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Wastes Agricultural Biomass: a Potential Adsorbents in Oil Removal from Water

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بسم الله الرحمن الرحيم

صدق الله العظيم

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الاهداء

بدأنا بأكثر من يد وقاسينا اكثر من هم وعانينا الكثير من الصعوبات وها نحن اليوم والحمد لله نطوي سهر الليالي وتعب الايام وخلاصة مشوارنا بين دفتّي هذا العمل المتواضع.

الى منارة العلم الذي علّم العالمين الى سيّد الخلق الى رسولنا الكريم سيدنا محمد (ﷺ).

الى من سعى وشقى بأنعم الراحة والهناء الذي لم يبخل بشيء من أجل دفعي في طريق النجاح الذي علمني ان ارتقي سلم الحياة بحكمة وصبر الى والدي العزيز.

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(كن عالماً فأن لم تستطع كن متعلماً، فأن لم تستطع فأحب العلماء فأن لم تستطع فلا تبغضهم)

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طلبة البحث

اقرار المشرف وترشيح رئاسة قسم التقانة الاحيائية

اشهد بان اعداد هذا البحث الموسوم:

Wastes Agricultural Biomass: a Potential Adsorbents in Oil Removal from Water

الذي قدمه الطالبات/الطلبة (زهراء سلمان كاظم، مروة حسين صادق، ازهار رعد سعد، زينب اسماعيل ابراهيم، احمد يعقوب يوسف، محمود عبد الكريم عبد) قد جرى تحت اشرافي في قسم التقانة الاحيائية/كلية العلوم/جامعة ديالى، وهو جزء من متطلبات نيل درجة البكالوريوس في علوم التقانة الاحيائية.

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بناء على التوصيات المتوافرة ارشح هذا البحث للمناقشة

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اقرار لجنة المناقشة

نشهد باننا اعضاء لجنة المناقشة، اطلعنا على هذا البحث الموسوم:

Wastes Agricultural Biomass: a Potential Adsorbents in Oil Removal from Water

الذي قدمه كلا من الطالبات والطلبة (زهراء سلمان كاظم، مروة حسين صادق، ازهار رعد سعد، زينب اسماعيل ابراهيم، احمد يعقوب يوسف، محمود عبد الكريم عبد) في محتوياته وفيما لها علاقة به، ونعتقد بانهم جديرون بالقبول لنيل درجة البكالوريوس في علوم التقانة الاحيائية بتقدير (   ).

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مصادقة رئاسة قسم التقانة الاحيائية

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Abstract

Water is a vital tool in the lives of people who both benefit from its use and are affected by its abuse and unpredictability. Consumption of contaminated water puts our life and livelihoods at risk because there is no replacement for water. There are many ways in which water intended for human use can be contaminated. Organic pollutants include hydrocarbons (oils), dyes, textile waste, tanning, pharmaceutical waste, inorganic pollutants such as heavy materials and biological pollutants such as certain microorganisms and parasites. Agricultural waste primarily contains cellulose, lignin and hemicellulose. Agricultural waste has loose and porous structures and contains functional groups such as the carboxyl group and the hydroxyl group, so that it can be used as a biological adsorption material. Agricultural waste benefits from a wide variety of sources, low costs and renewable energy.

Keywords: Wastewater, agro-waste, adsorption, oil.

TABLE OF CONTENTS

LIST OF FIGURES

CHAPTER ONE

WATER POLLUTION

1. Introduction

Water is the most vital component of life's origin. Existence is not possible without water. However, it has been polluted with numerous poisonous, inorganic industrial contaminants, resulting in a variety of problems such as unhealthy human use and irrigation operations. This leads to water scarcity as it limits its supply to humans and the environment. Water contamination is the key cause behind the water crisis. It should not be polluted below a certain level for use for irrigation and drinking water purposes. The problem of social justice is exacerbating the water crisis; poor people are more likely to lack clean water and sanitation than rich people in similar areas (Singh et al., 2020).

Up to 9% of all diseases and 6% of all deaths could be prevented by enriching water health, hygiene and sanitation worldwide. Apart from the global water-borne disease crisis, global water quality is affected by chemical contamination from farming, manufacturing, urban and mining activities. Some environmental contaminants have significant health consequences, although many others have long-term effects that are not well known. More than 40,000 water bodies in the U.S. currently have an EPA definition of "impaired" that indicates that they can not sustain a healthy environment or meet water quality requirements. Water pollution is the contamination of water by the accumulation of a material that can cause damage to humans and to wildlife (Dwivedi, 2017).

Pollutants arrive in water supplies from various types of point sources that are easily recognizable and relatively small, or non-point sources that are larger and more diffuse. Point emission sources include farms in an animal factory that produce large numbers of livestock and high densities, such as cows, pigs and chickens. Collective drainage systems that bring together street sewage and storm water runoff that handle drainage may be a major point pollutant source. Storm water runoff can overload sewer capacity during heavy rainfall, cause it to back up and directly spill untreated sewage into surface waters (Sophocleous, 2002). Agricultural lands, towns and abandoned mines are non-point sources of pollution. Rainfalls flow through the soil and through the soil for the accumulation of pollutants from farm fields and lawns such as herbicides, pesticides and fertilizers; tar, animal waste and industrial road salt; and acid and radioactive materials from abandoned mines. This waste is then passed to the soil and to groundwater (Figure 1.1) (Dwivedi, 2017).

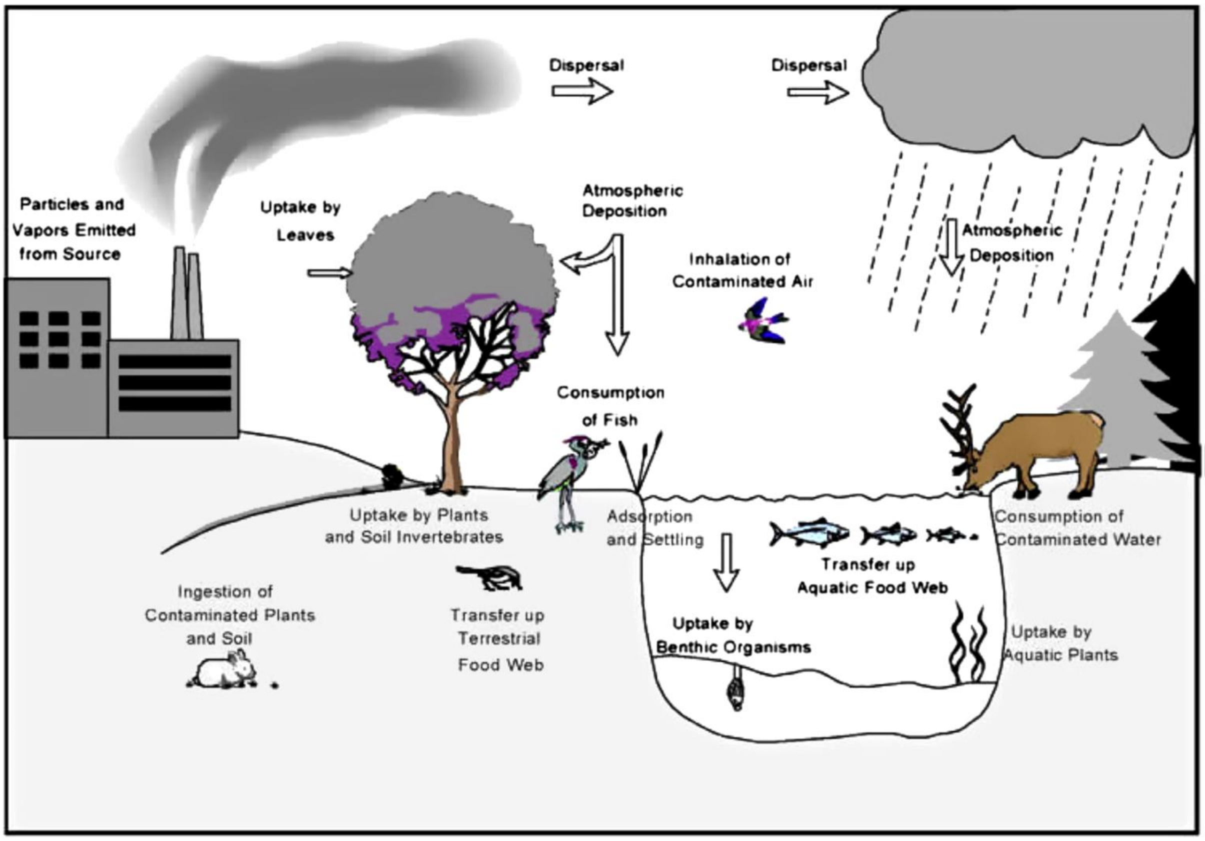

Figure 1.1 Transportation of chemicals in the environment. Chemicals are released from the source (in this case the factory smoke stack) and dispersed throughout the area (adapted from Schweitzer & Noblet, 2018).

1.1. What is water pollution?

Water pollution is the presence of chemical, physical or biological components or factors that cause the water body to be polluted by any beneficial use. The amount of pollution required to harm the water source is highly dependent on the type of water body, its location and the types of beneficial uses it serves. Water deemed unfit for human consumption can be ideal for other uses, such as agriculture, irrigation or recreation. While some natural events can cause water pollution, the emphasis here will be on the anthropogenic sources of pollution, that is, pollution from human activities (Schweitzer & Noblet, 2018). Figure 1.2 shows an oil slick in the Tigris River caused by an act of sabotage to one of Iraq’s oil pipelines.

Figure 1.2 An oil spill in the Tigris River caused by an act of sabotage to one of Iraq's oil pipelines (adapted from https://www.toxicremnantsofwar.info/iraqs-continuing-struggle-with-conflict-pollution/).

In waters which receive waste discharges, whether by design or by accident, one or more of these variables may come to lie outside the limits which can be tolerated by one or more of the species which live there, and consequently the biological characteristics of the water are altered. Water pollution is an undesirable change in the state of water, contaminated with harmful substances. Polluted water is not only unsafe for drinking and other consumption purposes, but it is also unsuitable for agricultural and industrial uses (Sadek et al., 2017).

With expansion of the oil business the level of environmental pollution risk is inevitably increasing. Ruptured oil pipelines, ship collisions or groundings, overfilling of gas tanks, bilge pumping from ships, leaking underground storage tanks, oil-contaminated runoff from streets and parking lots during rain storm are considered from the environmental oil pollutions (Svanberg, 2006). But when oil spills in water, toxic chemicals from the oil mix with the water and stay there for a long time. Cleanup and recovery from an oil spill is difficult and depend upon many factors, including the type of oil, the temperature of the water (affecting evaporation and biodegradation) and the types of shorelines and beaches involved (George & Shah, 2003).

1.1.1. Sources of water pollution

Water pollution may occur from two sources:

1. Source point
2. Origin of non-point

Point sources of pollution are those with a direct, identifiable source. Types include pipes connected to the warehouse, oil spills from the truck, chemical effluents. Pollution sources include wastewater effluent (both municipal and industrial) and storm sewer discharges, most of which affect the area nearby. Whereas non-point sources of pollutants are those originating from various sources of origin and the number of ways in which chemicals enter groundwater or surface water and arrive in the atmosphere from different non-identifiable sources. Examples include runoff from farm fields, industrial waste, etc. Occasionally, waste that reaches the atmosphere in one location has an impact hundreds or even thousands of miles away. This is known as cross-border emissions. One example is the radioactive waste that passes from nuclear reprocessing plants to neighboring countries across the oceans. Water pollutants may be (a) organic and (b) inorganic water pollutants (Singh & Gupta, 2016; Walker et al, 2019).

1.1.2 Aim of the project

The aim of this project was to illustrate the negative effects of oil spills on aquatic environments and addressed the general methods used for oil removal, in particular the biological methods using local plants and agro-waste plants.

1.2. Water pollutants

Water is the most vital component of life's origin. Existence is not without water It's true. However, it has been polluted with numerous poisonous, inorganic industrial contaminants, resulting in a variety of problems such as unhealthy human use and irrigation activities. This leads to water scarcity as it limits its availability to humans and the environment. The problem of social justice is compounding the water crisis; poor people are more likely to lack clean water and sanitation than rich people in similar areas. Up to 9% of all diseases and 6% of all deaths could be avoided by enriching water health, hygiene and sanitation worldwide. Apart from the global water-borne disease crisis, global water quality is affected by chemical contamination from farming, manufacturing, urban and mining activities. Some chemical pollutants have serious health effects, while many others have long-term effects that are not well known (Singh et al., 2020)

1.3. Classification of water pollutants

The various types of water pollutants can be classified into the following major categories: (1) Organic pollutants, (2) Pathogens, (3) Nutrients and agriculture runoff, (4) Suspended solids and sediments, (5) Inorganic pollutants (salts and metals), (6) Thermal pollution, (7) Radioactive pollutants, and (8) Nanopollutants (Ghangrekar & Chatterjee, 2018) (Figure 1.3).

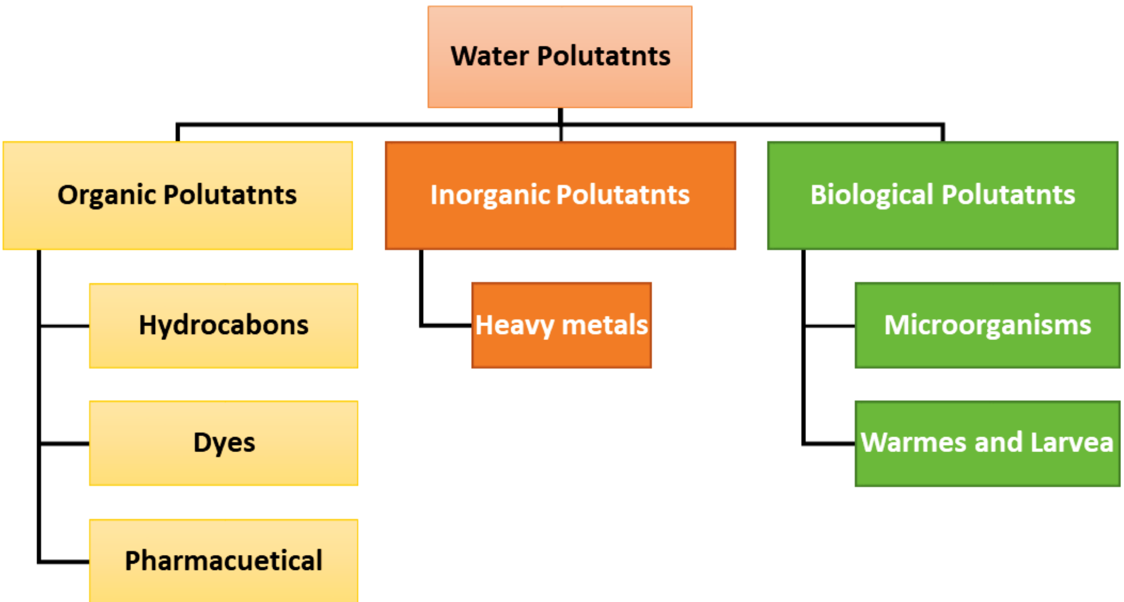

Figure 1.3 Classification of water pollutants.

1.3.1. Organic pollutants

1.3.1.1. Hydrocarbons (oils)

With industrial growth, there is an rise in the amount of oil used, but numerous technological and management innovations have lagged behind-and there are other factors that are not ideal and bring a lot of oil into the water, causing pollution. The treatment of oily wastewater sources is very large, as oil in the oil industry, oil refining, oil storage, transportation and petrochemical industries produce a lot of oily wastewater in the production process. Oily wastewater pollution is mainly manifested in the following aspects (Yu et al., 2017):

1) Affecting drinking water and groundwater resources, endangering aquatic resources;
2) Endangering human health;
3) Atmospheric pollution;
4) Affecting crop production;
5) Destructing the natural landscape, and even probably because of coalescence of the oil Burner safety issues that have arisen.

In view of oily wastewater pol-lution background China provides a maximum permissible emission of 10 mg / L of oily wastewater. In today's field of environmental engineering, oily wastewater treatment is desperately needed. Domestic and international research institutions have continuously researched in-depth and debated strategies for the treatment of oily wastewater, with the purpose of extracting significant quantities of oil, taking into account the elimination of dissolved organic matter, suspended solids, soaps, pH, sulphide, ammonia, etc (Yu et al., 2017).

Oil properties

This research was conducted to investigate the sorption activity of two separate types of oils: crude oil and diesel oil. Crude B oil produced by Alex Petroleum Company has a specific gravity at 60/60 ° F (D1298) of 0.878, viscosity = 17.18 Cs and API gravity equal to 29.66. The higher API value (> 10) means that the oil is less concentrated and floats on the surface. At the other hand, diesel oil has a density of 15oC = 0.82g / cm3 and a viscosity of 12.8 Cs. By fact, when oil spills, lighter hydrocarbons begin to evaporate, resulting in an increase in oil viscosity. This phenomenon is rapidly occurred before any possible clean-up process can take place . So, in order to minimize experimental error resulted from this situation, oil

samples were placed on a tray (in a layer of a 5 mm thick) and was situated in open air for 1day weathering (weight loss: 21.78%) and 7d weathering (weight loss: 47.47%) (Hussein et al., 2013; Santos et al., 2014).

The fate of crude oil spills

Crude oil hydrocarbons are naturally occurring sub-positions derived from marine algae laid down over millions of years. These are often made of compounds with varying solubility , stability and biodegradability susceptibility. Spilled oil includes aliphatics (such as alkanes and al-kenes) and aromatics that are susceptible to degradation and asphalt fraction with double covalent bonds and aromatics with more compact rings that are more resistant to biodegradation. For order to effectively address the oil spill, it is important to identify the oil hydrocarbons and forecast the fate and the short-term and long-term actions of the oil spills. In addition to occasional large-scale spills that have a major impact on shorelines and habitats, numerous smaller spills occur annually on habitats and waterways causing acute and chronic toxicological effects on flora and fauna. If an oil spill enters the marine system, it is subjected to a range of compositional changes influencing its physical and toxic properties. Most harmful and volatile elements are re-moved by evaporation, while a small percentage of them are oxidized by UV radiation in sunlight. Many toxic compounds with low molecular weight are dissolved in water and rapidly degraded. Some of them attach to the small particles in the water and settle down to the bottom (Atlas & Hazen, 2011; Board & National Research Council, 2013).

The environment impacts of crude oil spills

Crude oil spillage (Figure 1.4) may have harmful impacts on both water and soil habitats. Lakes, rivers and wetlands have important resources and marine ecosystems that can be endangered by oil spills. The lethal and sub-lethal effects of petroleum hydrocarbons on fish have been identified. Abnormal neuron growth, genetic damage, physical deformities as well as changes in biological processes such as feeding, reproduction and migration are examples of adverse effects. Seabirds are also obvious victims of hydrocarbon spills. Only 10 ml of oil slick will affect the microstructure of the feathers of birds and lead to a lethal reduction in thermoregulation. The negative effects of oil contamination on shellfish, turtles, and some coastal vertebrate species such as sea ducks and otters have been also reported (Chang et al., 2014; Saadoun, 2015; Yu et al., 2017).

Figure 1.4 Pollution of water by oil spill (adapted from https://phyohankyaw19.wordpress.com/category/pollution/).

1.3.1.2. Dyes (Textile and Tannery)

The tannery industry is considered to be the most polluting activity due to the wide range of chemicals used during the conversion of animal skins into leather. Chromium salts, phenols, tannins, organic matter, among other products, are constantly released to the environment in tannery wastewater. Such contaminants pose environmental threats to marine life and human health (Chandra et al., 2011; BORRELY et al., 2019).

In China, high concentrations of NH4-N and Ge were identified as impacts and residues for the local environment and human health. Pathogenic and non-pathogenic bacteria are part of the organic matter of the effluent (coliforms, anaerobic spore-forming bacilli. Streptococci, Staphylococci, etc) (Yadav et al., 2016). There are more than 3,000 tanneries in India and most of them (nearly 80 per cent) are made in chrome tanning. Health risks linked to this manufacture have been shown in Figure 1 and have been discussed by numerous scholars. Brazil is also a major exporter of blue-leather tanning. Several attempts have been made by various countries to minimize environmental and human health threats because this operation is very significant to the economy and the positive impacts of the successful interventions have been discussed during the discussion segment (Tarantola, 2014; BORRELY et al., 2019).

1.3.1.3. Pharmaceutical Products

Increased pharmaceutical use has contributed to the designation of human and veterinary pharmaceuticals as emerging environmental pollutants. Sewage is the main route of pharmaceuticals to aquatic ecosystems (including veterinary medicines, agriculture and industry). Pharmaceuticals are continuously discharged but not always effectively removed, so most of them remain in the environment. After ingestion, they are excreted in a biologically active form as residues or active metabolites. Mainly due to incomplete degradation of treatment systems, chemical contaminants and metabolites occur of rivers, lakes and ponds, groundwater, and even in drinking water (Figure 1.5) (Santos et al., 2016; Varano et al., 2017).

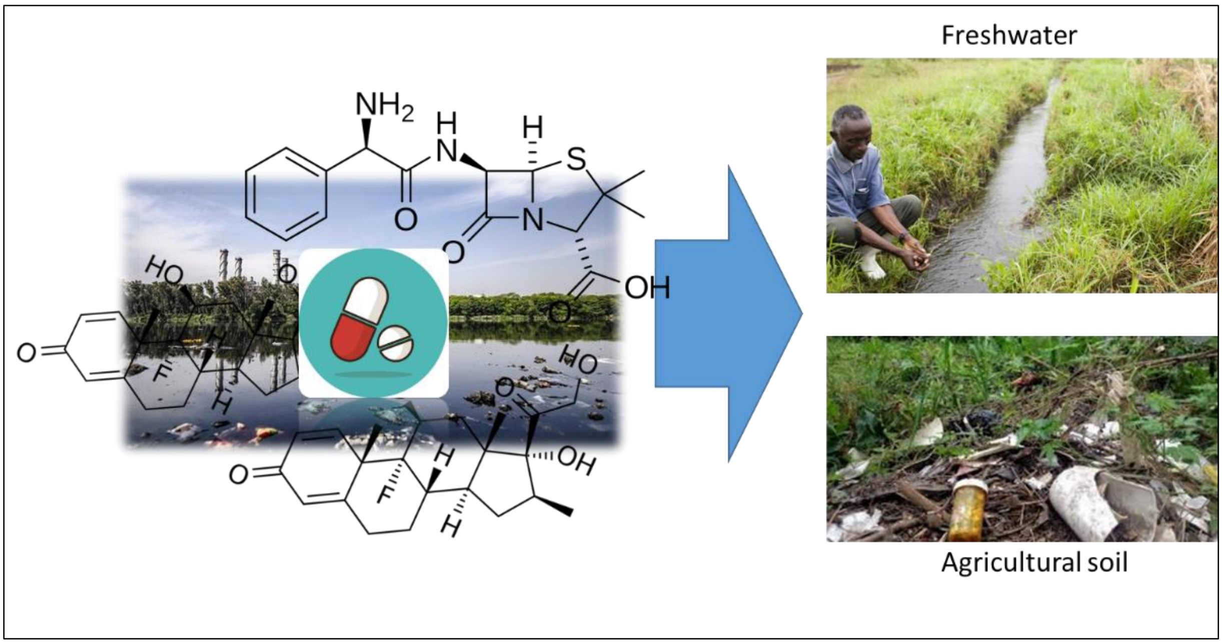

Figure 1.5 impact of pharmaceutical residues on environment.

Steroidal estrogens have become an emerging and serious concern. Worldwide, including estrone, estradiol, and estriol. They pose serious threats to soil, plants, water resources, and humans. Environmental concentrations of pharmaceuticals have been reported in the range of 10-1000 ng.L-1. Pharmaceutical risks are persistent because they are engineered to induce complex biological reactions to living organisms and can thus cause lethal effects even at low concentrations. Aquatic species are typically exposed to mixtures of contaminants and can interact, produce synergistic or toxic effects on individual components. The cumulative effects of mixtures should be understood and the chemical threats to marine organisms should

be discussed in this dynamic exposure situation. Consequences of environmental pharmaceutical mixtures are identified as one of the top priority research needs to understand the risks of long-term exposure to pharmaceuticals (Rudd, 2014; BORRELY et al., 2019).

Pharmaceutical products for humans or animals and their associated metabolites (degradation products) end up in the aquatic environment after use. Latest studies have shown that small amounts of pharmaceuticals can be found in industrial wastewater, surface water, groundwater and even drinking water. Nothing is known about the impact and risk of long-term exposure to low concentrations of pharmaceuticals in aquatic species. The presence of pharmaceuticals in soil, waste, drinking water and sediments is not well documented except for two preliminary studies, which assessed the levels of pharmaceuticals in the atmosphere, published in 1977 and in 1985. The presence of several pharmaceuticals in effluents was soon confirmed in The Netherlands, Switzerland, United Kingdom; France, Greece, and Sweden; Spain; USA; Canada; Brazil and Australia (Yadav et al., 2016; Varano et al 2017).

In world wide ranges of pharmaceuticals are 12,000 human and 2,500 veterinary pharmaceuticals. Each pharmaceutical consists of an active substance, mixed with a number of auxiliary substances to make it possible to handle and dose the pharmaceutical. From an environmental point of view, especially the active substances are of interest. The relatively recent awareness of pharmaceutical products impact on environment is reflected in literature since the 1990s through the exponentially increasing number of studies concerning this emergent class of water pollutants. Pharmaceutically active compounds are produced and used in very large volumes and their use and diversity is increasing every year (Yadav et al., 2016).

The majority of studies on pharmaceutical products in the aquatic environment relate to their study, occurrence and fate in wastewater and wastewater treatment plants, with an focus on process efficiency with regard to their removal. As the majority of organic micropollutants, the origin of the pollution is predominantly anthropogenic and continually released into wastewater or directly into the atmosphere. Evidence has shown that pharmaceuticals can be found in untreated and chemically treated industrial wastewater, surface water and very little in drinking water. Such results sparked a series of inquiries into the existence of both human and veterinary pharmaceutical products (Sui et al., 2015).

1.3.2. Inorganics pollutants

1.3.2.1. Heavy metals

The word "heavy metals" refers to any metallic material that has a fairly high density and is toxic or harmful even at low concentrations. "Heavy metals" is a general collective concept that refers to a category of metals3and metalloids with a nuclear density of less than 4 g/ cm or 5 times or more than water. However, being a heavy metal has nothing to do with density, but is related to chemical properties. Heavy metals include lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag) chromium (Cr), copper (Cu) iron (Fe) and platinum group components. Environment is defined as the totality of the circumstances surrounding the specific organism or group of organisms survival of organisms (Duruibe et al., 2007).

Heavy metal contamination is an anthropogenic, unavoidable problem that society has failed to tackle. Heavy metal is a loosely defined term that refers to a group of elements with a density greater than 4 g cm−3, including metals and metalloids such as arsenic. While naturally occurring and some are biologically important (for example, copper and chromium are micro nutrients), pollution emissions increase the concentration of these elements in natural environments to dangerous concentrations. Figure 1.6 shows that heavy metals are the key contaminants in European soils and groundwater. Non-essential heavy metals are harmful to living organisms, as are essential metals at high concentrations (Vareda et al., 2019).

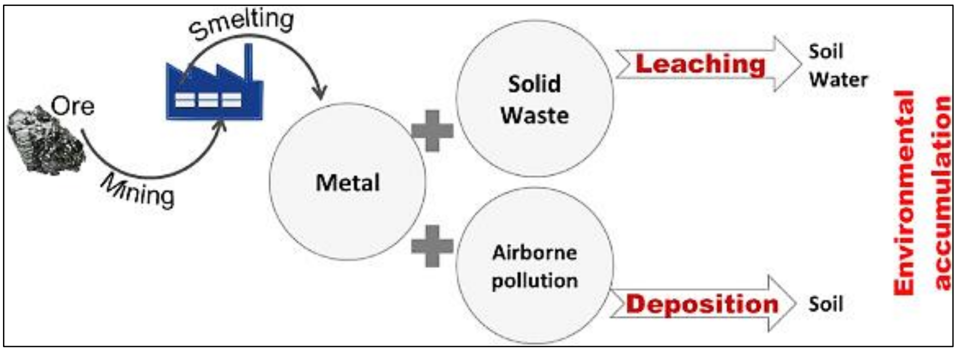

Figure 1.6 Schematic illustration of heavy metal emissions from mineral extraction and processing (adapted from Vareda et al., 2019).

The speciation of heavy metals plays a key role in their persistence in the environment; mobile forms can easily leach, spread to different media, and are more bioavailable, absorbed by living organisms. Since heavy metals are not degradable, bioaccumulation occurs at all

levels of the food chain (being especially important for humans, located at the top of their food chain), causing multiple diseases and poisoning. Bioavailable and mobile sources of heavy metals are released by anthropogenic practices such as mining, a variety of factories, fossil fuel combustion and pesticide use. Metal processing and mining contribute to 48% of the overall release of pollutants by the European industrial sector (Pandey et al., 2016; Vareda et al., 2019).

1.3.3. Biological pollutants

The main criterion for the identification of pollutants is their ability to reduce the survival fitness of a certain level of biological organization (from cell to ecosystem). If it is accepted that the term biological pollutant is accurate, it would be important to decide if such a reduction in fitness can be observed and then to consider how this applies to a wide variety of species which could be considered to be pollutants. It is fairly straightforward to include viruses, bacteriophages and bacteria; they are apparently released from wastewater discharges into the sea to kill them, but they may accumulate in sediments and filter feeders, most possibly altering the microbial floral population in these media (Elliott, 2003).

Microbiological water pollution is typically a natural source of water pollution caused by microorganisms. Various forms of microorganisms live in water and cause the sickness of fish, land animals and humans. Microorganisms such as bacteria, viruses and protozoa Dangerous diseases such as cholera are caused by microorganisms that live in water. These diseases typically affect the health of people in developing countries, because they do not have facilities to treat contaminated water. Generally speaking, contamination occurs when any part of the system, product or medicine comes into contact with microbiological pathogens where it is expected to be sterile. For example, if the surgical instrument is contaminated with pathogens (Bomoi et al., 2020).

CHAPTER TWO

WASTEWATER TREATMENT METHODS

2. Wastewater treatment methods

The treatment of wastewater is a relatively modern practice. The first mechanical and biological processes designed to treat municipal waste- water emerged early by the end of the 19th century. The technology of industrial wastewater treatment uses both mechanical and physicochemical methods as well as biological ones (Figure 2.1) (Zajda & Aleksander-Kwaterczak, 2019).

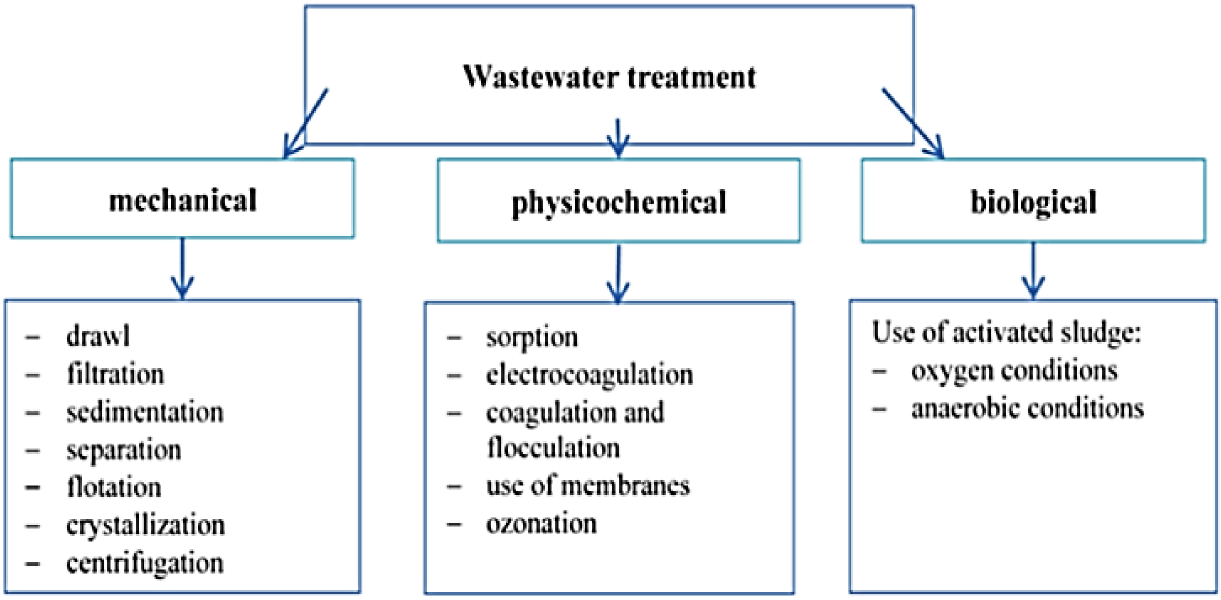

Figure 2.1 Wastewater treatment methods (adapted from Zajda & Aleksander-Kwaterczak, 2019).

2.1. Mechanical treatment

Mechanical wastewater treatment, this so- called first stage of purification, are intended to eliminate larger floating and dragged solids, granular particles with a diameter greater than 0.1 mm, and easily falling suspensions, oils and fats. This is achieved through the use of two techniques (Raouf et al., 2019; Zajda & Aleksander-Kwaterczak, 2019):

(a) Screening: This approach is one of the oldest methods of treatment. It eliminates gross pollutants from the waste stream to protect downstream machinery from destruction, avoids interference with plant operations and prevents hazardous suspended materials from reaching the primary sewage tanks.

(b) Filters: Filters can be classified as biological rather than mechanical methods. The most commonly encountered aerobic attachment-growing biological treatment process used for the removal of organic matter from wastewater may be considered.

2.2. Physicochemical treatment

(a) Sorption

The sorption cycle involves two phenomena. The first is adsorption, which involves the binding of molecules to the surface of a solid or liquid. The second is absorption, which consists of the sorption of one material by another into some continuous process. Methods using the adsorption process are considered to be one of the most competitive because they are not complicated and do not require high operating temperatures (Crini et al., 2018).

Activated carbon is a substance that very easily absorbs organic compounds. This is due to its large surface area, porosity and resistance to chemical and thermal changes. For this reason, it is the most flexible adsorbent used in wastewater treatment. It decreases the BOD and COD values by more than 90%. The key downside of its use is the high cost of processing and recycling, as well as the problems of disposal. That's why scientists are looking for cost-effective and more environmentally friendly sorbents with similar properties to carbon (Fraga et al. 2019).

(b) Coagulation and flocculation

In wastewater treatment, these methods are mainly used to remove suspended solids and organic compounds. The effectiveness of processes depends on the selection of suitable coagulant. The most popular are aluminium and iron salts as well as active silica. In the case of wastewater from the food industry, the use of ferrous sulphate as a coagulant can cause a reduc- tion of BOD from about 33% to 58% and COD from about 30% to 53%. While the use of limes led to slightly larger improvement aerobic con- ditions (BOD: 34%-66% and COD 32%-59%) (Vanerkar et al. 2013; García-Morales et al. 2018).

Vanterkar et al. (2013) conducted an experiment in which they used as a coagulant: lime, alum, ferrous sulphate or ferric chloride in combination with different polyelectrolytes as lime 200 mg/L + anionic-synthetic polyelectrolyte (Magnafloc - E-207), lime 200 mg/L + nonionic - synthetic polyelectrolyte (Zetag - 7650) and lime 300 mg/L + cationic - synthetic polyelec- trolyte (Oxyfloc - FL-11). The analysis showed that 0.3 mg/L Magnafloc E-207 in combination with the optimal dose of lime 200 mg/L, was very effective in the reduction of COD - 67.6% and BOD - 71.0%.the reduction of COD by 90% and of the colour by 93.5% (Sahu 2017). The integrated electro- coagulation process using aluminium sacrificial anodes

and the sand filtration process as a pre- treatment of wastewater from the chocolate al- lowed reducing turbidity, colour and COD by about 96%, 98% and 39%, respectively. What is more, hybrid electrodes are safe to operate and economical (García-Morales et al. 2018).

2.3. Biological methods

(a) The use of activated sludge

Wastewater treatment with activated sludge under aerobic conditions is one of the most widely used techniques, but procurement and maintenance costs can still be too high for industrial applications. Enabled sludge is a biological mechanism that includes both physical processes and biochemical reactions. Macroscopically, it is a suspension consisting of flocculating agglomerations of heterotropic bacteria. Physical processes exist on the surface of flocks, which are based on the adsorption of organic compounds and, as a result, decompose into smaller fragments. They are then absorbed by the microbial cells in which they are further transformed. Bacteria (Scholz, 2016; Zajda & Aleksander-Kwaterczak, 2019).

(b) Treatment under anaerobic conditions

Anaerobic treatment is based on a microbiological process, such as methane fermentation, during which well-chosen bacterial strains convert organic waste from sewage into biogas (methane and CO2). The bacteria involved in this process are found in anaerobic sludge: flocculent and granular. (Yakout & El-Deen, 2016; Senés-Guerrero et al., 2019). Many wastewater treatment systems are based on anaerobic technologies. An-aerobic digestion has been used to handle not only many forms of waste but also biosolids. The Up-flow Anaerobic Sludge Blanket (UASB) reactor has become very common in recent years and has been widely used for the treatment of various forms of wastewater. The benefits of using this reactor are due to high removal performance even at low temperatures, low energy consumption and low space requirements. It is very useful in the treatment of organic wastewater due to its high concentration of biomass and its rich microbial diversity (Yakout & El-Deen, 2016; Daud et al., 2018).

CHAPTER THREE

REMOVAL OF OILS FROM WASTEWATER USING AGRICULTURAL WASTES AS ADSORBENTS

3. Biological methods using agro-waste biomass

Increasing oil consumption in modern society has contributed to further generation of oil / oil refining waste. Fuel treatment wastewater / waste contains high amounts of aliphatic, aromatic petroleum hydrocarbons, etc. The direct release would have an effect on the vegetation and marine life of surface and ground water supplies. Due to its chemical origination, its fluid nature and its toxic effects, treatment of wastewater prior to discharge is essential. The biological treatment cycle is usually used to reduce the effects of petrochemical waste. Stringent regulations have inspired researchers to develop innovative treatment facilities that provide high treatment performance, low maintenance, footprint and operating costs. Biological anaerobic, anoxic and aerobic digestion (or a mixture of each other) has been done to treat petrochemical wastewater.

Optimizing the pretreatment process using physicochemical processes is also essential for the provision of sufficient pretreatment wastewater for effective biological secondary treatment. The description and update of petrochemical wastewater treatment processes would contribute to the theoretical and practical growth of awareness (Ghimire & Wang, 2018). Biological treatment technologies have become increasingly common in the treatment of wastewater oil fields due to their high quality, cost-effectiveness and environmental friendliness (Hussein et al., 2013).

Oil sorption by sorbents is one of the most inexpensive and effective methods for preventing oil spills. Oil sorbents are capable of absorbing and converting liquid oil to a semi-solid or solid form, which can then be separated from the water and treated in a comfortable manner without substantial oil drainage. Preferred sorbent materials are those that, in addition to being cheap and readily available, show rapid oil sorption, high oil sorption. Availability (oleophilicity or lipophilicity), low water absorption, high oil retention potential during transit, high absorption oil with simple methods, good reusability, high buoyancy and excellent physical and chemical resistance (Lim & Huang, 2007).

Conventional methods for removing oil from oil spills are time-consuming and expensive. For this reason, the need to find oil adsorbents that are easy to handle, can adsorb the oil quickly, and have a large adsorption capacity has increased in recent years. Water contaminated with oil cannot be used for drinking, industry, or irrigation. In addition, the

spilled oil settles on beaches, killing coastal creatures, and sinks to the seabed, killing benthic organisms such as crabs (Bejarano & Michel, 2016; Khade et al., 2017).

Consequently, in order to protect the environment and human health, contaminants must be extracted rapidly and efficiently after an oil spill. Of the different methods of oil recovery, sorption technology is one of the most successful solutions to the management of oil spills. Synthetic materials, such as polypropylene and polyurethane, are used to reduce environmental effects and increase treatment efficiency. Nonetheless, this process of adsorption and removal of oil is expensive and requires non-biodegradable material, making land filling difficult and resulting in a high cost of incineration and potential air pollution (Ogbu et al., 2016).

Recently, focus has been drawn to environmentally friendly oil adsorbents such as natural charcoal, rice straw, peat, pine nuts and tree roots. While the main benefit of these plant-derived adsorbents is their environmentally friendly properties, their drawbacks include low oil adsorption performance, higher hydrophobicity and less buoyancy than conventional adsorbents such as polypropylene. However, as most plant adsorbents are typically hydrophilic, they absorb more water than oil and are not sufficiently dimensionally stable due to the activity of the hydroxyl groups. The goal of this study was therefore to find a way to adsorb and extract crude oil from aqueous solution by using dried corncob, which has less hydroxyl activity than other plant adsorbents (Choi, 2019).

3.1. Oil removal by adsorption technique

Absorption is the uptake of a substance into the bulk sorbent via the pore structure by diffusion, whereas adsorption is a surface phenomenon by either physical forces or chemical bonding (Figure 3.1). The two processes (absorption and adsorption) inevitably occur simultaneously, and are jointly referred to as sorption. Sorbents to be used on water should have oleophilic properties, i.e. it attracts large amount of oil without sinking. Moreover, the sorbent should be easy to handle, and non-toxic to the environment. It is generally an advantage if the sorbent is biodegradable or can be disposed of by burning without large amounts of black smoke or toxic fumes. Sorption influenced by several factors; these are physical and chemical attraction between sorbent and sorbet, surface geometry or morphology of sorbent, surface area of sorbent, contact time, density ratio of sorbent/sorbet,

and environmental factors including ambient temperature, pH and salinity (Hussein et al., 2013).

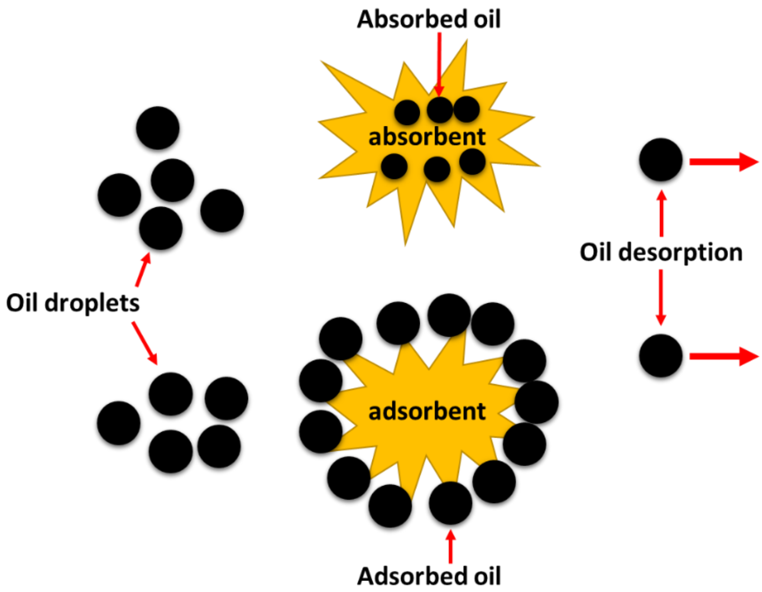

Figure 3.1 Oil absorption and adsorption processes.

Adsorption is considered to be one of the most advanced techniques used for wastewater treatment as it is an effective, economical and environmentally friendly treatment technique. This is good enough to meet the duty to conserve water and the high levels of runoff in the industries. Adsorption is basically a method of mass transfer by which the metal ion is moved from the solution to the sorbent surface and is bound by physical and/or chemical interactions. Functional groups therefore play an important role in determining the effectiveness, efficiency, selectivity and reusability of these adsorbents (Raouf et al., 2019).

In general, the key steps involved in the adsorption of contaminants on solid adsorbents are:

1) Shift the metal ion from the bulk solution to the outer surface of the adsorbent.
2) Internal mass transfer from the outer surface of the adsorbent to the inner surface of the porous structure.
3) Adsorption of adsorbate to active sites of adsorbent pores.
4) The overall rate of adsorption is determined either by film formation or by intra-particle diffusion, or both as the last stage of adsorption is very fast compared to the other two steps.

3.2 Types of Sorbents

Sorption is a physical and chemical mechanism by which one material is bound to another. This type of attachment is set out in the following (Raouf et al., 2019):

1) Absorption: the incorporation of a substance in one state into another of a different state (e.g., liquids being absorbed by a solid or gases being absorbed by a liquid);
2) Adsorption: the physical adherence or bonding of ions and molecules onto the surface of another phase (e.g., reagents adsorbed to a solid catalyst surface);
3) Ion exchange: an exchange of ions between two electrolytes or between an electrolyte solution and a complex.
4) Commonly, in physical adsorption, the attractive forces between adsorbed molecules and the solid surface are Van der-Waals forces of attraction and reversible adsorption (Desorption) occurs when they are weak in nature.
5) (Ad) sorption at a solid–liquid interface is a complex process playing a critical role in several industrial applications as well as in the fate and passage of chemical pollutants in the environment. In industry, the sorption techniques concerning solid sorbents are widely used to remove certain classes of chemical pollutants from waters, especially those that hard and resistant.

3.3. Agricultural wastes as effective sorbents

Organic sorbents (i.e. agricultural waste) have been widely used because they are readily available and relatively inexpensive. Their sorption potential is just as strong as other inorganic sorbents as they can pick up 5 to 15 times their oil weight. Some of these materials must be processed in such a way that they are oleophilic. In order to combine the advantages of biological treatment with sorption methods, this research used agricultural waste as an organic sorbent, enhanced by bacterial organisms, to clean up spilled oil. The studied parameters affecting the sorption capacity were. Oil type (i.e. diesel oil and crude oil), Oil film thickness (i.e. 1, 3 and 5 mm), Bacterial doses (i.e. 1, 3 and 5 mm), and sorbent materials (i.e. corn stalk, cotton, and composting of 1:1 corn stalk: cotton) (Hussein et al., 2013).

Recently, special attention has been paid for the utilization of the available-in-nature, abundant, and eco-friendly sorbents to replace the conventional and expensive sorbents based on economic and environmental point of views. These substances are mostly synthesized and developed by the pyrolysis of carbonaceous materials of plants and agricultural

residues/wastes such as coconut shells, walnut shells , palm shells date stones almond shells spent tea leaves (STL) , and cotton stalks (followed by either physical or chemical activation of the chars obtained from them).

Agricultural wastes mainly include cellulose, lignin, and hemicellulose. The contents of these chemical components in various types of crops are different. For example, the cellulose, lignin, and hemicellulose contents of crop residue are 35–50%, 20–30%, and 15–30%, respectively. Lignocellulose is an abundant source of biomass. Cellulose, formed by β-(l→4)-glycosidic bonds, is a linear syndiotactic polymer of glucose. Hemicellulose is composed of a variety of uronic acid groups, which is a branched heteropolymer of D-xylose, L-arabinose, D-galactose, D-glucose, D-mannose, and D-glucuronic acid. These monomers are connected in the form of C-C bonds, and C-O-C bonds. Lignin is a crosslinked aromatic polymer compound that is consisted of p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol.

In recent years, various industrial activities have caused serious pollution to the environment. Due to the low operating costs and high flexibility, adsorption is considered as one of the most effective technologies for pollutant management (Figure 3.2). Agricultural waste has loose and porous structures, and contains functional groups such as the carboxyl group and hydroxyl group, so it can be invoked as biological adsorption material. Agricultural waste gets the advantages of a wide range of sources, low cost, and renewable. It has a good prospect for the comprehensive utilization of resources when used for environmental pollution control (Dai et al., 2018).

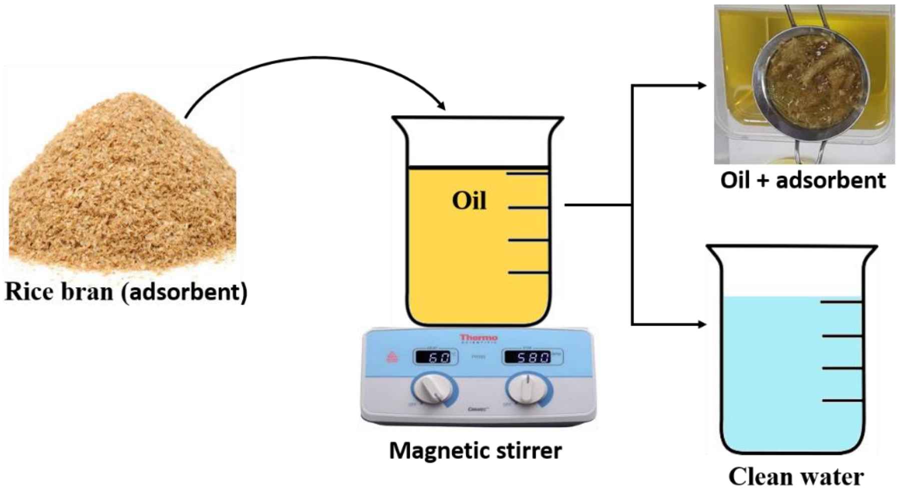

Figure 3.2 schematic represent oil removal from water using rice bran as adsorbent.

CHAPTER FOUR

CONCLUSIONS AND RECOMMENDATIONS

4.1. Conclusions

With the continuous improvement of environmental requirements, the consistency of oily wastewater treatment effluent must be improved in order to upgrade existing methods which have not been able to meet current human and environmental requirements, a modern, more effective approach is required. Oily wastewater treatment systems will concentrate on the following areas for future trends:

1) Considering the existing challenges of technology and systems, study and development of a new hybrid process and exploiting the benefits of various approaches in order to escape its limitations.
2) A strong theoretical basis offers an in-depth analysis of oily wastewater degradation mechanism, enhancing the performance of oily wastewater treatment and the production costs.
3) In this work, we have focused on water pollutants and their origins, as well as methods for the treatment of water pollution, and we have come closer to methods for the treatment of water pollution by plants and agricultural waste, which essentially all seek to tackle an environmental crisis that endangers the lives of living organisms at risk.

4.2. Recommendations

1) Carry out effective studies to identify and resolve the environmental problems in Iraqi aquatic systems especially near the petroleum sites.
2) Drawing an environmental strategy to resolve and control oil spill.

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الخلاصة

تعتبر المياه أداة حيوية في حياة الأشخاص الذين يستفيدون من استخدامها ويتأثرون سلبا بإساءة استخدامها وعدم القدرة على التنبؤ. إن استهلاك المياه الملوثة يعرض حياتنا وسبل عيشنا للخطر بسبب عدم وجود مصادر نظيفة بديلة. هناك العديد من الطرق ومصادر التلوث التي يمكن أن تتلوث بها المياه المخصصة للاستخدام البشري. تشمل تلك المصادر الملوثات العضوية الهيدروكربونات (الزيوت)، والأصباغ، ونفايات صناعة النسيج، والدباغة، والنفايات الدوائية، والملوثات غير العضوية مثل المواد الثقيلة والملوثات البيولوجية مثل بعض الكائنات الحية الدقيقة والطفيليات. تحتوي المخلفات الزراعية في المقام الأول على السليلوز واللكنين والهيموسيليلوز. تمتاز النفايات الزراعية من بين مجموعة متنوعة من المصادر انها رخيصة ومتجددة. تحتوي النفايات الزراعية على تراكيب رخوة وذات مسامية وتحتوي ايضا على مجموعات وظيفية فعالة مثل مجموعة الكربوكسيل والهيدروكسيل، بحيث يمكن استخدامها كمواد امتزاز حيوية واعدة.

الكلمات الدالة: الملوثات الزيتية، المخلفات الزراعية الممتزة، الامتزاز.

وزارة التعليم العالي والبحث العلمي
جامعة ديالى/كلية العلوم
قسم التقانة الاحيائية
الدراسة الصباحية

مخلفات الكتلة الحيوية الزراعية: ممتزات كفوءة في ازالة الزيت من الماء

بحث تخرج مقدم الى

مجلس قسم التقانة الاحيائية/كلية العلوم/جامعة ديالى

وهو جزء من متطلبات نيل درجة البكالوريوس في التقانة الاحيائية

من قبل

زهراء سلمان كاظم
احمد يعقوب يوسف
ازهار رعد سعد
مروة حسين صادق
محمود عبد الكريم عبد
زينب اسماعيل ابراهيم

باشراف

د. عصام حامد حميد

2020م – 1441هـ