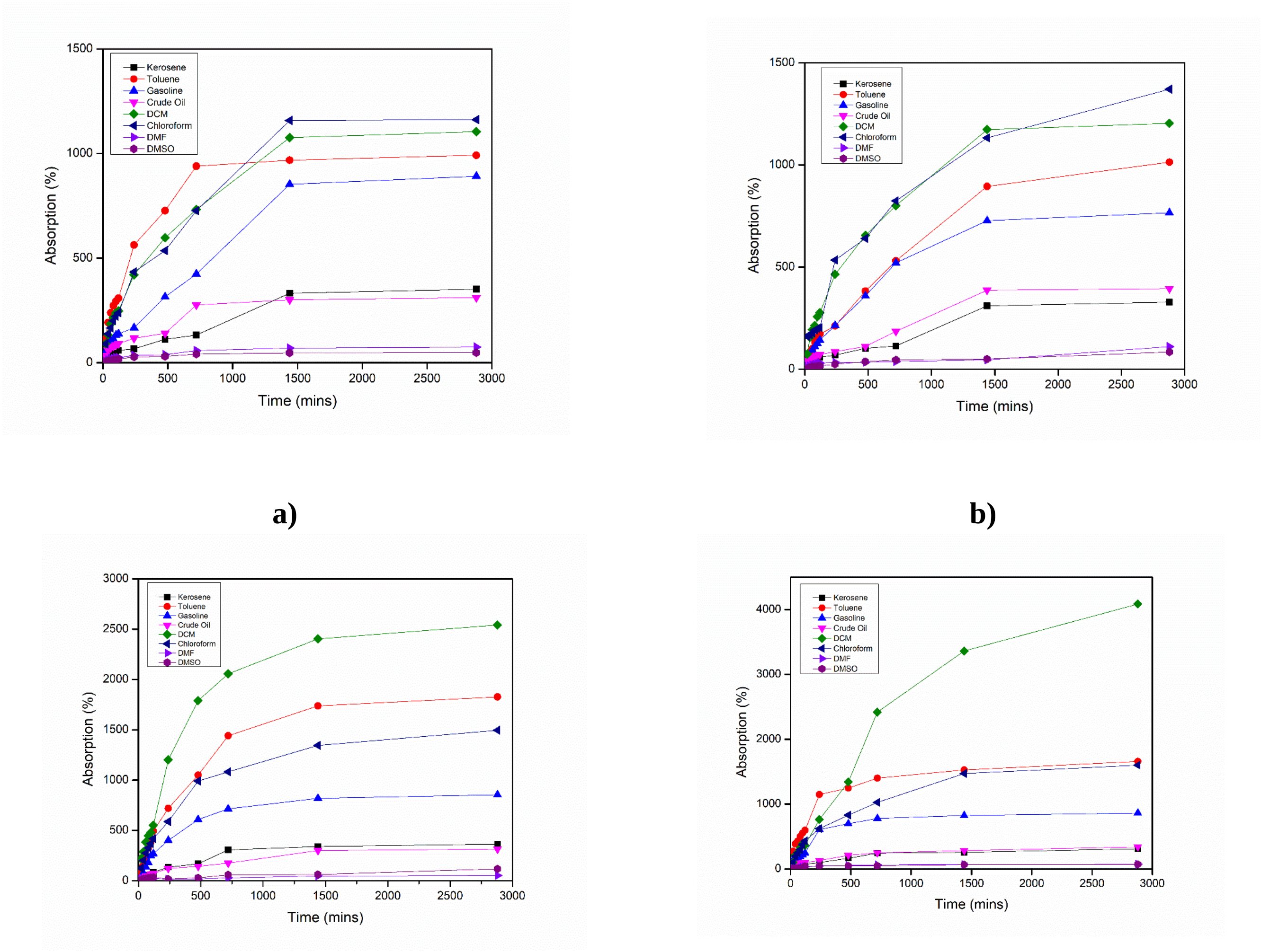


Fig. 4.8 Reusability of BENN5 for continuous absorption-desorption cycles

4.3.10 Absorption Kinetics

The mechanism of absorption by the synthesized nanocomposites was illustrated by the absorption kinetic study using the oils and solvents under study. A time vs absorption plot (Fig. 4.9) elucidates the absorption kinetics of the nanocomposites in various oils as well as organic solvents. It was observed from the kinetic curves (fig. 4.9) that absorption occurs with a rapid rate during the early phase of the absorption reaction. However, as the lattice of the nano composites saturates with the oils and solvents, the rate of reaction drops and equilibrium is reached after about 24 hours. This absorption rate remains almost constant till 48 hours. To determine the rate constant associated with the absorption process, plots between ln $W_\infty/(W_\infty - W_t)$ vs t (equation 3) and t/W_t vs t (equation 5) were obtained. The plot of t/W_t vs t from the experimental data demonstrated a straight line graph according to the second-order kinetic equation having correlation factor (R^2)~0.99 (Fig. 4.10) whereas no such linearized plots are observed in the case of first-order kinetic equation which clearly suggests that the rate of reaction follows the second order kinetics. The pseudo-second-order parameters for BEN3, BEN5, BENN3, and BENN5 are shown in Table 4.2.



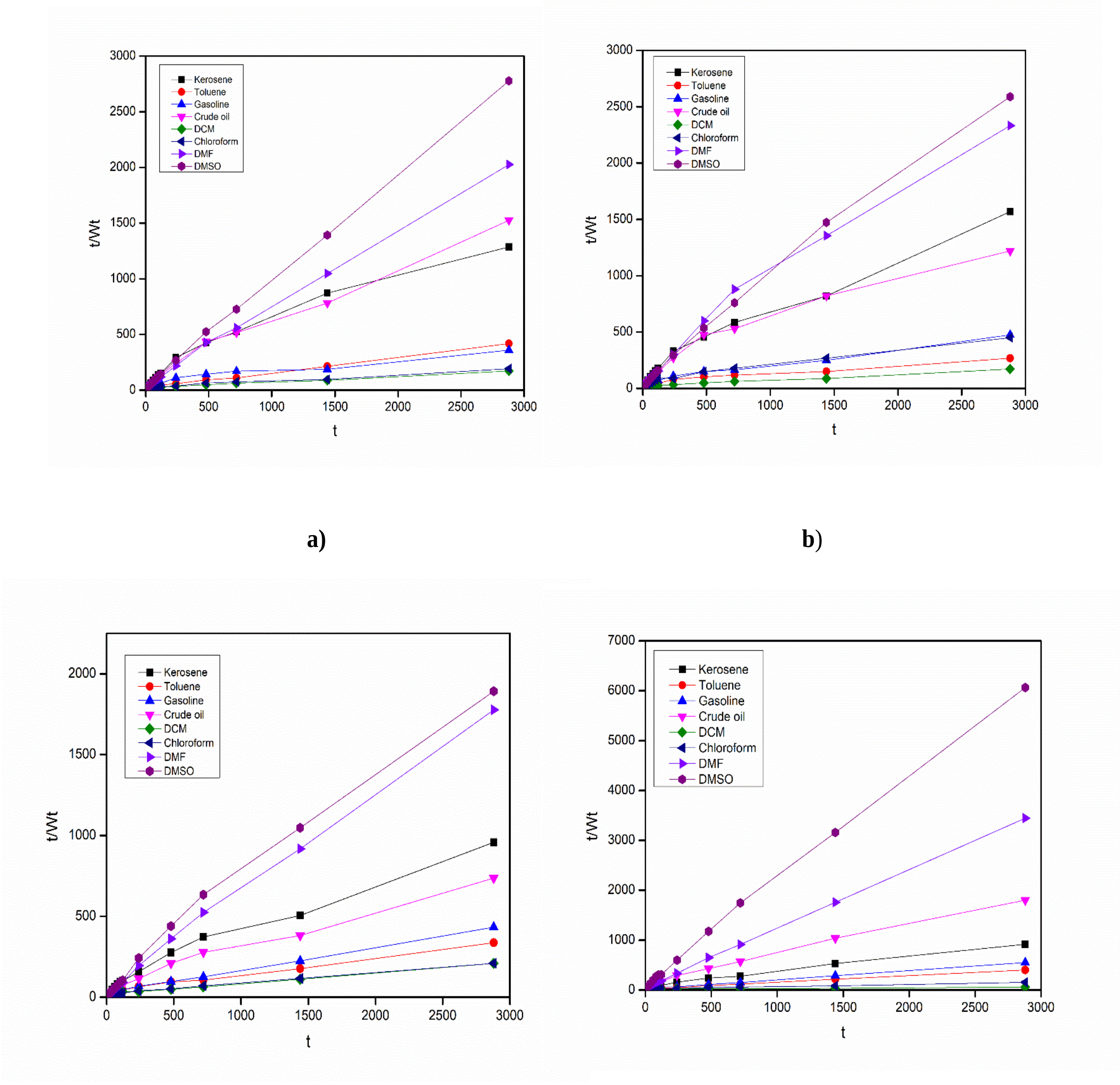
a)

b)

c)

d)

Fig. 4.9 Absorption kinetics for a) BEN3 b) BEN5 c) BENN3 d) BENN5



a) **b)**

c) **d)**

Fig. 4.10 Absorption kinetics showing pseudo-second-order absorption for a) BEN3 b) BEN5 c) BENN3 d) BENN5

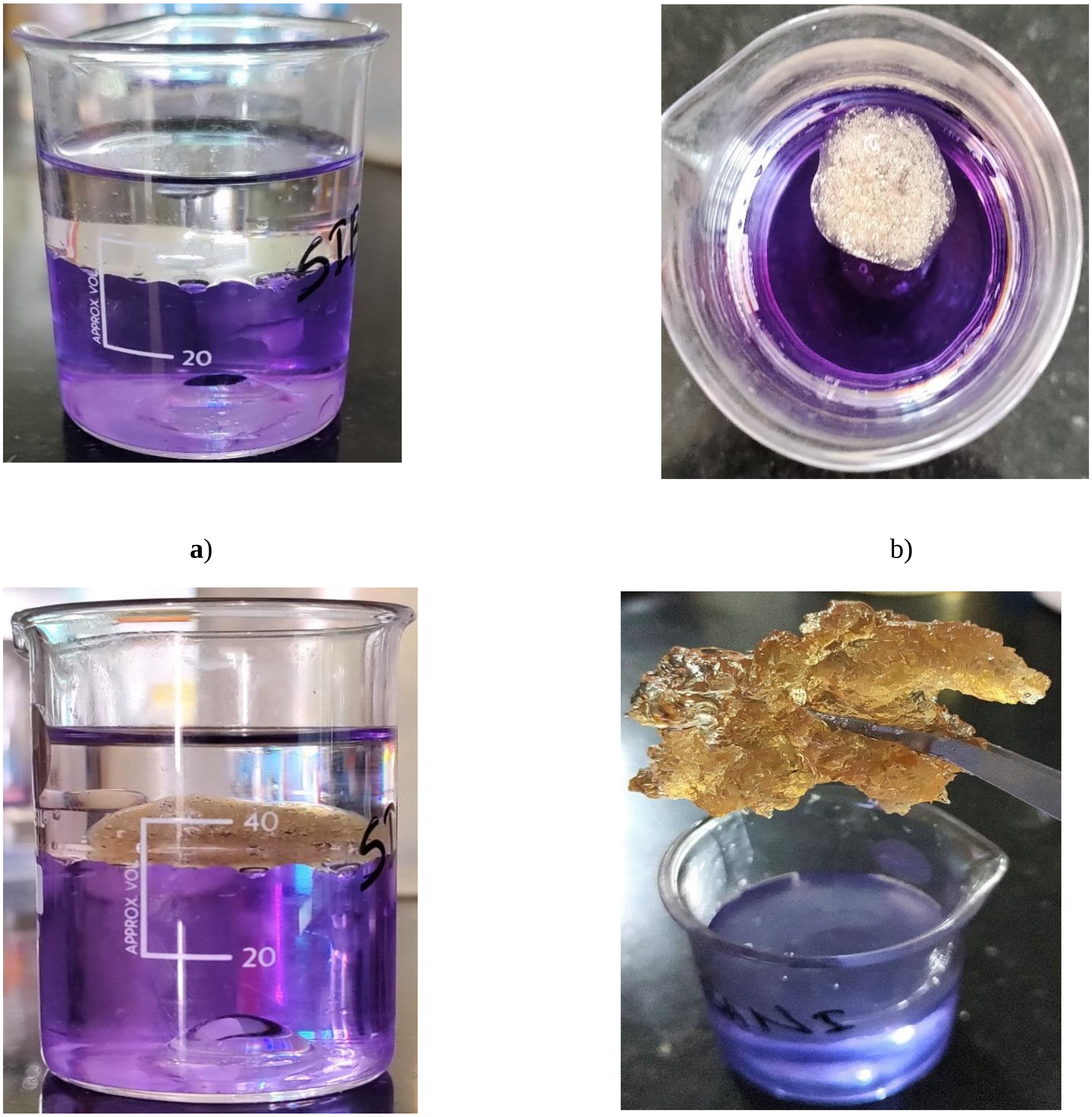
Table 4.2 Pseudo-second-order rate constant and correlation coefficients for BEN3, BEN5, BENN3 and BENN5

Oils/ Solvents	Rate constant of absorption kinetics (K_{2})				R^2 value (Correlation coefficients)			
	BEN3	BEN5	BENN3	BENN5	BEN3	BEN5	BENN3	BENN5
Toluene	9.0X10-4	1.90X10-4	3.26X10-4	9.01X10-4	0.997	0.974	0.994	0.998
Gasoline	2.6X10-4	4.80X10-4	7.10X10-4	1.19X10-3	0.988	0.990	0.998	0.996
Crude Oil	3.32X10-3	1.54X10-3	1.32X10-3	4.39X10-3	0.985	0.986	0.986	0.991
Kerosene	1.70X10-3	2.29X10-3	1.51X10-3	1.92X10-3	0.954	0.977	0.990	0.989
DMF	1.34X10-2	7.43X10-3	1.33X10-2	3.22X10-2	0.998	0.986	0.997	0.999
DMSO	3.27X10-2	1.44X10-2	8.43X10-3	4.45X10-2	0.999	0.995	0.990	0.998
DCM	2.0X10-4	1.9X10-4	2.72X10-4	1.52X10-5	0.986	0.987	0.994	0.991
Chloroform	1.9X10-4	3.9X10-4	2.71X10-4	1.59X10-4	0.974	0.986	0.994	0.986

4.3.11 Selective separation of oils and different organic solvent from the surface of water

The selective removal of oil from water surface as well as stability in oils and organic solvents is another important factor that determines the potential of an absorbent in environmental treatment applications. Fig. 11 and Fig. 12 demonstrates the experimental procedures conducted to determine such selective removal ability of our prepared nanocomposite BENN5 which has shown the best absorption performance in our absorption studies. It was observed that the nanocomposite samples absorbed most of the solvents or oils from the water surface within 30 mins of application leaving behind water in the beaker. Therefore, the prepared nanosorbents have a tremendous potential to be exploited in practical applications of oil spill removal and water treatment.

A) Selective removal of Toluene from Water-Toluene mixture:

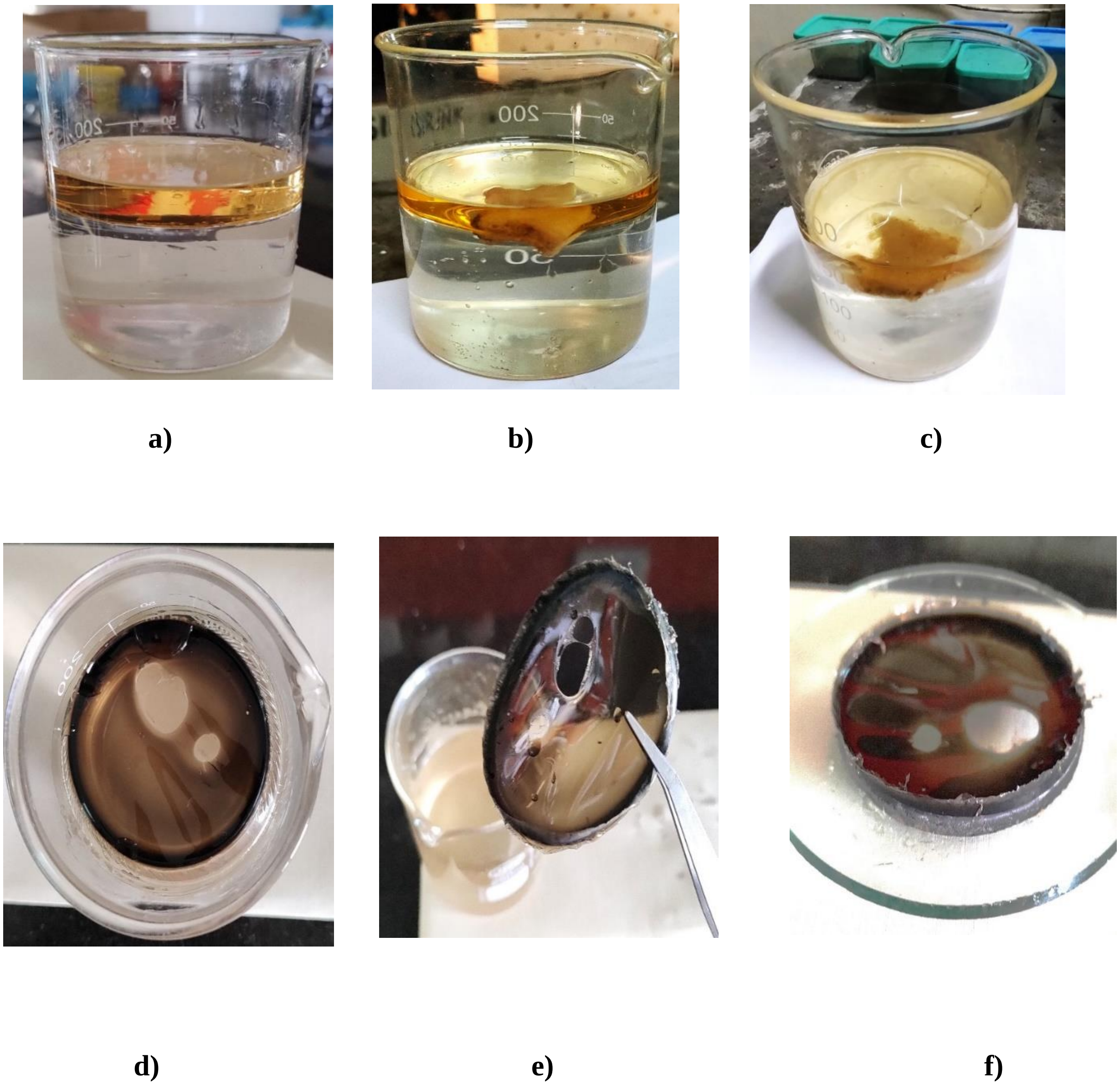


a) b)

c) d)

Fig. 4.11 Sequence of events during selective removal of toluene from water surface by BENN5: a) Oil-Water mixture; Water has been colored blue for observation, b) BENN5 nano composite immersed in the mixture, c) Toluene absorption by BENN5 after 15 min, d) BENN5 sample after absorbing entire toluene from the water surface

B) Selective removal of Gasoline from Water-Gasoline mixture:



a) **b)** **c)**

d) **e)** **f)**

Fig. 4.12 Sequence of events during selective removal of gasoline from water surface by BENN5

4.4 Conclusion

Significantly improved hydrophobic porous EVA/OMMT composites were prepared by incorporating nano clay into poly (ethylene co-vinyl acetate). The nanocomposites thus prepared showed excellent absorbing capacity in various oils and different organic solvents. BENN5 with

5 wt.% filler has displayed the best result in the absorption studies absorbing 40 g of DCM per gram of the composite. SEM study has effectively shown the development of pores by NaCl leaching which has drastically improved the absorption capacity of the composites. The recycle efficiency of the composites has been improved with the addition of OMMT and the composites could be reused for more than 30 absorption-desorption cycles. The nanocomposite could also effectively separate oils and various organic solvents from water surface which has significant practical application in an oil spill and water treatment.

4.5 References

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CHAPTER 5

DESALINATION OF WASTEWATER USING ION EXCHANGE METHOD

5.1. Introduction

Environmental pollution has turn out to be a matter of concern from the last decade and several stringent norms on the disposal of wastes to the environment have come up recently [1]. One of the foremost sources of environmental pollution has been the contaminated water produced from the oil and gas wells during hydrocarbon exploration [2]. This water termed as produced water contains huge quantity of organic and inorganic elements together with various suspended particles, oils and grease [3,4]. Now in order to make this produced water beneficial and support human as well as aquatic life, this water needs to be treated so that the various salts, organic and inorganic elements gets separated from the water. The characteristics of this water produced from the hydrocarbon extraction can be subject to several factors including method of drilling, the geographical location, nature of the reservoirs and the geochemistry of the formation layers [4]. Saline nature of the produced water depends on the formation layer from where extraction is performed. The main constituents which determine salinity in water are sodium and chloride along with potassium, magnesium, calcium and sulphates. Salinity levels in this water various significantly depending on the geographical location as well as depending on the lifetime of the well. Sometimes salinity of produced water has been found to be as high as 2,00,000 mg/l based on the geography and nature of the extracted hydrocarbon [5].

Innumerable technologies have been developed to eradicate these contaminants from the water to protect our water reserves and fulfil the environmental standards. These include precipitation, coagulation, floatation, flocculation, reverse osmosis, evaporation, adsorption etc. Bernabe et al. [6]had prepared poly (acrylamide-co-methacrylic acid) resin and estimated the adsorption capacity for Hg (II), Pb (II), and Al (III) ions. Polyacrylamide and hybrid silica-polyacrylamide aerogels for adsorbing mercury (II) was developed by Hiba et al. [7] and found that the aerogels had economic applications and good reusable characteristics. Hydroxyethyl starch-g-polyacrylamide (HES-g-PAM) was studied and synthesized by De et al. [8] and studied its potential to remove ferrous and copper ions from wastewater. Hamid et al. [9] developed ion exchange resins from polyamidoxime and studied its removal efficiency in case of Th (IV) with respect to pH, time of agitation and dosage. Yasemin et. al [10] investigated and studied the eradication of sulphate ions from water by means of ion exchange resins and reported that the resin could remove 60% of sulphate from the processed water.

From the environmental perspective, it is very essential to remove salinity from the produced water. Although Chemical precipitation has been found to be the most economic method but it has not been used in industrial applications owing to its slow rate of removal and high amount of waste production. Adsorption has been considered to be the most effective technology for desalting wastewater. Amberlyst A21 ion exchange resin was used by Guimaraes and Leao [11] for removing sulphate and found the adsorption capacity to be 11.6 mg sulphate per ml of resin. Duolite A161, Amberlite IRA67 and Duolite A375 anion exchange resins were used for removing Br^-, F^-, Cl^- and SO_4^{2-} ions. These resins were found to reveal similar adsorption characteristics and bring down the ion concentration to acceptable limits. Ion exchange resins in GYP-CIX process reported to reduce sulphate ions from 1500 - 200 mg/l and calcium ions from 500 - 50 mg/l in tailing water [12].

In this study, Amberlite IR 120 is used as the cation-exchange resin to remove Na^+ from water and Amberlite IR 400 was used as an anion exchange resin to remove ions present in water in a batch separation process. The adsorption capacity of the resins was studied in detail using synthetic water having different concentrations of sodium (Na^+) and chloride (Cl^-) ions. The reusability of the resins was also studied for 4 adsorption-desorption cycles and hence this resin system can be used potentially for elimination of salts from waste impure water in water treatment systems.

5.2 Experimental

5.2.1 Materials

Amberlite IR 120 was obtained from sigma Sigma Aldrich and used for the removal of cations whereas Amberlite IR 400 was used as an anion exchanger and obtained from Merck. Specifications of the obtained resins were described in Table1.

Synthetic water was prepared in the experiment by dissolving 3 gm of NaCl (obtained from Merck) in 500 ml of distilled water to make 0.1 M stock solution of sodium chloride. The cation (Na^+) concentration present in the treated water was obtained using atomic absorption spectrometer whereas the anion (Cl^-) ion concentration was measured by the Mohr's method [13].

5.2.2 Adsorption Test

Amberlite IR 400 was supplied in the chloride form as per specification. Therefore. its form was changed from chloride to hydroxide since using the resin in the chloride form may affect its efficiency and lead to corrosion problem in water plants when used in large scale (Shukla & Arya, 2018). Moreover, Amberlite IR 120 supplied in the Na^+ form was also converted to H^+ form for better adsorption efficiency. To convert the Cl^- form of the Amberlite IR 400 to OH^- form, the anion exchange resin was immersed completely in a 1N NaOH solution taken in a beaker and stirred for 45 mins. The process was timely repeated with other fresh dose NaOH solution several times until no Cl^- ions are identified in the solution. In a similar process, the cation exchange resin was changed from Na^+ form to H^+ form by mixing it in a 1N HCl solution for 45 mins quite a few times until no Na^+ ions are detected in the solution. The resins are now washed several times with distilled clean water and subsequently dried in the air for 4 hours at room temperature and then stored in the desiccator for further experimental process.

5.2.3. Optimization of time of contact and adsorption capacity

The adsorption experiment was conducted to investigate the salt removal efficiency of IR 120 and IR 400 where time of contact and the adsorption capacity were optimized. The contact time was optimized by mixing 1g of the resin with 250 ml of 0.1 M NaCl solution and stirred with the magnetic stirrer for 3 hours. 5 ml of the solution was collected every 30 mins of mixing for chemical analysis to study the rate of adsorption. To estimate the adsorption capacity of the resins, the resins were immersed in beakers holding 250 ml of solutions having varying concentrations of Na^+ and Cl^- ions for 45 mins. In order to determine the adsorption capacity of the ion exchange resin a synthetic stock solution was prepared using NaCl with Na^+ and Cl^- being the main ions under study. 1 g of the resin was concocted with 250 ml of the stock solution for a minimum of 45 mins and eventually, the final concentration of the ions was estimated. Reusability is also another important property that determines the efficiency of ion exchange resins. Therefore, the desorption study of the ions from the ion exchange resins was also performed to determine its reusability.

5.2.4 Regeneration of resins

Regeneration capacity is another factor that determines the efficiency of an ion exchange resin. Here the resins were first used in the desalting process using synthetic NaCl solution and the remaining concentration of ions in the synthetic water was determined. For regeneration of the cation exchange resin (Amberlite IR 120), the preloaded resin was concocted with 250 ml of 1N HCl solution for 1 hour after which the ion concentration in the regeneration solution was measured. This process of recharging the resin was repeated upto five cycles. Similarly, to regenerate the anion exchange resin, the resin preloaded with the Cl^- ions was mixed with 1N NaOH solution for 1 hour after which the ion concentration of the regenerated NaOH solution was estimated and the process of recharging the anion exchange resin was repeated for five different cycles.

5.3 Results and Discussion

5.3. Mass of adsorbent and its effect on ion removal capacity

Fig. 5.1 describes the effect of mass of adsorbent on the elimination capacity in the ion exchange process. In this process, 0.4, 0.6, 0.8, 1 and 1.2 g of both the resins were immersed in 100 ml of the stock solutions for 4 hours and then the ion removal percent was calculated. It is apparent from the Fig. 1 that as the mass of the adsorbent rises the ion removal efficiency also increases. This may be due to the elevation in surface area as the mass of the resins elevates. However, the ion removal efficiency stabilizes and becomes almost constant at a particular mass of the adsorbent.

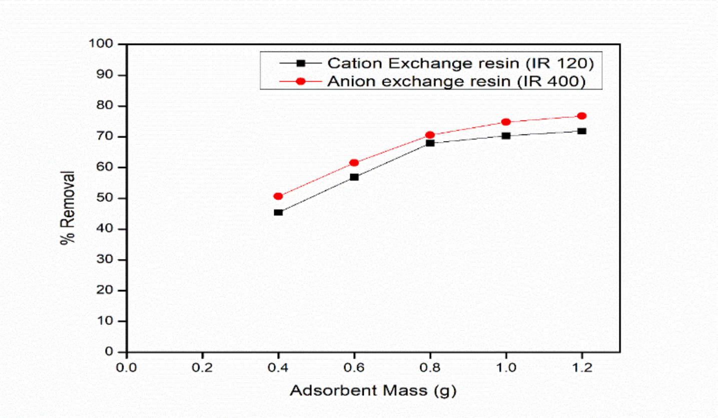


Fig. 5.1 Relation between mass of adsorbent and ion removal capacity

5.3.2 Relation between time of contact on adsorption

Fig. 5.2 delineates the resultant effect of time of contact of the resins on the adsorption of Na^+ and Cl^- on amberlite IR 120 and amberlite IR 400 respectively. The adsorption starts briskly in both the cases within the first 30 mins however the rate of adsorption slows down eventually and a smooth and steady adsorption curve is obtained indicating the equilibrium adsorption state. The equilibrium adsorption is reached in 90 mins for the cation exchange resin and 120 mins for the anion exchange resin.

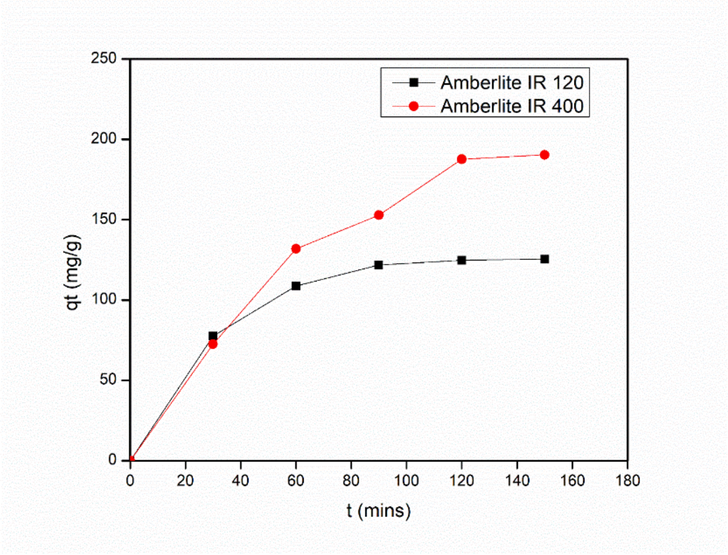
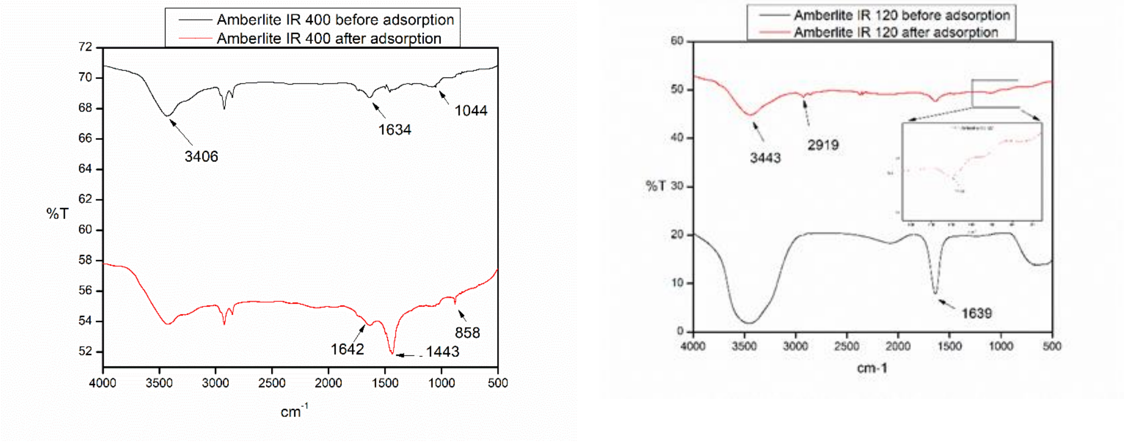


Fig. 5.2 Contact time vs adsorption of Na^+ and Cl^- on Amberlite IR 120 and Amberlite IR 400 respectively

5.3.3 FTIR analysis

To determine the functional groups, present in the Cation exchange resins (Amberlite IR 120) and the anion exchange resins (Amberlite IR 400) before and after adsorption, FTIR analysis was performed. In the FTIR curves of Cation exchange resin (Amberlite IR 120), a strong and sharp peak identified at 3443 cm^{-1} which may be ascribed to the -OH groups. A band present at 2919 cm^{-1} signifies the C-H stretching vibration. The absorption band observed at 1639 cm-1 represents –C=O stretching vibration. The band of sulfonate ($–SO_3 -$) groups which participate in cation exchange are located in the wave range from 1035-1153 cm^{-1} for the amberlite IR 120 resin. The peak intensity visible at 1103 and 1026 cm-1 was changed in the cationic resin after adsorption due to the formation of metal complex of sodium ions and the sulfonate groups existing in the resin [15]. In the FTIR curves for anion exchange resin, a broad peak observed at 3406 cm^{-1} signifies the -OH groups. There is a shift of the stretching vibration peak of –C=O from 1634 cm^{-1} before adsorption to 1642 cm^{-1} after adsorption. The chlorinated anion exchange resin after adsorption shows definite peak at 858 cm^{-1} due to the stretching vibration of C-Cl [16]. The peaks observed at 1443 and 1044 cm^{-1} corresponds to the amine groups present in the anionic resin.

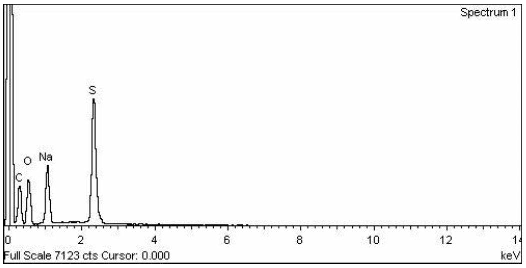


a) **b)**

Fig. 5.3 FTIR curves for a) Amberlite IR 120 before and after adsorption b) Amberlite IR 400 before and after adsorption

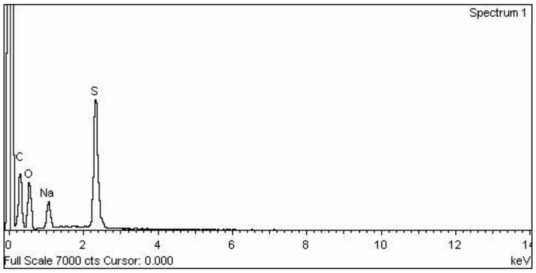
5.3.4 EDX analysis

The EDX spectrum of the cation exchange and anion exchange resins are presented in fig. 5.4. In the EDX spectrum of Amberlite IR 120 it is observed that the initial weight percent of Na^+ ions before adsorption was 3.09 % which has increased to 9.05 % after the cation exchange process. Thus the EDX spectrum indicates the intake of Na^+ ions from the stock solution thus removing these ions from the water. The other major elements present in the resin as observed from the EDX are carbon, oxygen and Sulphur. From the EDX spectrum of Amberlite IR 400, it is observed that the initial weight percent of Cl^- ions before adsorption was 5.72% which has increased to 14.23% after the anion exchange process. Other major elements in the anionic resin as observed from the EDX are carbon and oxygen. From the EDX interpretation it can be concluded that the resin system can be efficiently used in the desalting of wastewater.



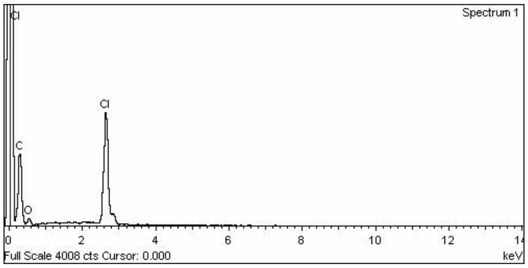
Element	Weight%	Atomic%
C K	43.82	55.57
O K	33.64	32.02
Na K	9.05	5.99
S K	13.5	6.41
Totals	100	

a)



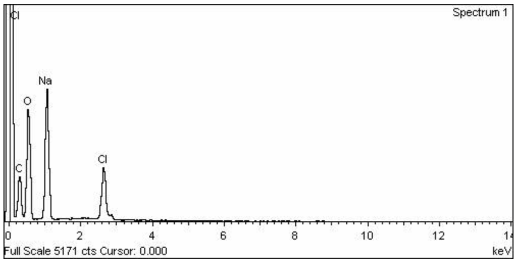
Element	Weight%	Atomic%
C K	49.75	60.78
O K	33.73	30.94
Na K	3.09	2.55
S K	13.43	5.74
Totals	100	

b)



Element	Weight%	Atomic%
C K	77.32	87.38
O K	8.45	7.17
Cl K	14.23	5.45
Totals	100	

c)



Element	Weight%	Atomic%
C K	28.34	37.58
O K	46.83	46.62
Na K	19.1	13.23
Cl K	5.72	2.57
Totals	100	

d)

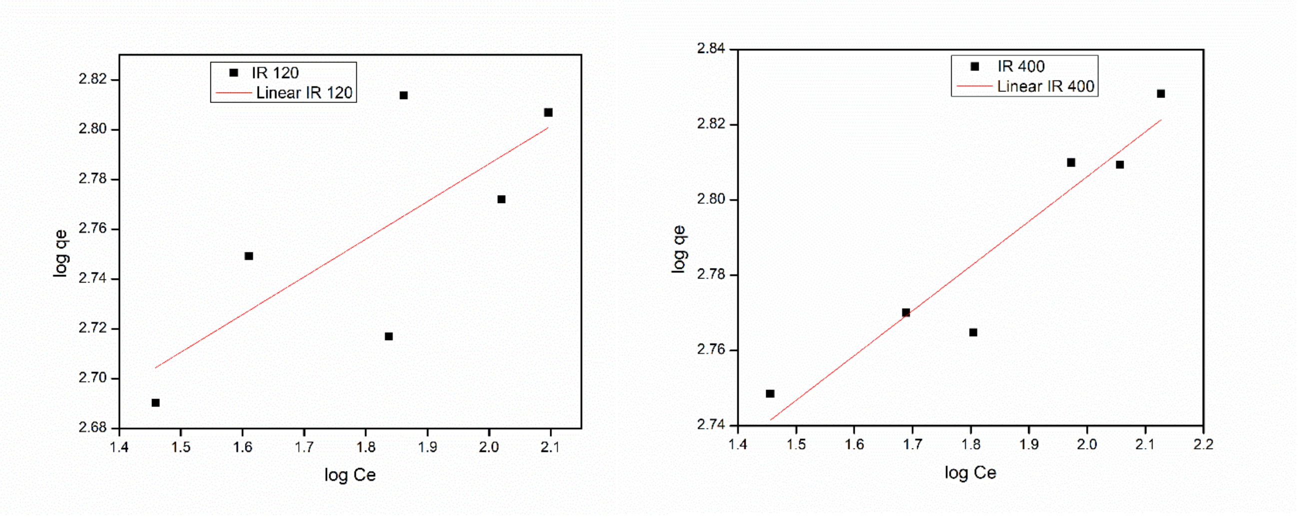
Fig. 5.4: EDX spectrum of a) Cation exchange resin after adsorption b) Cation exchange resin before adsorption c) Anion exchange resin after adsorption d) Anion exchange resin before adsorption

5.3.5 Adsorption isotherms

Freundlich and Langmuir isotherms are interpreted to describe the adsorption process. In Freundlich isotherm various spectrum of binding energy are assumed to exist on the adsorbent surface. Freundlich isotherms were developed by using different concentration of the stock solution with a known constant weight of the adsorbent for 6 hours although it was observed that the equilibrium was obtained in 90 mins in case of cation exchange resin (Amberlite IR 120) and 120 mins in case of anion exchange resin (Amberlite IR 400). Equation 1 represents the Freundlich equation [17]:

$$\log q_e = \log K_f + (1/n) \log C_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where q_e is the equilibrium measure of ion adsorbed by the adsorbent in mg/g. The Freundlich isotherm is an indication of the ease with which the adsorption process occurs. A linear plot of log q_e and log C_e represents the Freundlich isotherm. Fig. 5.5 (a, b) represents the Freundlich isotherms for the adsorption of cations (Na^+) onto IR 120 and anions (Cl^-) onto IR 400 respectively. The values pertaining to K_f and n are derived from the measured slope and intercept of the plot (Table 5.1).



a) b)

Fig. 5.5 Freundlich isotherm for the adsorption of a) Na^+ onto amberlite IR 120 b) Cl^- onto amberlite IR 400

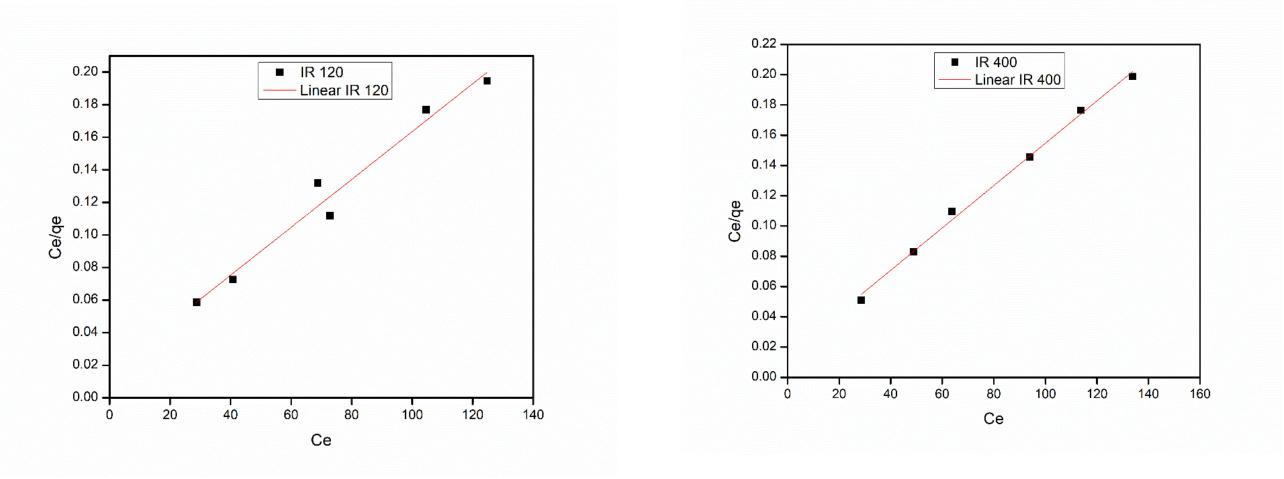
Langmuir model was also applied in the study of adsorption process. Equation 2 represents the Langmuir isotherm:

$$(C_e/q_e) = (1/b\ Q_o) + (C_e/Q_o)\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Where C_e relates to the equilibrium concentration (mg/L) of stock solution. Q_o is a constant that represents the adsorption capacity in terms of (mg/g) and b signifies the energy associated with the adsorption process (L/mg). A dimensional constant equilibrium parameter can be used to modify the Langmuir equation, expressed as equation 3.

$$R_L = \frac{1}{1+bC_o}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Where b represents the Langmuir constant, C_0 is the maximum original salt concentration (mg/L). R_L indicates whether the isotherm is linear, favourable, unfavourable or irreversible. For R_L =1, the isotherm resembles a linear nature, for R_L >1, the isotherm represents an unfavourable nature, for $0<R_L<1$ the isotherm is favourable and for R_L=0, the isotherm shows an irreversible nature. The plot of C_e vs C_e/q_e for the adsorption of Na^+ and Cl^- onto the Amberlite IR 120 and Amberlite IR 400 respectively indicates that the adsorption resembles to Langmuir isotherm (Fig 6). The values of Q_o and b are derived with the slope and intercept of the established plot (Tablea)



a) **b)**

Fig. 5.6 Langmuir isotherm related to the adsorption of a) Na+ onto amberlite IR 120 b) Cl- onto amberlite IR 400

Both Freundlich isotherm and Langmuir isotherm was plotted for the adsorption process. The value of n specifies the favorability of the adsorption process whereas K_f indicates the capacity related to the system. When the magnitude of n lies between 1 and 10 the adsorption process is beneficial [18]. Here the n value for both the cation exchange as well as the anion exchange process lies between 1 and 10 indicating a favorable adsorption. The dimensionless equilibrium parameter (R_L) is also placed between 0 and 1 which further indicates to a favorable adsorption. However, the correlation coefficient value r_f^2 for the Freundlich isotherms are lower than the values of r_L^2 for Langmuir isotherm which indicates that the Langmuir adsorption isotherm are best fitted isotherm for the adsorption reaction of Na^+ and Cl^- ions onto the cation exchange and anion exchange resins respectively.

Table 5.1 Langmuir and Freundlich parameters obtained for the adsorption of Na^+ and Cl^- ions on cation exchange and anion exchange resins respectively

Adsorbents	Langmuir Constants				Freundlich Constants		
	Q_0 (mg/g)	b (L/mg)	R_L	r^2_L	n	K_f	r_f^2
Amberlite IR 120	161.290	4.217	0.004719	0.985	6.622	301.995	0.776
Amberlite IR 400	233.644	3.057	0.006499	0.995	8.403	369.828	0.88

5.3.6 Adsorption kinetic studies

The kinetic data were processed to comprehend the kinetics of the adsorption process and determine the order of the rate constant. Both pseudo first order and second order models were employed to the kinetic data. The first order kinetics has the following differential form:

$$\frac{dq_t}{dt} = K_1(q_\infty - q_t) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

where q_t is the quantity of ions adsorbed by the resin (mg/g) at time t, and q_∞ is the quantity of the ions adsorbed after adsorption reaches the equilibrium (mg/g) .

Integrating Eq. (4), we get,

$$\log (q_\infty/(q_\infty - q_t) = K_1/2.303t \ldots\ldots\ldots\ldots\ldots\ldots(5)$$

After rearranging, equation (5) can be written as

$$\log(q_\infty - q_t) = \log(q_\infty - K_1)/2.303t \ldots\ldots\ldots\ldots\ldots\ldots(6)$$

If the graph obtained by a plot between log (q_∞-q_t) vs t represents a straight line the adsorption process follows first-order kinetics.

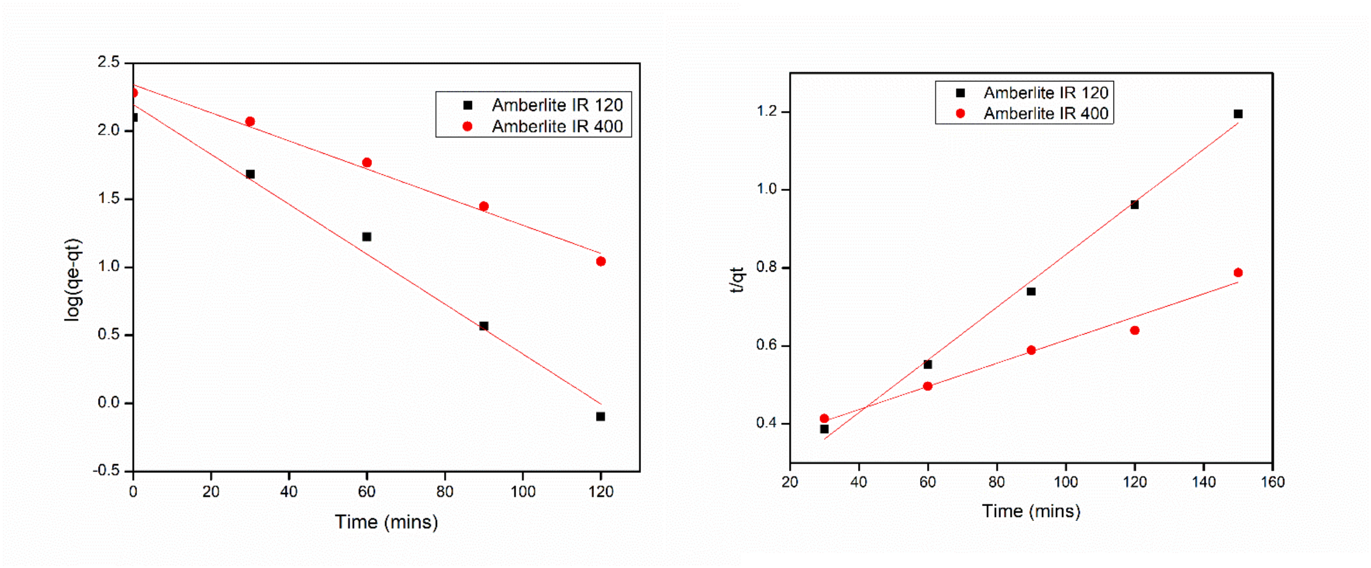
The second order kinetics has the following differential form:

$$\frac{dq_t}{dt} = K_2(q_\infty - q_t)^2 \ \ldots\ldots\ldots\ (7)$$

Integrating Eq. (7), we get,

$$\frac{t}{q_t} = \frac{1}{K_2 q\infty^2} + \frac{1}{q\infty}t \ \ldots\ldots\ldots\ldots\ldots\ (8)$$

If the graph attained by a plot between t/q_t vs t is a straight line, we can conclude that the absorption process follows second-order kinetics.



a) b)

Fig. 5.7 a) Pseudo first order adsorption kinetics

b) Pseudo second order adsorption kinetics

The first order and the second order parameters as obtained from the adsorption kinetic curves a) and b) for cation exchange and anion exchange resins are tabulated in the Table 5.2. From these parameters it is clear that both the adsorption process follows the second order kinetic model related to the adsorption of Na^+ and Cl^- ions onto amberlite IR 120 and amberlite IR 400 respectively as the correlation coefficient for the second order model is on the higher side than the first order. It is also evident that q_∞ value pertaining to the second order is higher than the first order values which indicate that the second order kinetic model precisely fits the desalting process.

Table 5.2 Parameters involved in the first-order and second-order kinetics for the applied cation exchange resin and anion exchange resin.

Adsorbent	First order Kinetic model			Second Order Kinetic model		
	q_∞	K_1	r_1^2	q_∞	K_2	r_2^2
Amberlite IR 120	8.986	1.22×10^{-4}	0.926	147.929	2.87×10^{-4}	0.998
Amberlite IR 400	10.396	6.88×10^{-5}	0.934	336.7	2.77×10^{-5}	0.978

5.3.7 Regeneration study

Fig. 8 represents the reusability nature of the resins. It could be concluded from the adsorption-desorption study that the adsorption capacity of the resins remains almost unchanged even after 5 adsorption-desorption cycles. This indicates that the resin system has excellent reusability character and the same system can be operated several times without much hindrance to its adsorption desorption performance.

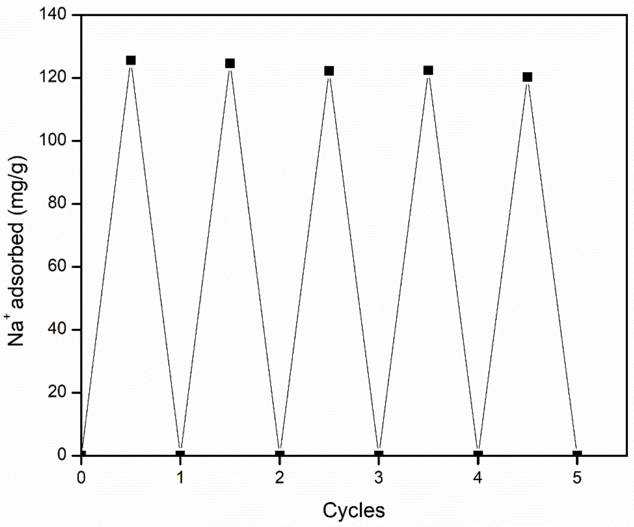


Fig. 5.8 Reusability study of Amberlite IR120 for various adsorption-desorption cycles

5.4 Conclusion

Integrated cation exchange and anion exchange resin system has been found to have excellent potential for desalting of wastewater. Here Amberlite IR 120 and Amberlite IR 400 showed excellent adsorption measurements of 161.29 mg/g and 233.64 mg/g respectively. The equilibrium data on adsorption were interpreted using Langmuir and Freundlich isotherms. The parameters attained from these isotherms indicate that the Langmuir model precisely fits to the adsorption process and there is close agreement with the experimental and the model data. The kinetic study reveals that the adsorption process behaves according to the second order kinetic model having R^2 value close to 0.99 for both the cation exchange and the anion exchange resins involved in the system. The cation exchange resin could be effectively regenerated by the use of regeneration solution of 1N HCl solution whereas the anion exchange resin could be effectively regenerated by the use of regeneration solution of 1N NaOH. The resin system could also be reused for multiple adsorption desorption cycles which further enhances the efficiency of the system. Hence this system has the potential to be used for removing salts from wastewater and therefore, finds in application in advanced fields of environmental protection like wastewater treatment**.**

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CHAPTER 6

CONCLUSION AND FUTURE SCOPE

6.1 Overall Conclusion

The thesis provides an elaborative summary on contaminated water and deals with the problem of water scarcity. This unabated water scarcity problem directly impacts human life and various forms of flora and fauna. One of the darker sides of rapid industrialization is the discharge of various pollutants into the water making it unsuitable for use one. One of the principal sources of contaminated water is the produced water coming out during drilling operations during onshore and offshore petroleum extraction since this water contains oils and other minerals as the primary pollutants. Moreover, oil spills in the marine environment are another associated problem that contaminates the marine environment and leads to detrimental effects on the land and terrestrial flora and fauna. The basic aim of this thesis is to study and develop a polymer-based absorbent that can eradicate the oils as well as organic solvents from the contaminated water by a green method of mixing ie. melt blending. Various factors like hydrophobicity, absorbate and absorbent interaction, pore size etc. are the main driving force in selecting the polymer material and other additives which can perform the adsorption phenomenon effectively. Moreover, a suitable ion exchange system is required for the desalination purpose, thus making the contaminated water oil free reducing the salinity to acceptable limits so that the water could be discharged off to the environment safely and also can be utilized for various beneficial purposes. The most challenging part of the work is to maintain the stability of the polymeric absorbent by means of curing at an optimum temperature without compromising the overall properties. Another significant part of the work is the reusability of the absorbents and the resins. From the environmental as well as economic point of view, the absorbents and the resins should have good recycling characteristics to be applied for water treatment operations. The effect of sodium chloride porogen on the absorbent was studied in detail and found to enhance the overall absorbing characteristics of the absorbents. The effect of nanoparticles such as organically modified montmorillonite clay on the characteristics of the polymer absorbent was studied in detail. The ion absorbing capacity of the ion exchange system in the desalination of water was also investigated thoroughly.

The significant features that can be derived from the present work are summarized below.

In the first study, elastic and hydrophobic reusable crosslinked Poly (ethylene-co-vinyl acetate) (EVA) copolymer modified with cetyl alcohol-based sorbent has been successfully prepared. In this first investigation on the oil absorption capacity of Poly (ethylene-co-vinyl acetate), a novel crosslinked Poly (ethylene-co-vinyl acetate) based absorbent was prepared by the grafting of maleic anhydride and cetyl alcohol in the presence of benzoyl peroxide. The melt mixing was carried out in the Brabender mixture at 120^0C. The grafted polymer was post-cured in the hot air oven at 100^0C for 24 hours. The post-cured sorbent showed excellent absorption capacity in Toluene (2200%), Gasoline (1720%), Crude Oil (1105%), and Kerosene (390%). The absorption properties of this hydrophobic composite remain stable even after 10 absorption/desorption cycles with absorption capacity remaining constant. The wettability study in terms of contact angle shows good hydrophobic character. EVA contains both hydrophobic ethylene groups as well as hydrophilic vinyl acetate groups. Due to the presence of hydrophobic ethylene groups, weaker adhesion interaction occurs between the ethylene groups and the water surface, and hence the hydrophobicity increases. With the incorporation of CA in the absorbents, the contact angle increases from 60.8^0 to 123^0 indicating an increase in hydrophobic nature.

In the second study, an attempt has been made to prepare porous crosslinked poly (ethylene-co-vinyl acetate) polymer (C-EVA). The porous C-EVA was prepared by grafting of maleic anhydride and cetyl alcohol onto the polymer backbone with addition of NaCl as porogen in the brabender mixture at 120^0C and 80 rpm. This was followed by leaching of NaCl with water extraction to generate a highly porous polymer structure which was evident from its SEM micrographs. The polymer was found to have excellent swelling capacity in various oils and organic solvents with 27.39 g/g in case of toluene and also showed good selective absorption capacity. The reusability of the synthesized polymer was studied and it was found that it could be reused for more than 30 absorption desorption cycles without undergoing much change in its absorption capacity. Although the synthesized polymers show hydrophobic nature, however it was observed from the contact angle measurement that as the NaCl porogen concentration was increased there was a decline in the contact angle. This could be attributed to the fact that with the addition of NaCl, larger pores are formed on the polymer surface which allows liquid drops to diffuse through them, thus elevating the wetting characteristics of the polymer. In the SEM images, significant pores are visible which are formed as the NaCl particles are pulled out from the polymer matrix by leaching. The pore size increases from 107 µm to 136 µm as the porogen concentration increases in the adsorbents.

In our third study, we studied the effect of incorporating nanoclay in the polymer matrix. poly(ethylene-co-vinyl acetate was blended with organically modified montmorillonite (OMMT) nanoclay following a green pathway by melt blending in the Brabender plasticoder. The nanocomposites thus prepared were found to have excellent absorption capacity in various oils and organic solvents. To further increase the absorption capacity of the nanocomposites NaCl was added as porogens in the melt mixing process, which was followed by leaching of NaCl in water to generate a highly porous nanocomposite material. The absorption test also revealed excellent absorption efficiency in various oils and organic solvents with absorption capacity of 40 g per gram of absorbent in dichloromethane (DCM) and 9 g per gram in gasoline. The nanocomposites also demonstrated excellent recycling capability and could be reused for more than 30 absorption-desorption cycles.

In our fourth investigation, a novel integrated ion exchange resin system has been developed to remove salts from waste water. Amberlite IR 120 and amberlite IR 400 has been utilized as the cation exchange and the anion exchange resins respectively which exchanges the cations and the anions from the wastewater and consequently makes the water free from salts. The adsorption isotherms for the process were studied for both Langmuir and Freundlich model and the adsorption kinetics were established. Amberlite IR 120 and amberlite IR 400 showed excellent adsorption capacity of 161.29 and 233.64 mg/g respectively. The regeneration of the resins was also studied and it was found that the resin system could be applied and regenerated multiple times in the desalting process.

Thus, it can be concluded that poly (ethylene-co-vinyl acetate) based adsorbents can be used as an excellent candidate for oil adsorption. Since poly(ethylene-co-vinyl acetate) (EVA) is an important widely used commercial synthetic material, the synthesis of high swelling capacity and reusable absorbent proposes its application in a new field of oil absorption. In addition to its high absorption capacity, its reusable nature makes it a potential candidate for use in various practical industrial fields such as water treatment and environmental cleanups.

6.2 Future Scope

The thesis discussed a systematic investigation into the development and modification of poly (ethylene-co-vinyl acetate) based absorbent employing various additives (porogen) and nano-fillers. Advancement in the field of polymeric absorbent particularly poly (ethylene-co-vinyl acetate) based absorbent has a bright future ahead of it. However, both the application and optimization aspects have a lot of room for further investigation. Below are a few key points to consider.

I. In laboratory research, the poly (ethylene-co-vinyl acetate) based absorbents have shown significant oil adsorption characteristics and improvement in a variety of characteristics. However, further extensive research is required before the material can be commercialized and used in a practical oil spill environment.
II. Extensive studies on increasing the stability of the absorbents are another scope of improving the efficiency of the absorbents.
III. Although there has been a significant improvement in the recycling capability of the absorbents, the scope for further improvements in recycling characteristics still exists.
IV. The synergistic impact of several types of nano-fillers on the characteristics of the absorbent might be explored.
V. Studies on blending various waste materials with poly (ethylene-co-vinyl acetate) absorbents can also be attempted to prepare composites having excellent absorption efficiency.
VI. Desalination studies on the contaminated water using different ion exchange resin systems could be made to further upgrade the desalting capacity of the resin system.

Therefore, it may be anticipated that investigation into novel polymeric absorbents may lead to new perspectives on global challenges and may be effective as a replacement for traditional waste water treatment process, broadening the scope of applications.