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

SYNOPSIS SUBMITTED BY

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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.

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.

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.

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.

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.

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

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.

Biological treatment: Biological treatment is the application of microbial metabolism for separation of dissolved colloidal organic contaminants from the wastewater. These applications have 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 have 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.

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.

Absorbents: Absorption is a mechanism of transferring pollutants from one phase to another, which necessitates additional methods for removal from the environment. Absorptions 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 absorbent 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 develops between the adsorbate surface and adsorbent surface.

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** which provides a detail study on 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

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.

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