Review

A Review on Adsorption Process for the Treatment of Oily Wastewater

Teow Yeit Haan [1, 2, *], Puteri Mimie Isma Nordin [1], Nur 'Izzah Ahmad Juanda [1], Muhammad Afiq Mohd Shafi [1], Pavithiran Krishnan [1]

1. Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor Darul Ehsan, Malaysia; E-Mails: yh_teow@ukm.edu.my; A167654@siswa.ukm.edu.my; A169074@siswa.ukm.edu.my; A168983@siswa.ukm.edu.my; A169303@siswa.ukm.edu.my
2. Research Centre for Sustainable Process Technology (CESPRO), Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor Darul Ehsan, Malaysia

* **Correspondence:** Teow Yeit Haan; E-Mail: yh_teow@ukm.edu.my

Abstract

Oil-contaminated or oily wastewater (OW) is generated from various industrial and domestic premises. It consists of fats, oils, and greases and may contain petroleum fractions such as diesel oil, gasoline, and kerosene. It is regarded as one of the most hazardous wastewaters, causing serious environmental and health threats to ecosystems and human beings. The global increase in the discharge of OW coupled with stringent regulations for effluent discharge and incessant drive for the reuse of treated wastewater necessitate the need for the treatment of the OW. Conventional approaches employed in the past are inept for OW treatment due to low separation efficiency, high operational cost, creating secondary pollution, and long treatment hours. Comparatively, the adsorption process is considered a better alternative because of its simple design and can involve low investment in terms of both initial cost and land required. Thus, the adsorption process is widely applied as a

promising alternative to existing treatment methods for OW. The adsorption process is an effective technique for OW treatment. Super adsorbents with ultrahigh adsorption capabilities are highly desired for efficient OW treatment in a new revolution of adsorption technology to meet present and future needs. This review provides insights into advanced and emerging state-of-the-art technologies of the adsorption process as a safe and efficient treatment of OW. Strength, weakness, opportunities and threats (SWOT) analysis was conducted to identify and analyze internal strengths and weaknesses and external opportunities and threats that shape the current and future operation of the adsorption process for the treatment of oily wastewater for developing strategic goals. Super adsorbents with ultrahigh adsorption capability such as P-GSC and P-PKS discussed are highly desired. The extraordinary properties of P-GSC and P-PKS can provide leap-forward opportunities to revolutionize traditional adsorption technology. However, scale-bridging and optimization study of these innovated super adsorbents is required for the real application. It shows a bright future of P-GSC and P-PKS towards OW treatment.

Keywords
Oily wastewater; adsorption; wastewater treatment; super adsorbent; separation

1. Introduction

The industrial sector's increasing population and rapid growth have become the root of increased wastewater production. In Malaysia, it is estimated that the volume of wastewater generated by municipal and industrial sectors is 2.97 billion m^3 per year [1]. According to the United Nations Educational, Scientific and Cultural Organization (UNESCO), 2.21 trillion m^3 of wastewater is released into the environment annually [2]. One of the major concerns in treating wastewater is oil-contaminated wastewater discharged from various industrial and domestic premises [3]. The petrochemical and metal processing industries generate a large volume of oily wastewater (OW) [4]. The volume of global OW generated by oil and gas industries was 7.95 billion m^3 per year in 2009 [5]. Municipal sources such as kitchen waste, oil leakage from mechanical devices, and human activities have potent resources for OW production [3].

OW consists various fats, oil, and greases [6]. It may also contain petroleum fractions such as diesel oil, gasoline, and kerosene [7]. OW is carcinogenic and mutagenic to human health [4]. Toxic compounds such as phenols, petroleum hydrocarbons, and polyaromatic hydrocarbons present in OW are inhibitors for plant and animal growth [8]. Besides, OW that is discharged to the water bodies without proper treatment would increase the biological oxygen demand (BOD) and chemical oxygen demand (COD) of the water, generate an unpleasant odor, and reduce sunlight penetration into the water thus disrupting the aquatic ecosystem [3]. Moreover, the viscous nature of oil and grease in OW might cause blockage of drainage and sewer lines. Hence, it is important to treat OW before release due to its harmful environmental effects.

Various treatment methods are available to remove the oil impurities in OW, such as electrochemical treatment, membrane filtration, biological treatment, flotation, and chemical coagulation [9]. Unfortunately, these technologies suffer several drawbacks, including low

separation efficiency, high energy cost, long-term operation, and secondary pollution [10]. For instance, aerobic digestion, flotation, and chemical coagulation results in large amount of bio-solids, or sludge, which require disposal. Electrochemical oxidation has low efficiency and the anodes service life is short due to a limited electro-active surface area and poor stability [11]. The membrane is high-cost and slow in filtration speed [12]. The major disadvantage of floatation and coagulation is the operational cost. Considerable quantities of coagulant and flocculant are needed to achieve the required level of flocculation. The cost can escalate, particularly with a large volume of wastewater.

Adsorption is considered a potential treatment method for OW [13]. Comparatively, the adsorption process is considered a better alternative because of its simple design and can involve low investment in terms of both initial cost and land required. Thus, the adsorption process is widely used to treat industrial wastewater from organic and inorganic pollutants and meets the great attention of researchers [14]. Adsorption involves the contact of the free aqueous phase with the rigid solid phase (adsorbent) that can remove one or more adsorbates selectively. The adsorbent selection is important for efficient adsorption in treating OW [15]. Hence, this review will focus on adsorption processes for treating OW as an advanced alternative to other treatment methods. The review starts by emphasizing the problem of oily wastewater. This includes the characteristics of oil-contaminated wastewater and the sources of oil in wastewater. Subsequently, the category of adsorbents was reviewed, including natural adsorbents (earth crust and bio-adsorbents) and non-natural adsorbents (lab synthesis and commercial).

This review will also discuss highly desired super adsorbents, an adsorbent with superior adsorption capacity yet a simple and sustainable synthesis process. Kinetics and isotherms used in describing the adsorptions system are also deliberated to understand concepts and engineering aspects of the adsorption process. On top of that, strength, weakness, opportunities and threats (SWOT) analysis was applied in this review to identify and analyze internal strengths and weakness and external opportunities and threats that shape current and future operation of adsorption process for the treatment of oily wastewater for developing strategic goal.

2. Oil Contaminated Wastewater

Oil in wastewater could be free oil, dispersed oil, emulsified oil or dissolved oil. The emulsified oil is either oil in water (O/W) emulsion or water in oil (W/O) emulsion [15]. In O/W emulsion, the oil droplets are dispersed in a continuous water phase (>30% water) while in W/O emulsion, a continuous oil phase contains droplets of water (<25% water) [16].

Oil-contaminated wastewater is mainly in O/W emulsions [16]. The source of OW is very broad, it is commonly emitted by metal processing industries, slaughterhouses, dairy industries, restaurants, poultry processing industries, edible oil refineries, petrochemical industries, and tannery industries [6]. Oil refineries and petrochemical industries are the largest sources of OW emissions. When a tonne of oil is processed for foreign refineries, about 0.5 to 1 tonne of OW is produced while 0.7 to 3.5 tonnes are manufactured for domestic refineries [17]. Malaysia and some other countries have developed the specific discharge limit of oil and grease in wastewater to minimize the harmful effect of OW on the environment as summarized in Table 1.

Table 1 Specific discharge limit of oil and grease in wastewater.

Bodies or regulation	Oil and grease discharge limit	Reference
Department of Environment, Environment Quality Act 1974 in Malaysia	10 mg/L	[18]
Central Pollution Control Board (CPCB) of India	Surface water: 10 mg/L Coastal water: 20 mg/L	[19]
Oslo-Paris (OSPAR) Convention in North Sea region	Upper limit to the sea: 30 mg/L	[5]
Paris convention	Upper limit to the sea, Offshore fields: 40 mg/L On-land fields: 5 mg/L	[20]
China government	10 mg/L	[21]

2.1 Sources of Oil in Wastewater

2.1.1 Industrial Sources

One of the industrial sources of OW is the metal industry, where the sources of OW are from cooling lubricants in metalworking processes such as metal rolling, metal cutting, wire drawing, and scouring baths for cleaning the metal parts [16]. On the other hand, the petroleum processes industry like the chemical treatment of lubricating oils, waxes, burning oils, barometric condensers, and desalting processes had also generated OW due to condensate and wash water coming into contact with the petroleum products at some stage of the processing. OW is also produced in coke plants from cooling, quenching, or scrubbing gases. Additionally, industrial OW may generate from leaks, spills, or cleaning operations of the transportation industry [15].

Vegetable oil mill effluents are another major source of industrial OW. One of the most problematic OW in Malaysia is palm oil mill effluent (POME). POME is a colloidal suspension that contains 95-96% water, 0.6-0.7% oil and grease, and 4-5% total solids. The oil droplets in POME occur in two phases, either as a suspended solid or floating in the supernatant. According to Ahmad et al. [22], approximately 2,000 mg/L of residue oil exists in the supernatant of POME. Table 2 summarizes the source of industrial OW with its respective oil concentration.

Table 2 Source of industrial OW.

Industrial process	Oil concentration (mg/L)	Reference
Petroleum refining	20-4,000	[23]
Metal processing and finishing (grinding oils, cutting oils, lubrication fluids, and coolant-oil water emulsion)	100-20,000	[23, 24]
Aluminum rolling	5,000-50,000	[23]
Copper wire drawing	1,000-10,000	[23]
Food processing (meat, fish, and poultry)	500-14,000	[23, 24]
Edible oil refining (palm oil mill effluent)	4,000-6,000	[22]
Paint manufacturing	1,000-2,000	[23]

Leather processing (tannery effluents)	200-40,000	[23]
Wool scouring	1,500-12,500	[23]

2.1.2 Municipal Sources

Municipal sources of OW can be of large varieties too. One of the sources is domestic wastewater, produced by human activities in households, including food preparation, garbage disposal, and cleaning. Laundry washing and household cleaning produced OW from the oil and grease stains. Soaps and detergents used in cleaning and washing also contain oil and fat, which mostly turn into emulsion in the wastewater. Domestic wastewater contains 10-50 mg/L of oil and grease [15]. There has been a huge increase in the amount of OW produced from domestic wastewater, mainly due to rapid growth in the population [25] and the outbreak of COVID-19 where lockdown and home activities are applied.

Vegetable oils that are not only used in food preparation in households but also used in cosmetic and pharmaceutical products as well as paints are also the sources of municipal OW. The demand to look for new resources such as biomass fuel in diesel engines had drastically increased the usage of vegetable oils. Moreover, OW from hotels, restaurants, and other commercial food services consisting of fats, oil and grease as well as surfactant from the dishwashing detergent is commonly directly discharged to the drainage system without any treatment [26]. Due to a large number of customers, high operating temperature, and mixed kitchen waste, the strength of OW from these sources is higher than the residential water. Yearly, around 50,000 tonnes of municipal OW dominant by wasted cooking oil are disposed to the environment without proper treatment in Malaysia [27]. In comparison, 10 million tonnes of municipal OW per year are being produced by the United States, which is the top producer in the world [28].

2.2 Classification of Oil and Water Mixture

The concentration and nature of oil in wastewater will influence the degree of oil removal in a treatment process. Therefore, it is important to understand the characteristics of the oil and water mixture for an efficient treatment process. Oil in OW can be classified as free (floating) oil, dispersed oil, emulsified oil, and soluble (dissolved) oil.

Free oil is usually produced in the petroleum process industry, aircraft washracks, and the spills of lubricating, hydraulic, and turbine oils [15, 29]. It is normally present as a floating mass or in the form of oil droplets which arises quickly to the surface of the water under settled conditions [10]. Therefore, free oil is not a big problem for OW treatment as it can be separated by gravitation, skimmed off or removed by an overflow weir in a tank [15]. Whereas, dispersed oil is usually produced by aircraft and vehicle maintenance operations [29]. Dispersed oil contains polyaromatic hydrocarbons and alkyl phenols less soluble in water [10]. It is an array of fine droplets that are stabilized by their electrical charges without surfactants.

Emulsified oil has a similar distribution to dispersed oil but has better stability. The high stability of emulsified oil is mainly due to the interactions with surfactants present in the OW interface [16]. The emulsified oil is usually generated from industrial and municipal sources such as petroleum and edible refineries, soap manufacturing, food processing, and domestic wastewater [16, 22, 30]. Due to the high stability of emulsified oil in the aqueous phase, the emulsified oil droplets do not go through spontaneous coalescence into larger flocs, making its separation by the simple gravity

method a hard and time-consuming process [22]. On the other hand, soluble or dissolveed oil is water-soluble oil, which is translucent and transparent [10]. Hence, it is not present as visible droplets, but truly dissolved chemically or dispersed in extremely small droplets. Soluble oils can contain materials like phenolic-type aromatic compounds or cutting oil used in metalworking [15]. It is produced during metal processing and ballast water from ships [15, 29]. Table 3 summarizes the classification of the oil and water mixture and its source.

Table 3 Classification of oil and water mixture and its source [15, 16, 29, 31].

Type of oil	Droplet diameter, D_p (μm)	Characteristics	Sources of oil
Free (floating) oil	$\geq$150	Droplets that float on the surface of aqueous medium due to the difference density of oil and water	Petroleum process and aircraft washrack
Dispersed oil	20-150	Droplets that stabilized by its electric charges	Aircraft and vehicles maintenance operation
Emulsified oil	$\leq$20	Droplets that stabilized by the chemical action of surface active agent	Petroleum and edible oil refineries, soap manufacturing and food processing
Soluble (dissolved) oil	$\leq$5	Droplets that are very fine and not visible, dissolved in aqueous medium	Metal processing and ballast from ships

3. Adsorption as a Treatment Method for Oily Wastewater

Adsorption is a common method used for the treatment of OW. The adsorption of oil molecules happens when they adhere to the surface of the solid adsorbent when they come in contact. Adsorbent plays an important role in adsorption as different adsorbent might involve different adsorption mechanisms, and leading to variation in adsorption efficiency. Generally, the adsorbent is classified into two classes; natural adsorbents and non-natural adsorbents. Natural adsorbents are further classified into earth crust and bio-adsorbents, whereas non-natural adsorbents consist of laboratory-synthesized adsorbents and commercial adsorbents. Figure 1 below shows the overview of the classification of adsorbents.
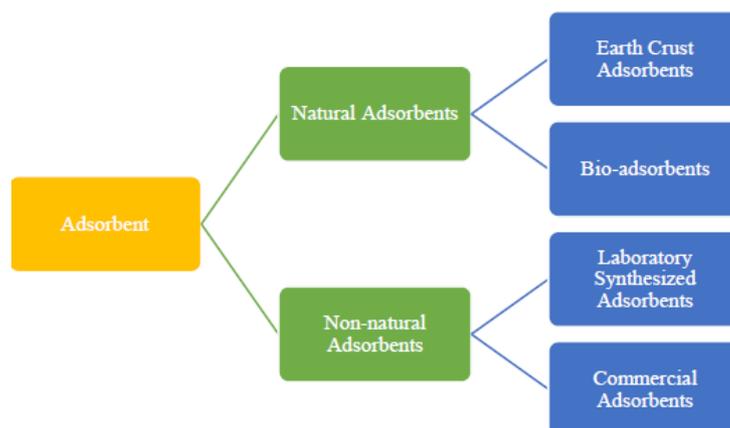
Figure 1 Classification of adsorbents.

3.1 Natural Adsorbents

Natural adsorbents are obtained naturally, and include charcoal, clays, clay minerals, zeolites, and ores. Natural adsorbents are relatively cheap, abundant in supply, and have significant potential for modification to enhance their adsorption capabilities [14]. Natural adsorbents are classified into two subclasse: earth crust adsorbents and bio-adsorbents.

3.1.1 Earth Crust Adsorbents

Earth crust adsorbents are originated from the earth's crust and mantle. Goethite derived naturally is a type of earth crust adsorbent. Winnipeg et al. [32] investigated the effect of crude oil coating on goethite to remove arsenate, As (V) in water to assess environmental implications. This is because wastewater from oil fields is frequently released into marine and freshwater bodies. The adsorption of goethite was fast and the oil did not affect the kinetics of the adsorption process. However, As (V) adsorption was significantly reduced on oil-covered goethite. This could have an important effect on the cycling and the biogeochemistry of As (V) and other oxyanions in water with high oil loads. Alternatively, Takeuchi et al. [33] used engine oil-water emulsion as a model-produced water to evaluate the oil sorption properties of exfoliated graphite (EG). It was found that 100 mg/L of oil in the emulsion can be reduced to a concentration of 0.1-few mg/L using received commercially available EG and surface-modified EG subjected to an additional oxidation treatment. EG sorbs oil preferentially and the oil concentration of the sorbed phase in EG was estimated to be about 200 times that of the initial untreated emulsion, comparable to that achieved by nanofiltration (NF) or reverses osmosis (RO) membrane treatment. This confirms the potential of EG in practical use. Besides single-layer graphite, graphene is another good choice of natural adsorbent. The high adsorption capacities of graphene-based adsorbents are mainly determined by their unique nanostructures, high specific surface areas, and tailorable surface properties, which make them suitable for the storage or capture of various molecules relevant to OW treatment.

Clay minerals such as sepiolite, attapulgite, bentonite, and organoclay are present in the Earth's crust just like goethite and have been tested for the adsorption of waste oil. Zheng et al. [34] modified sepiolite with single-chain and double0chain organic cation surfactants, stearyl trimethyl ammonium bromide (STAB) and dimethyl dioctadecyl ammonium bromide (DDAB) for investigating

the adsorption behavior of modified sepiolite towards emulsified oils in produced water. The surfactant-modified adsorbents improved emulsified oils adsorption and oil-water separation efficiency where the emulsified oils removal exceeded 99%. The maximum adsorption capacitates were reported as 957.0 mg/g for STAB-sepiolite and 1031.5 mg/g for DDAB-sepiolite, respectively. The work conducted by Zheng et al. [34] has provided a theoretical foundation for the design of high-efficiency and low-cost organoclay adsorbents. Table 4 presents the study conducted by researchers on the application of earth crust adsorbents for different OW treatments with their respective performances.

Table 4 The application of earth crust adsorbents for OW treatment.

Absorbent	OW	Performance	References
Graphene oxide	Laundry wastewater	Adsorption capacity: 87.58-97.90% Rejection: COD = 70-85% BOD = 85%	[35]
Attapulgite	Domestic sewage	Adsorption capacity: 155 mg oil/g adsorbent Rejection: COD = 84.54%	[36]
Chitosan	Textile wastewater	Rejection: COD = 90% Oil = 96.35%	[37]
Sepiolite	Organic wastewater	Rejection: COD = 50% BOD = 55-65% Oil = 99%	[38]
Bentonite	POME	Rejection: COD = 88-93% Oil = 96.5%	[39]

3.1.2 Bio-adsorbents

Bio-adsorbents can be found in either agricultural operations or food chain waste. Examples of bio-adsorbents are banana peel, corn straw, palm oil branches, date seeds, rice husks, wheat straw, rape straw, sawdust and eggshells. Alkherraz et al. [40] synthesized activated carbon (AC) from olive branches for removing heavy metals such as lead, zinc, copper, and cadmium from aqueous solutions. The biosorption of AC from olive branches was found to be pH dependent. The maximum metal ion biosorption was achieved at pH 5 for lead, copper, and cadmium ions and pH 3 for zinc ions.

On the other hand, the extent of the metal ions adsorption was increased with the temperature and initial metal ions concentration. Alternatively, Kunjirama et al. [41] carried out a study investigating the potential application of oil palm empty fruit bunches (OPEFB) as adsorbents to remove organic methylmercury, MeHg(II) and inorganic Hg(II) from aqueous solution. The OPEFB was functionalized with an amine-containing ligand namely 3-ureidopropyltriethoxysilane (UPTES) aiming for better adsorption performance towards both mercury ions. The adsorption was pH, concentration, temperature, and contact time dependent. The maximum adsorption capacities of Hg(II) adsorption onto OPEFB and UPTES-OPEFB were 0.226 and 0.773 mmol/g, respectively.

However, the maximum adsorption capacities of MeHg(II) onto OPEFB were higher than UPTES-OPEFB. UPTES-OPEFB offered higher selectivity towards both mercury ions than OPEFB. Table 5 presents the study conducted by researchers on the application of bio-adsorbents for different OW treatments with their respective performances. Generally, wooden residue-based bio-adsorbents are preferable to fruit-based bio-adsorbents. This is because wooden residue-based bio-adsorbents showed better stability in regeneration cycles, making them more robust in applications [42].

Table 5 The application of bio-adsorbents for OW treatment.

Adsorbents	Target	Performance	References
Date palm	Oil adsorption	Adsorption capacity: 1330-1425 mg-oil/g-adsorbent	[43]
Activated date-pit	Phenols from petroleum wastewater	Adsorption capacity: 88 mg-phenol/4g-adsorbent	[44]
Date seeds	Dissolved organic carbon (DOC) in produced water	Equilibrium adsorption capacity: 5.75-19.85 mg/g Rejection: DOC = 70-82%	[45]
Banana peel	Oil removal from produced water	Rejection: Oil = 194 mg/L-oil/267mg-banana peel	[46]
Pomegranate peel	Oil removal from produced water	Adsorption capacity: 555 mg/g	[47]

3.2 Non-natural Adsorbents

Adsorbents synthesized in a laboratory or acquired by purchasing them from commercial companies are considered non-natural adsorbents. Commercial AC, deposited carbon, zeolite, and carbon nanotubes (CNTs) are the non-natural adsorbents used to treat OW.

3.2.1 Laboratory Synthesized Adsorbents

Laboratory synthesized adsorbents are described as evolving adsorbents discovered via laboratory experiments. Nanotechnology-based adsorbents were perceived as noteworthy laboratory-synthesized adsorbents for the treatment of OW. It was reported that particles with smaller sizes would drastically increase the chemical activity and adsorption capacity [48]. Nano-adsorbents are classified into several categories based on their function in the adsorption process. Nanoparticles (NPs), nanostructured mixed oxides (NMOs), magnetic NPs, and metal oxide NPs are among them. On the other hand, carbon nanomaterials, carbon NPs, and carbon nanosheets are some of the most recent developments. Furthermore, various ranges of silicon NPs are utilized as nano-adsorptive silicon nanotubes, silicon NPs, and silicon nanosheets.

Franco et al. [49] synthesized hydrophobic silica NPs and silica NPs functionalized with a petroleum vacuum residue (VR) to reduce oil in oil-brine and oil-water emulsion. The study showed 100% oil removal for all the systems studied and better performance was achieved for oil-saltwater emulsion. Besides, Franco et al. [50] also synthesized alumina-based adsorbents and investigated oil adsorption onto hydrophobic alumina NPs and alumina NPs functionalized with petroleum VR. Comparatively, alumina-based adsorbents have a more prominent affinity towards oil molecules in OW treatment. The polarity of silica NPs contemplated this.

On the other hand, Fard et al. [51] synthesized and evaluated novel iron-oxide/CNTs nanocomposites for oil-water separation. The CNTs were doped with different loadings of iron oxide NPs using a wet impregnation technique. The increasing iron oxide loading on the surface of CNTs had increased the removal of the emulsified oil from the water. The sorption capacities of doped CNTs were greater than 7 g/g for gasoline oil. They reached maximum sorption capacity after 15 minutes, one of the fastest minimum contact times reported by all oil sorbent materials. Table 6 shows the laboratory-synthesized adsorbents and their performance in OW treatment.

Table 6 Laboratory synthesized adsorbents and its performance.

Adsorbent	Target	Performance	Reference
Silica NPs	Oil saltwater	93% oil removal	[49]
	Oil freshwater	93% oil removal	[49]
Alumina NPs	Oil saltwater	185.76 mg-oil/g-adsorbent	[50]
CNTs	Oil	87% oil removal	[51]

3.2.2 Commercial Adsorbents

Commercially accessible adsorbents are frequently used in OW treatment. AC is the foremost broadly utilized commercial adsorbent. It is also the oldest known adsorbent [52]. Besides OW treatment, AC is also use to eliminate various pollutants such as heavy metals and dyes from wastewater. AC has the advantage of simple operation. However, its broad application in wastewater treatment is restricted by its high production cost and relatively low adsorption capacity, which needs frequent regeneration or disposal [53].

Zeolite is another commonly available commercial adsorbent. Zeolite is an inorganic substance with high porosity, wide surface area, high regeneration potential, strong acidic stability, and economics, making it a good adsorbent for OW treatment [54]. Jun et al. [54] reported that zeolite is exceptional for removing organic compounds and heavy metals in wastewater. It was also testified that zeolite displays incredible adsorption ability towards aerobic POME [55]. However, the poor permeability of zeolite necessitates an artificial transformation in practical applications [52].

Khader et al. [56] used AC and zeolite to absorb oil and COD from produced water by absorption experiments (continuous fixed-bed column). Two types of AC –powdered and granular were utilized. The results revealed that powdered AC obtained the highest removal of oil and COD (72.98% and 69.5%),   followed by granular AC (64.87% and 60.94%), and lastly zeolite (58.58% and 52.49%) at 1.25 mL/min, 0.5 g adsorbent dose, 40 ppm oil concentration, 1350 ppm COD, and 2 cm bed height. This arranged is related to the characteristics (surface area, pore volume) of the adsorbents that were used, where the surface area was 824.34, 504.35, and 303.45 m^2/g and pore volume was 0.753, 0.632, and 0.503 cm^3/g for powdered AC, granular AC, and zeolite, respectively. When the surface

area (large pore size) of the adsorbent is increased, the amount of adsorption capacity increases due to a decrease in the diameter of the adsorbent particles, because of increasing the active sites and the activity of adsorption kinetic for adsorbent to adsorb oil and COD from produces water and therefore the increased removal efficiency f organic pollutants.

3.3 Super Adsorbents

Super adsorbents with ultrahigh adsorption capabilities are highly desired for efficient OW treatment. However, most of the adsorbents with high adsorption capabilities are powdery adsorbents, showing inescapable limitations in practical application. Therefore, it is practically imperative that a simple yet reliable method for synthesizing adsorbents with ultrahigh adsorption capability and convenient column operation need to be developed. The superabsorbent that are going to discuss are palm oil mill effluent-based graphene sand composites (P-GSC) and palm oil mill effluent-based palm kernel shell (P-PKS).

3.3.1 Palm Oil Mill Effluent-based Graphene Sand Composite (P-GSC)

Graphene has gained popularity as an adsorbent due to its unique features of large surface area, high mechanical strength, low weight, high flexibility, and high chemical stability [57]. The incredible adsorption capability of graphene allows it to be used for OW treatment. Gupta et al. [58] developed a green method for synthesizing graphene material from cane sugar, a common disaccharide. Chemically synthesized graphene was immobilized on sand without needing any binder, resulting in a composited, referred to as graphene sand composite (GSC). GSC shows excellent performance in removing contaminates from water such as rhodamine 6G as a model dye and chlorpyrifos as a model pesticide to that of AC. On top of that, the GSC can be easily regenerated. Subsequently, Dubey et al. [59] studied the adsorption of GSC to remove hexavalent chromium, Cr (VI) the most toxic contaminant. The maximum adsorption capacity of GSC for Cr (VI) was found to be 2859.38 mg/g at room temperature which is claimed to be one of the exceptionally high values reported in the literature.

However, using graphic materials for large-scale and down-to-earth applications like water purification and wastewater treatment is quite challenging. This is mainly due to the difficulty in the large-scale synthesis of GSC, as the carbonaceous source of sugar is costly [60]. In general, an adsorbent can be termed as a low-cost adsorbent if it requires little processing, has an abundant carbonaceous source in nature, or the carbonaceous source is a by-product or waste material from the industry. Hence, a cheap and easily available carbonaceous source with a simple synthesis method to produce GSC is of utmost concern [61]. The palm oil industry is one of the major agro-industries in Malaysia. The palm oil extraction process consumes a huge amount of water for steam sterilizing the fresh oil palm fruit bunches (PFB) and clarifying the extracted oil which eventually ends up as POME, the single largest source of industrial wastewater in Malaysia [62]. Wan Mohammad Hamdan et al. [61] used POME as a low-cost carbonaceous source to synthesize P-GSC. Figure 2 presents FESEM micrographs of the synthesized P-GSC. P-GSC surface was rough, irregular, and covered with a thin sheet of graphene layers that could have contributed to high adsorption capability. The synthesized P-GSC was used as the adsorbent in the adsorption treatment process to remove the undesirable constituents in POME. This concept echoes the increasing importance of sustainable development, where the waste (POME) was converted into a value-added product (P-

GSC) to treat the waste (POME). Small size P-GSC (0.30–0.60 mm) had the best performance in removing COD, color, turbidity, and total dissolved solids (TDS) from diluted aerobic POME up to 94.7%, 92.3%, 83.3%, and 51.5%, respectively. The concept of sustainable waste-to-treat-waste has been proven throughout this study. Results from this study appear to be an attractive practice that could be economical and eco-friendly beneficial.
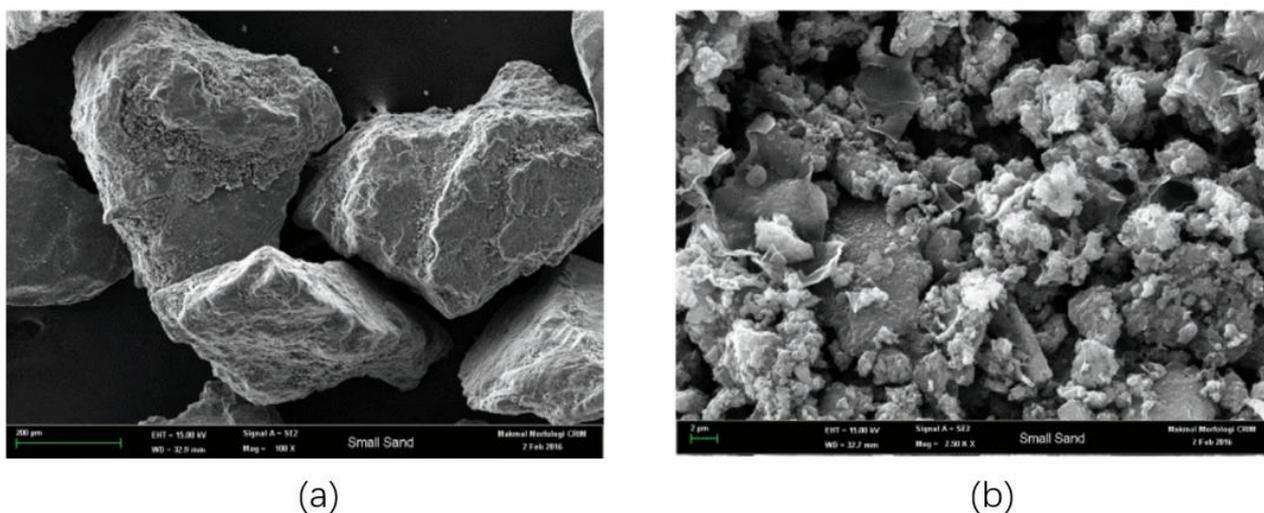

(a)

(b)

Figure 2 FESEM micrographs of small size P-GSC at the magnification of (a) 100× and (b) 2.5 k× (Adapted from [61]).

3.3.2 Palm Oil Mill Effluent-based Palm Kernel Shell (P-PKS)

Oil palm kernel shells (PKS) are another biomass produced by the palm oil industry. PKS with its large cavities and porosity, low cost, widespread accessibility, and adsorption affinity, is an excellent organic sorbent for pollution removal. Previous research used PKS to remove heavy metals, dyes, persistent organic pollutants, and contaminants [54]. However, raw PKS is lacks efficiency and stability, hence not applicable in actual wastewater treatment. Efforts have been underway by Teow et al. [62] to develop an adsorbent; the synthesis of which uses two wastes (POME and PKS) from the palm oil industry for the synthesis of P-GSC. Similar to the study by Wan Mohammad Hamdan et al. [61], POME was used as a low-cost carbonaceous source, coating onto PKS for P-GSC synthesis. The synthesized PKS was examined for removing methylene blue (MB) dye by adsorption. The batch column study demonstrated that small-sized synthesized P-GSC from PKS as a base material could remove up to 98.5% for concentration. Alternatively, Teow et al. [63] explored P-GSC synthesis with oil palm frond (OPF) juice as the natural carbon source and with oil palm kernel shell as the base material. The adsorption performance was evaluated by studying the effect of synthetic MB solution concentration and the P-GSC mass. 75.45%–99.13% removal of MB ions from synthetic MB solution after 20 h of adsorption performance study suggested the applicability and effectiveness of the synthesized P-GSC in treating dye-containing wastewater. The concept of deploying POME as the carbonaceous source to produce P-GSC, and then, deploying the resultant P-GSC as the adsorbent for MB dye removal has presented promising practical potential. This green technology can significantly contribute to the body of knowledge on sustainability, economic growth, and mitigating environmental degradation; thus, the environmentally friendly reuse of waste materials is envisioned to promote a 'zero-waste industry.

4. Adsorption Isotherms and Models

4.1 Kinetics

Adsorption kinetics needs to be understood before the applicability of any adsorbent. The mass transfer from the solution to the adsorption sites at the adsorbent's surface is constrained by mass transfer resistance that determines the time required to reach the state of equilibrium [64]. The time progress of the adsorption process is referred to as adsorption kinetics [65].

Diffusion processes usually limit adsorption rate toward the external adsorbent surface and within the porous adsorbent particles. Based on the model, the adsorption mechanism can be identified [66]. Typically, adsorption equilibria are not established instantaneously. This is particularly true for porous adsorbents. The surface complexity of the adsorbent solute concentration and flow influences kinetics. From the many different kinetics models, the most common models for the OW adsorption process are the Pseudo-first order (PFO), Pseudo-second order (PSO), and intraparticle diffusion model [67].

The PFO model is also known as the Lagergren model. PDF describes the adsorption of adsorbate onto adsorbent following the first-order mechanism [68]. It assumes that the rate of solute uptake is directly proportional to concentration, which is generally applicable at the initial stage of an adsorption process [69]. Eq. (1) represents the PFO model:

$$(q_e - q_t) = \ln q_e - (k_1 t) \tag{1}$$

where q_t is adsorbate absorbed onto adsorbent at time t (mg/g), q_e is equilibrium adsorption capacity (mg/g), and k_1 is rate constant per min. The linear plot of ln (q_e - q_t) against time is used to determine the rate constant k_1.

The PSO model assumes of the adsorbate's adsorption rate proportional to the available sites on the adsorbent. The reaction rate depends on the amount of adsorbate attached to the surface of the adsorbent [70]. The PSO model is described based on the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{2}$$

where q_t and q_e are the amounts of adsorbate adsorbed onto the adsorbent at equilibrium (mol/cm^3) and k_2 is the PSO rate constant (g/mg/min). The linear plot of t/q_t against time is used to determine q_e and k_2 from the slope and intercept, respectively. PSO and PFO do not explain adsorbate diffusion into the adsorbent [71]. Therefore, before any conclusion is made about the adsorption mechanism, diffusion models should be concerned.

The intraparticle diffusion model is the most popular formula to describe diffusion-controlled processes. It was widely applied to describe the liquid/solid adsorption kinetics. The intraparticle diffusion model is presented in Eq. (3):

$$q_t = K_{dif} t^{0.5} + C \tag{3}$$

where, q_t is the adsorbate concentration at time t (mg/g), K_{dif} is the intraparticle diffusion rate constant (mg/g min$^{0.5}$), C is the thickness of the boundary layer (mg/g), and t is the time taken for diffusion (min).

4.2 Isotherms

The equilibrium relationship between the adsorbent and the adsorbate is explained through various isotherms to quantify the amount of adsorbate at a constant temperature [72]. The most commonly used isotherm models are Langmuir, Freundlich and Tempkin isotherms.

4.2.1 Langmuir Isotherm

Langmuir isotherm is one of the oldest empirical models used to describe the adsorption equilibrium relationship [72]. Langmuir isotherm assumes monolayer adsorption in which adsorption only occurs at a finite number of sites. All adsorption sites are equivalent and adsorbed adsorbates do not interact with each another [67]. Eq. (4) is the Langmuir isotherm in the linear form:

$$\frac{Ce}{Cads} = \frac{1}{Qb} + \frac{Ce}{Q} \tag{4}$$

where C_e is the equilibrium concentration of adsorbent (mg/L), C_{ads} is the amount of adsorbate adsorbed at equilibrium (mol/cm^3), Q_b is the maximum adsorption constant (L/mg) at a given temperature, related to the energy of adsorption, and Q is the maximum adsorption capacity (mg/g).

4.2.2 Freundlich Isotherm

Freundlich isotherm describes adsorption processes that occur on the heterogeneous surface. Active sites with different energies promote multilayer adsorption in achieving equilibrium [73]. Eq. (5) is the Freundlich isotherm in the linear form:

$$lnQ = lnK_f + \frac{1}{n}lnC_e \tag{5}$$

where K_f is the Freundlich isotherm constant (L/g), n is the adsorption intensity (mg/L), C_e is the equilibrium concentration of adsorbate (mg/L).

4.2.3 Tempkin Isotherm

Tempkin isotherm contains a factor that considers the interaction between adsorbates [74]. The isotherm assumes that the heat of adsorption of all binding molecules in the adsorbent layer decreases linearly rather than logarithmically with coverage at average concentrations. The heat of adsorption is characterized by a uniform distribution of binding energies up to some maximum binding energy [67]. The model is expressed as follows:

$$q_e = \frac{RT}{b_T}\ln A_T + \left(\frac{RT}{b_T}\right)\ln C_e \tag{6}$$

where A_T is the Tempkin isotherm equilibrium binding constant (L/g), b_T is the Tempkin isotherm constant, R is the universal gas constant (8.314 J/mol/K), T is the temperature at 298 K, and C_e is the equilibrium concentration (mg/L). A_T and (RT/b_T) are determined from the intercept and slope of the plot of q_e against ln C_e, respectively.

5. Strength, Weakness, Opportunities and Threats (Swot) Analysis

SWOT analysis was conducted to identify and analyze internal strengths and weakness and external opportunities and threats that shape current and future operation of adsorption process for the treatment of oily wastewater for developing strategic goals. Table 7 summarized the SWOT analysis of adsorption process for oily wastewater treatment.

Table 7 SWOT analysis of adsorption process for the treatment of oily wastewater.

	Helpful To achieving the objective	Harmful To achieving the objective
Internal origin	Strengths ● Simple design ● Low cost ● Small footprint ● No secondary pollution	Weakness ● Weak specificity ● Regeneration needed or excessive waste product need to be charged ● Efficiency affected by operation conditions (such as pH and flow rate)
External origin	Opportunities ● Common oily wastewater treatment method ● Concepts, theory, and engineering aspects of the technologies are well developed	Threats ● Stringent discharge limit of oil and grease in wastewater ● Up-scaling of super adsorbent production

6. Conclusion

Pollution of OW has become a global phenomenon, causing adverse environmental and health hazards to the ecosystems. Over decades, adsorption technology has been engineered to curb this menace. Implementation of adsorption technology to treat OW provides an efficient approach to meeting stringent discharge limits of oil and grease in wastewater.

A detailed review of the adsorption process for the treatment of OW was presented. There is a vast array of natural adsorbents and non-natural adsorbents. However, most of the adsorbents with high adsorption capabilities are powdery adsorbents. Although powdery adsorbents have a high surface area for adsorption, they show inescapable limitations in practical application as a subsequent separation step is needed to retain the powdery adsorbents. Super adsorbents with ultrahigh adsorption capabilities such as P-GSC and P-PKS discussed in this paper are highly desired. The extraordinary properties of P-GSC and P-PKS can provide leap-forward opportunities to revolutionize traditional adsorption technology. However, scale-bridging and optimization study of these innovated super adsorbents is required for the real application. It shows a bright future of P-GSC and P-PKS towards OW treatment.

List of Abbreviations

AC	Activated carbon
BOD	Biological oxygen demand
CNTs	Carbon nanotubes
COD	Chemical oxygen demand
CPCB	Central Pollution Control Board
DDAB	Dimethyl dioctadecyl ammonium bromide
DOC	Dissolved organic carbon
EG	Exfoliated graphite
GSC	Graphene sand composite
MB	Methylene blue
NF	Nanofiltration
NMOs	Nanostructured mixed oxides
NPs	Nanoparticles
OPEFB	Oil palm empty fruit bunches
OPF	Oil palm frond
OSPAR	Oslo-Paris
OW	Wastewater or oily wastewater
O/W	Oil in water
PFB	Palm fruit bunches
PFO	Pseudo-first order
P-GSC	Palm oil mill effluent-based graphene sand composites
PKS	Palm kernel shells
POME	Palm oil mill effluent
P-PKS	Palm oil mill effluent-based palm kernel shell
PSO	Pseudo-second order
RO	Reverse osmosis
STAB	Stearyl trimethyl ammonium bromide
SWOT	Strength, weakness, opportunities and threats
TDS	Total dissolved solids
UNESCO	United Nations Educational, Scientific and Cultural Organization
UPTES	3-ureidopropyltriethoxysilane
VR	Vacuum residue
W/O	Water in oil

Acknowledgements

Author Contributions

Teow Yeit Haan has made a substantial contribution to the concept or design of the article, critical revision of the article for important intellectual content, and approved the version to be

published; Puteri Mimie Isma Nordin, Nur 'Izzah Ahmad Juanda, Muhammad Afiq Mohd Shafi, and Pavithiran Krishnan collected, analyzed, and interpreted data and drafted the article.

Competing Interests

The authors have declared that no competing interests exist.

References

1. Mat EA, Shaari J, How VK. Wastewater production, treatment and use in Malaysia. Proceedings of the Safe Use of Wastewater in Agriculture 5th Regional Workshop Southeast and Eastern Asia; 2013 March 5-7; Bali, Indonesia. Gevena: WHO.
2. World Water Assessment Programme. The United Nations world water development report 2017. Wastewater: The Untapped Resource. Paris: UNESCO; 2017.
3. Putatunda S, Bhattacharya S, Sen D, Bhattacharjee C. A review on the application of different treatment processes for emulsified oily wastewater. Int J Environ Sci Technol. 2019; 16: 2525-2536.
4. Abuhasel K, Kchaou M, Alquraish M, Munusamy Y, Jeng YT. Oily wastewater treatment: Overview of conventional and modern methods, challenges, and future opportunities. Water. 2021; 13: 980.
5. Dickhout JM, Moreno J, Biesheuvel PM, Boels L, Lammertink RG, De Vos WM. Produced water treatment by membranes: A review from a colloidal perspective. J Colloid Interface Sci. 2017; 487: 523-534.
6. Adetunji AI, Olaniran AO. Treatment of industrial oily wastewater by advanced technologies: A review. Appl Water Sci. 2021; 11: 98.
7. Jamaly S, Giwa A, Hasan SW. Recent improvements in oily wastewater treatment: Progress, challenges, and future opportunities. J Environ Sci. 2015; 37: 15-30.
8. Njoku KL. Responses of accessions of Zea mays to crude oil pollution using growth indices and enzyme activities as markers. Pollution. 2017; 4: 183-193.
9. Teow YH, Kam LM, Mohammad AW. Synthesis of cellulose hydrogel for copper (II) ions adsorption. J Environ Chem Eng. 2018; 6: 4588-4597.
10. Yalcinkaya F, Boyraz E, Maryska J, Kucerova K. A review on membrane technology and chemical surface modification for the oily wastewater treatment. Materials. 2020; 13: 493.
11. Chaplin BP. Advantages, disadvantages, and future challenges of the use of electrochemical technologies for water and wastewater treatment. In: Electrochemical water and wastewater treatment. Oxford: Butterworth-Heinemann; 2018. pp. 451-494.
12. Qin Z, Liu HM, Ma YX, Wang XD. Developments in extraction, purification, and structural elucidation of proanthocyanidins (2000–2019). Stud Nat Prod Chem. 2021; 68: 347-391.
13. Moreno-Castilla C. Adsorption of organic molecules from aqueous solutions on carbon materials. Carbon. 2004; 42: 83-94.
14. Rashed MN. Adsorption technique for the removal of organic pollutants from water and wastewater. In: Organic pollutants-monitoring, risk and treatment. Rijeka: IntechOpen; 2013. pp. 167-194.
15. Kundu P, Mishra IM. Treatment and reclamation of hydrocarbon-bearing oily wastewater as a hazardous pollutant by different processes and technologies: A state-of-the-art review. Rev

Chem Eng. 2019; 35: 73-108.

16. Coca J, Gutiérrez G, Benito J. Treatment of oily wastewater. In: Water purification and management. Dordrecht: Springer; 2011. pp. 1-55.

17. Hui L, Yan W, Juan W, Zhongming L. A review: Recent advances in oily wastewater treatment. Recent Innov Chem Eng. 2015; 7: 17-24.

18. Liew WL, Kassim MA, Muda K, Loh SK, Affam AC. Conventional methods and emerging wastewater polishing technologies for palm oil mill effluent treatment: A review. J Environ Manage. 2015; 149: 222-235.

19. Zolfaghari R, Fakhru'l-Razi A, Abdullah LC, Elnashaie SS, Pendashteh A. Demulsification techniques of water-in-oil and oil-in-water emulsions in petroleum industry. Sep Purif Technol. 2016; 170: 377-407.

20. Holdich RG, Cumming IW, Smith ID. Crossflow microfiltration of oil in water dispersions using surface filtration with imposed fluid rotation. J Membr Sci. 1998; 143: 263-274.

21. Yu L, Han M, He F. A review of treating oily wastewater. Arab J Chem. 2017; 10: S1913-S1922.

22. Ahmad AL, Sumathi S, Hameed BH. Chitosan: A natural biopolymer for the adsorption of residue oil from oily wastewater. Adsorp Sci Technol. 2004; 22: 75-88.

23. Patterson JW. Industrial wastewater treatment technology. 2nd ed. Oak Ridge: U.S. Department of Energy; 1985.

24. Yang CL. Electrochemical coagulation for oily water demulsification. Sep Purif Technol. 2007; 54: 388-395.

25. Kalla S. Use of membrane distillation for oily wastewater treatment–A review. J Environ Chem Eng. 2021; 9: 104641.

26. Turunawarasu D. A novel and sustainable approach in treating restaurant wastewater with kapok fiber through a compact biodegradable oil absorption filter system. Seri: IskandarUniversiti Teknologi PETRONAS; 2012.

27. Daud MS, Ngadiman NI, Suliman MS. The awareness of recycling the used of cooking oil. J Crit Rev. 2020; 7: 30-32.

28. Azahar WN, Bujang M, Jaya RP, Hainin MR, Mohamed A, Ngad N, et al. The potential of waste cooking oil as bio-asphalt for alternative binder--An overview. J Teknol. 2016; 78: 54917941.

29. Guyer JP. An introduction to oily wastewater collection and treatment. Scotts Valley: Guyer Partners; 2018.

30. Hanafy M, Nabih HI. Treatment of oily wastewater using dissolved air flotation technique. Energ Source Part A. 2007; 29: 143-159.

31. Pintor AM, Vilar VJ, Botelho CM, Boaventura RA. Oil and grease removal from wastewaters: Sorption treatment as an alternative to state-of-the-art technologies. A critical review. Chem Eng J. 2016; 297: 229-255.

32. Wainipee W, Weiss DJ, Sephton MA, Coles BJ, Unsworth C, Court R. The effect of crude oil on arsenate adsorption on goethite. Water Res. 2010; 44: 5673-5683.

33. Takeuchi K, Fujishige M, Kitazawa H, Akuzawa N, Medina JO, Morelos-Gomez A, et al. Oil sorption by exfoliated graphite from dilute oil–Water emulsion for practical applications in produced water treatments. J Water Process Eng. 2015; 8: 91-98.

34. Zheng Y, Liu W, Wang Q, Sun Y, Li G, Wu T, et al. Study of STAB-and DDAB-modified sepiolite tructures and their adsorption performance for emulsified oil in produced water. Colloids Interface Sci Commun. 2020; 34: 100231.

35. Bezerra de Araujo CM, Filipe Oliveira do Nascimento G, Rodrigues Bezerra da Costa G, Santos da Silva K, Salgueiro Baptisttella AM, Gomes Ghislandi M, et al. Adsorptive removal of dye from real textile wastewater using graphene oxide produced via modifications of hummers method. Chem Eng Commun. 2019; 206: 1375-1387. DOI: 10.1080/00986445.2018.1534232

36. Qu SS, Zhang PP, Wang YM. Experiment with modified attapulgite clay on the treatment of domestic sewage. Proceedings of the 2010 International Conference on Challenges in Environmental Science and Computer Engineering; 2010 March 6-7; Wuhan, China. New York: IEEE.

37. Hossain S, Hossain F. Chitosan: An effective material for textile waste water management. Int J Adv Res. 2020; 8: 26-34.

38. Rytwo G, Rettig A, Gonen Y. Organo-sepiolite particles for efficient pretreatment of organic wastewater: Application to winery effluents. Appl Clay Sci. 2011; 51: 390-394.

39. Dewi R, Sari R. The effect of the natural bentonite to reduce COD in palm oil mill effluent by using a hybrid adsorption-flotation method. IOP Conf Ser Mater Sci Eng. 2017; 210: 012016.

40. Alkherraz AM, Ali AK, Elsherif KM. Removal of Pb(II), Zn(II), Cu(II) and Cd(II) from aqueous solutions by adsorption onto olive branches activated carbon: Equilibrium and thermodynamic studies. Chem Int. 2020; 6: 11-20.

41. Kunjirama M, Saman N, Johari K, Song ST, Kong H, Cheu SC, et al. Adsorption affinity and selectivity of 3-ureidopropyltriethoxysilane grafted oil palm empty fruit bunches towards mercury ions. Environ Sci Pollut Res. 2017; 24: 15167-15181.

42. Song ST, Saman N, Johari K, Mat H. Surface chemistry modifications of rice husk toward enhancement of Hg(II) adsorption from aqueous solution. Clean Technol Environ Policy. 2014; 16: 1747-1755.

43. Sueyoshi M, Al-Maamari RS, Jibril B, Tasaki M, Okamura K, Kuwagaki H, et al. Preparation and characterization of adsorbents for treatment of water associated with oil production. J Anal Appl Pyrolysis. 2012; 97: 80-87.

44. El-Naas MH, Al-Zuhair S, Alhaija MA. Removal of phenol from petroleum refinery wastewater through adsorption on date-pit activated carbon. Chem Eng J. 2010; 162: 997-1005.

45. Al.Haddabi M, Vuthaluru H, Znad H, Ahmed M. Removal of dissolved organic carbon from oily produced water by adsorption onto date seeds: Equilibrium, kinetic, and thermodynamic studies. Water Air Soil Pollut. 2015; 226: 172.

46. El-Nafaty UA, Muhammad IM, Abdulsalam S. Biosorption and kinetic studies on oil removal from produced water using banana peel. Civ Environ Res. 2013; 3: 125-136.

47. Ibrahim TH, Gulistan AS, Khamis MI, Ahmed H, Aidan A. Produced water treatment using naturally abundant pomegranate peel. Desalination Water Treat. 2016; 57: 6693-6701.

48. Kalfa OM, Yalçınkaya Ö, Türker AR. Synthesis of nano B_2O_3/TiO_2 composite material as a new solid phase extractor and its application to preconcentration and separation of cadmium. J Hazard Mater. 2009; 166: 455-461.

49. Franco CA, Martínez M, Benjumea P, Patiño E, Cortés FB. Water remediation based on oil adsorption using nanosilicates functionalized with a petroleum vacuum residue. Adsorp Sci Technol. 2014; 32: 197-207.

50. Franco CA, Nassar NN, Cortés FB. Removal of oil from oil-in-saltwater emulsions by adsorption onto nano-alumina functionalized with petroleum vacuum residue. J Colloid Interface Sci. 2014; 433: 58-67.

51. Fard AK, Rhadfi T, Mckay G, Al-marri M, Abdala A, Hilal N, et al. Enhancing oil removal from water using ferric oxide nanoparticles doped carbon nanotubes adsorbents. Chem Eng J. 2016; 293: 90-101.

52. Yu C, Han X. Adsorbent material used in water treatment-a review. Proceedings of the 2015 2nd International Workshop on Materials Engineering and Computer Sciences; 2015 October 10-11; Jinan, China. Paris: Atlantis Press; 2015. pp. 286-289.

53. De Gisi S, Lofrano G, Grassi M, Notarnicola M. Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review. Sustain Mater Technol. 2016; 9: 10-40.

54. Jun KC, Raman AA, Buthiyappan A. Treatment of oil refinery effluent using bio-adsorbent developed from activated palm kernel shell and zeolite. RSC Adv. 2020; 10: 24079-24094.

55. Shavandi MA, Haddadian ZM, Ismail MH, Abdullah N, Abidin ZZ. Removal of Fe(III), Mn(II) and Z(II) from palm oil mill effluent (POME) by natural zeolite. J Taiwan Inst Chem Eng. 2012; 43: 750-759.

56. Khader EH, Mohammed TJ, Adnan SW. Reduction of oil and COD from produced water by activated carbon, zeolite, and mixed adsorbents in a fixed-bed column. Desalination Water Treat. 2021; 227: 216-227.

57. Gopalakrishnan A, Krishnan R, Thangavel S, Venugopal G, Kim SJ. Removal of heavy metal ions from pharma-effluents using graphene-oxide nanosorbents and study of their adsorption kinetics. J Ind Eng Chem. 2015; 30: 14-19.

58. Gupta SS, Sreeprasad TS, Maliyekkal SM, Das SK, Pradeep T. Graphene from sugar and its application in water purification. ACS Appl Mater Interfaces. 2012; 4: 4156-4163.

59. Dubey R, Bajpai J, Bajpai AK. Green synthesis of graphene sand composite (GSC) as novel adsorbent for efficient removal of Cr(VI) ions from aqueous solution. J Water Process Eng. 2015; 5: 83-94.

60. Teow YH, Nordin NI, Mohammad AW. Green synthesis of palm oil mill effluent-based graphenic adsorbent for the treatment of dye-contaminated wastewater. Environ Sci Pollut Res. 2019; 26: 33747-33757.

61. Hamdan WN, Haan TY, Mohammad AW. Sustainable approach in palm oil industry-green synthesis of palm oil mill effluent based graphene sand composite (P-GSC) for aerobic palm oil mill effluent treatment. J Eng. 2018; 1: 11-20.

62. Teow YH, Wan Mohammad Hamdan WN, Mohammad AW. Preparation of palm oil industry's biomass-based graphene composite for the adsorptive removal of methylene blue. Adsorp Sci Technol. 2021; 2021: 9130233.

63. Teow YH, Tajudin SA, Ho KC, Mohammad AW. Synthesis and characterization of graphene shell composite from oil palm frond juice for the treatment of dye-containing wastewater. J Water Process Eng. 2020; 35: 101185.

64. de Franco MA, de Carvalho CB, Bonetto MM, de Pelegrini Soares R, Féris LA. Diclofenac removal from water by adsorption using activated carbon in batch mode and fixed-bed column: Isotherms, thermodynamic study and breakthrough curves modeling. J Clean Prod. 2018; 181: 145-154.

65. Tefera DT, Hashisho Z, Philips JH, Anderson JE, Nichols M. Modeling competitive adsorption of mixtures of volatile organic compounds in a fixed-bed of beaded activated carbon. Environ Sci Technol. 2014; 48: 5108-5117.

66. Largitte L, Pasquier R. A review of the kinetics adsorption models and their application to the

adsorption of lead by an activated carbon. Chem Eng Res Des. 2016; 109: 495-504.

67. Foo KY, Hameed BH. Insights into the modeling of adsorption isotherm systems. Chem Eng J. 2010; 156: 2-10.

68. Apul OG, Wang Q, Zhou Y, Karanfil T. Adsorption of aromatic organic contaminants by graphene nanosheets: Comparison with carbon nanotubes and activated carbon. Water Res. 2013; 47: 1648-1654.

69. Saha D, Grappe HA. Adsorption properties of activated carbon fibers. In: Activated carbon fiber and textiles. Sawston: Woodhead Publishing; 2017. pp. 143-165.

70. Malakootian M, Ghadiri SK, Yousefi N, Fatehizadeh A. Isotherms and kinetics studies of biosorption nickel (II) and chromium (VI) from aqueous solution by dried activated sludge. Int J Environ Health Eng. 2012; 1: 2.

71. Cicek N, Winnen H, Suidan MT, Wrenn BE, Urbain V, Manem J. Effectiveness of the membrane bioreactor in the biodegradation of high molecular weight compounds. Water Res. 1998; 32: 1553-1563.

72. El-Khaiary MI. Least-squares regression of adsorption equilibrium data: Comparing the options. J Hazard Mater. 2008; 158: 73-87.

73. Balouch A, Kolachi M, Talpur FN, Khan H, Bhanger MI. Sorption kinetics, isotherm and thermodynamic modeling of defluoridation of ground water using natural adsorbents. Am J Anal Chem. 2013; 4: 31564.

74. Dada AO, Olalekan AP, Olatunya AM, Dada OJ. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk. IOSR J Appl Chem. 2012; 3: 38-45.