Poly(Methyl Methacrylate) Grafted Wheat Straw for Economical and Eco-friendly Treatment of Oily Wastewater.

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Poly(methyl methacrylate) grafted wheat straw for economical and eco-friendly treatment of oily wastewater.

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Abstract

The sustainable development of oil-gas and petrochemical industries necessitates the development of cost-effective and eco-friendly technologies to treat mass-produced oily wastewater discharge from these industries. This study applied a simple radical polymerization to enhance the oil adsorption efficiency of agricultural waste biomass wheat straw (WS) by grafting biocompatible PMMA. Diesel oil adsorption from oil-in-water emulsion using the PMMA grafted WS was thoroughly studied for the first time in the quest of developing an economical and eco-friendly adsorbent for the adsorptive treatment of oily wastewater. Initially, the pristine WS was subjected to alkaline hydrogen peroxide pre-treatment to remove the materials that can lead to secondary pollution during operation, to expose the reactive cellulose surface sites that can enhance grafting efficiency, and to break the inner interconnected tubular pore channel walls; otherwise, the tubular pore channels will not be accessible to viscous oil due to limited capillary penetration. The success of pre-treatment of pristine WS and the subsequent PMMA grafting were evaluated by SEM morphology, BET analysis, EDX and XPS elemental analysis, FTIR, and contact angle measurements. SEM images indicated that the inner interconnected tubular pore channels of WS are exposed significantly upon alkaline hydrogen peroxide pretreatment. PMMA grafting substantially improved oil adhesivity, as evident from the 0° oil contact angle for WS-g-PMMA film. Oil absorptivity was thoroughly evaluated by batch oil adsorption study using variable adsorbent dosages and oil emulsion concentrations. The WS-g-PMMA exhibited explicitly higher adsorption capacity (ca. 1129 mg/g) compared to that of the pristine (ca. 346 mg/g) and pretreated (ca. 741 mg/g) due to high accessibility to exposed inner interconnected tubular pore channels and strong hydrophobic interactions between the WS-g-PMMA surface and oil droplets. Langmuir and Freundlich adsorption isotherms were applied to evaluate the adsorption mechanism. The experimental data fit well with the Freundlich isotherm, clearly indicating the heterogeneity of adsorption sites, as well as multilayer adsorption of oil. The experimental adsorption data fit well
with the pseudo-second-order rate equation with $R^2$ as high as 0.999, which confirmed the multilayer adsorption of oil. The high oil adsorption capacity of the WS-g-PMMA makes it a very promising material for oily wastewater treatment. This will simultaneously resolve issues with the treatment of oily wastewater and facilitate the recycling of abundant quantities of waste WS. This study serves as a reference for analyzing the suitability of wheat straw for treating extremely challenging waste streams, such as SAGD produced water containing BTEX and PAHs that are also hydrophobic like diesel oil.

**Keywords:** Oily wastewater treatment; Adsorption; Wheat straw; Poly(methyl methacrylate); Free radical graft polymerization; Adsorption kinetics

1. **Introduction**

Oily wastewater discharge from oil/gas and petrochemical industries, commonly termed as produced water, poses a substantial threat to water bodies since it often carries several toxic and carcinogenic compounds, such as benzene, toluene, ethylbenzene, and xylene known as BTEX, phenols, and polycyclic aromatic hydrocarbons (PAHs) that are harmful to aquatic fauna (Pampanin and Sydnes 2013). Industrial wastewater discharges account for approximately 10% of the total wastewater discharges. Oil and grease are common pollutants in industrial discharges, and their concentration may range from 10 mg/L to 50,000 mg/L in various industrial sources, including petroleum refineries and aluminum rolling mills. Therefore, developing an efficient and economic oily wastewater treatment technology is pivotal for the sustainable growth of industries (Cheryan and Rajagopalan 1998).

Adsorption is a promising treatment technique since it is simple, sustainable, and cost-effective (Al-Majed et al. 2012; Sabir 2015; Zamparas et al. 2020). It is also found to be efficient in removing free, dispersed, and emulsified oil (Ibrahim et al. 2009; Li et al. 2018). Adsorption-based techniques are also suitable for treating diluted effluents (Sokker et al. 2011; Xavier et al. 2018). The desired criteria for oil adsorbents are high hydrophobicity, oleophilicity, surface area, and porosity (Adebajo et al. 2003; Al-Majed et al. 2012; Pintor et al. 2016; Zamparas et al. 2020), which are found in commonly used adsorbents, including activated carbon, graphene, and carbon nanotubes. The most common traditional adsorbent used for oil-water separation is activated
carbon (AC) (Pintor et al. 2016; Zamparas et al. 2020). Activated carbon systems, however, are not economical and require rigorous regeneration of spent activated carbon due to their microporous structure (Beall 2003; Pintor et al. 2016). Apart from that, its major drawback would be the carbon footprint, as estimations show that the consumption of each kg of AC can release approximately 0.7kg of carbon dioxide with the embodied energy of around 70MJ (Zanoletti et al. 2018). Other synthetic high-performance adsorbents such as graphene-based materials and carbon nanotubes are complicated and expensive to prepare (Pintor et al. 2016; Zamparas et al. 2020) and are also characterized by their high carbon footprint (Ali et al. 2019) and difficulty in disposing of used adsorbents.

In the context of exploring cheaper, environmentally benign, and low carbon-emitting adsorbents, the recent trend is to utilize renewable natural materials, such as agricultural by-products, as an alternative to traditional adsorbents (Al-Majed et al. 2012; Pintor et al. 2016; Zamparas et al. 2020). It is undoubtedly wise to develop processes that can resolve diverse issues at the same time. One such process development would be utilizing a waste by-product to treat another waste since it would simultaneously resolve the challenges of waste management involved in both cases. The spent biomass can also be easily regenerated and reused by washing with solvents with high solubility for oil (Lin et al. 2003; El-Naas et al. 2010). Agricultural wastes used as adsorbents for treating hydrocarbon-containing effluents include rice husk (Kudaybergenov et al. 2015), wheat straw (Sun et al. 2004; Lv et al. 2017), cotton fiber (Deschamps et al. 2003), Platanus Fruit Fibers (Yang et al. 2016), kapok fiber (Wang et al. 2012), and banana peels (Alaa El-Din et al. 2017).

Among the variant of natural bio-adsorbents, wheat straw is unique due to its highest abundance, relatively higher structural stiffness, and well-studied chemical structure and surface reactivity (Liu et al. 2005). The surface of the biomasses needs to be engineered to increase their adsorptive capacity (Adebajo et al. 2003). These materials can also result in secondary pollution by releasing their constituent organic compounds when used in pristine form (Ibrahim et al. 2009). Therefore, it is necessary to explore simple chemical modification methods that can enhance the oil absorptivity and prevent secondary pollution while retaining cost-effectiveness and biodegradability. Many reports have appeared on utilizing chemically surface-modified various types of straw for oil adsorption (Sun et al. 2002, 2004; Ibrahim et al. 2009, 2012; Li et al. 2013;
Lv et al. 2017; Tang et al. 2018; Xu et al. 2018). Some of the common surface modification methods applied on straw include surfactant modification of barley straw (Ibrahim et al. 2009, 2012), acetylation of rice straw (Sun et al. 2002), wheat straw (Sun et al. 2004; Lv et al. 2017), and corn straw (Li et al. 2013), esterification of wheat straw with palmitic acid (Tang et al. 2018), and impregnation of silica (SiO$_2$) and ZnO particles by octyltriethoxysilane or heptadecafluoro-decylalkyl trimethoxysilane coupling agents on corn straw fiber surface (Zang et al. 2016; Xu et al. 2018). As expected, the primary objective of such chemical modifications was to increase oil adsorption by increasing the surface hydrophobicity, oleophilicity, surface area, and/or porosity. The surfactant modification is based on the electrostatic interaction of cationic ends of the surfactants and the negatively charged sites on the adsorbent surface, leaving the surfactants susceptible to leaching into the treated water. Meanwhile, the acetylation (Sun et al. 2002, 2004; Li et al. 2013; Lv et al. 2017), esterification of wheat straw with palmitic acid (Tang et al. 2018), and silane coupling (Zang et al. 2016; Xu et al. 2018) reactions form ester and silyloxy bonds. These bonds are susceptible to hydrolysis under acidic or basic pH, making these surface modifications undesirable for the long-term treatment of alkaline oily wastewater, such as oil-gas produced water having pH in the range of 9-11. These reactions also involve excessive use of chemicals and/or multistep pre-treatment. The fluoro-silane modification for the SiO$_2$ impregnation approach also alters the biodegradability of straw, and the use of halogenated compounds should be avoided since these are deleterious for the atmosphere. In this context, it is important to explore surface modification methods that can retain the economic and environmental benefits of using waste biomass as an adsorbent.

Polymer grafting by free radical polymerization is one such technique. It does not involve a complicated process like esterification, acetylation, and silylation. In addition, polymer grafting also helps in retaining the unique properties of crystalline cellulose, which would otherwise be wrecked in other processes (Samal et al. 1986; Kim et al. 2020). However, free-radical mediated polymer grafting is scarcely explored for the modification of lignocellulosic biomasses, such as wheat straw (Russell 2002). Poly(methyl methacrylate) (PMMA) is an extensively used polymer for incorporating hydrophobic properties into a wide variety of materials, including cellulose (Rosli et al. 2015), wood (Fu et al. 2012), natural fibre (Chen et al. 2009), cotton fabric (Wang et al. 2020), multiwalled carbon nanotubes (nan Shen et al. 2013), and inorganic nanoparticles.
(Huang et al. 2009; Wang et al. 2011; Soleimani and Moghaddami 2018). Apart from the high hydrophobicity and oleophilicity, PMMA possesses high mechanical stability, chemical stability, thermal stability, resistance to acid/base hydrolysis, biocompatibility, and reasonable biodegradability (Hollick et al.; Yang et al. 2005; Alemdar et al. 2007; Maiti et al. 2013). PMMA grafted wheat straw has previously been used to increase flame retardancy (Mukherjee et al. 2017) and moisture resistance of straw biomasses (Thakur et al. 2013a, b). PMMA indeed has been shown to enhance the oil adsorptivity of natural rubber foam (Ratcha et al. 2014, 2015). Despite favorable criteria for large-scale oil adsorption treatment, PMMA grafted wheat straw (WS-g-PMMA) was not utilized for adsorbing oil from an oil-in-water emulsion.

This study is the first attempt to understand the potential of WS-g-PMMA for adsorptive removal of oil from an oil-in-water emulsion in a systematic way through batch adsorption studies. At first, the raw dried straw was mechanically ground into 250-425 µm size particles. Then, the straw was subjected to single-step pre-treatment with environmentally benign alkaline hydrogen peroxide (H$_2$O$_2$) to remove the constituents causing secondary pollution of water (wax and resins), to break the lignin shield for exposing reactive hydroxyl groups for PMMA grafting, and to break the inner interconnected tubular pore channel walls for allowing the access to oil. Afterward, a simple and efficient radical polymerization was applied to graft PMMA on the pretreated wheat straw. Cerium Ammonium Nitrate (CAN) was chosen as the reaction initiator to graft polymers predominantly on the surface and to simplify the modification reaction. The success of PMMA grafting was assessed by attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy, Energy-dispersive X-ray (EDX) spectroscopy, X-ray photoelectron spectroscopy (XPS). The percentage of PMMA grafting was evaluated by gravimetric analysis. Surface morphology was evaluated by scanning electron microscopy (SEM). Surface area and porosity were evaluated by BET analysis. Surface wettability was analyzed by water and oil contact angle measurements, while oil removal efficiency and adsorption capacity were systematically studied by batch oil adsorption experiments. Langmuir and Freundlich isotherms were applied to understand the adsorption mechanism. Finally, adsorption kinetics was studied by applying pseudo-first-order and pseudo-second-order kinetic models.
2. Experimental Method

2.1. Materials and Chemicals
Wheat straw was obtained from a farm in the Edmonton area. Methyl methacrylate (MMA) (99%), cerium ammonium nitrate (≥ 98%), and nitric acid were all obtained from Sigma Aldrich and were used as received. Acetone and methanol used for the purification of grafted material were purchased from Fisher Scientific. Ethanol (95%) was used for regenerating the spent column and was procured from Fisher Scientific. Sodium hydroxide pellets and hydrogen peroxide (30%) used for the pre-treatment of straw particles prior to grafting were purchased from Fisher Scientific. Diesel oil was obtained from a local fuel station.

2.2. Pre-treatment of wheat straw
Wheat straw was pulverized and sieved through 60 and 80 mesh screens to obtain particles in size range of 250-425 µm. The particles were rinsed ultrasonically with deionized (DI) water, followed by ethanol and DI water washing. The particles were then subjected to pre-treatment with NaOH and H₂O₂ to break the lignin shield enclosing the cell wall. Each 4 g of wheat straw particles was treated with 100 mL of 0.5 wt% NaOH and 3.5 mL of 30% H₂O₂ (Xu et al. 2018). The solution was stirred for 14 h at ambient temperature. The unreacted reagents and by-products were removed by rinsing the pretreated particles thoroughly with DI water and ethanol. Any excess alkaline residue in the solution was neutralized by adjusting the pH in the range of 6.5-7.0 using 6 mol/L HCl. At last, the pretreated particles were rinsed thoroughly with DI water and dried at 40 ºC until a constant weight was reached.

2.3. Preparation of WS-g-PMMA
The pretreated wheat straw was dispersed in a fixed volume of DI water. The volume of DI water was optimized during the initial reactions with the intention of keeping the amount of solvent as low as possible, just sufficient to disperse the straw particles. Optimizing the amount of solvent also helped in maintaining the good miscibility of all the reagents, providing favorable reaction kinetics, and facilitating the precipitation of PMMA grafted particles from the reaction mixture. Hence, a preliminary visual interpretation of the success of the reaction was achieved. The dispersion was stirred at 70 ºC for 1 h under a nitrogen atmosphere. Following that, MMA was
added dropwise using a syringe over a 30 min period while stirring the reaction mixture at 350 rpm. Finally, 10 mL of 2 mmol/L of CAN solution, prepared by dissolving CAN in 0.1 mol/L nitric acid, was added to the mixture, and stirred under the nitrogen atmosphere for 1 h. The weight ratio of WS/MMA was varied from 0.75 to 3.65 to optimize the amount of MMA required for the effective grafting of PMMA. The mixture was cooled to room temperature, and the grafting was terminated by pouring the mixture into excess methanol solution, followed by washing the precipitated WS-g-PMMA granules with DI water. The grafted particles were then dried at 40 °C until a constant weight was reached. The ungrafted homopolymer was extracted using acetone in a Soxhlet apparatus. The extracted sample was dried at 40 °C for 24 h. The grafting percentage (GP) was calculated as (Fakhru'L-Razi et al. 2001):

\[ GP = \frac{W_2 - W_1}{W_1} \times 100 \]  

(1)

where \( W_1 \) is the initial weight of wheat straw particles in g, and \( W_2 \) is the weight of WS-g-PMMA particles in g.

2.4. Characterization of WS-g-PMMA

The grafting of PMMA was evaluated by comparing the ATR-FTIR (Bruker, Equinox 55) frequencies and high-resolution C1s XPS (Kratos AXIS Ultra) spectra of WS-g-PMMA with that of pristine and pretreated WS. The surface morphology was analyzed by scanning electron microscopy (SEM) (FE-SEM, Zeiss, Oberkochen, Germany), and the elemental composition was determined by Energy-dispersive X-ray (EDX) (Bruker model) spectroscopy. Information on porosity and surface area were obtained by Brunauer-Emmett-Teller (BET) and Density Functional Theory (DFT) analysis by outgassing the samples with nitrogen at 150 °C for 2 h in physisorption/chemisorption analyzers (Quantachrome Autosorb iQ). The wettability of the samples was analyzed by measuring contact angles by the sessile drop method (Kruss GmbH). The wheat straw samples were pressed and compacted using an FTIR pellet press at room temperature to obtain pellets with approximately 5 mm diameter (Guettler et al. 2013). The pellets were firmly fixed on a glass side using double-sided tape. A 2 µl droplet of DI water or oil (diesel) was placed on the sample surface using a syringe, and the measurements were taken at three different spots to obtain an average value.
2.5. Preparation of oil-in-water emulsions

Three different concentrations (100, 200, and 300 ppm) of oil-in-water emulsions were prepared by placing 100, 200, and 300 mg of diesel in 1 L of DI water followed by probe sonication (Cole-Parmer ultrasonic processor) for 15, 25, and 35 min respectively at 60% amplitude in pulse mode (3s on and 1s off) (Diraki et al. 2018). Following that, the solutions were homogenized (Fisherbrand™ 150) at 10,000 rpm for 15 min. The stability of the emulsions was assessed by visual monitoring for 24 h. The dynamic light scattering technique (DLS, ALV/CGS-3 Compact Goniometer) was used to determine the size distribution of oil droplets in the emulsion. The oil emulsion of 300 ppm concentration was found to be monodisperse with a droplet size of 0.47 ± 4.15 µm.

2.6. Batch adsorption study

Oil removal efficiency and adsorption capacity of the pristine, pretreated, and WS-g-PMMA were studied by batch adsorption experiments. Three different variables considered for the adsorption study were the initial oil concentration, the adsorbent dosage, and the contact time. The experiments were carried out by varying the adsorbent dosage from 5 to 25 mg for each initial oil concentration of 100, 200, and 300 ppm, respectively. Centrifuge tubes with a capacity of 50mL were filled with 40 mL of emulsion and mixed at a constant shaking speed (160 oscillations/min) using a mechanical shaker (Eberbach 6000) for a total time of 1 h. The WS-g-PMMA samples were then centrifuged at 1000 rpm, and the remaining oil concentration was analyzed by measuring the scattering at 290 nm with a UV-visible spectrophotometer. A control tube with emulsion alone was also tested.

The adsorption capacity and oil removal efficiency were calculated using the formulas (Diraki et al. 2018):

\[ q_t = \frac{(C_0 - C_t) \times V}{W_g} \quad (2) \]

\[ \text{RE} = \frac{C_0 - C_t}{C_0} \times 100 \quad (3) \]

where \( C_0 \) is the initial oil concentration (ppm), \( C_t \) is the oil concentration (ppm) at time \( t \) after adsorption on WS samples, \( V \) is the volume of emulsion (mL), and \( W_g \) is the weight of adsorbent (mg).
2.7. Adsorption isotherms

Adsorption isotherm models were used to represent the equilibrium relationship of the adsorption process graphically. It describes the amount of oil being adsorbed by the WS samples as a function of adsorbent concentration at a constant temperature.

2.7.1. Langmuir isotherm

This model is mainly defined for monolayer adsorption (Xu et al. 2012), where the following assumptions are considered: (a) adsorption sites possess the same energy, and the number of adsorption sites remains constant (homogenous surface), and (b) adsorption is reversible. Therefore, at equilibrium, the rates of adsorption and desorption are assumed to be the same. The linearized form of the Langmuir equation is given by:

\[
\frac{C_e}{q_e} = \frac{1}{q_0b} + \frac{C_e}{q_m}
\]

where \(C_e\) is the concentration of oil (ppm) at equilibrium, \(q_e\) is the value of \(q\) at equilibrium (mg), \(q_m\) is the mass of adsorbate adsorbed per unit mass of adsorbent (i.e., mg adsorbate/g adsorbent), and \(b\) is an empirical constant. A plot of \(C_e/q_e\) versus \(C_e\) is used to determine the mechanism of adsorption.

2.7.2. Freundlich isotherm

The Freundlich model is a more comprehensive isotherm and deals with both homogenous and heterogeneous surfaces. In addition, the model applies for multilayer adsorption, i.e., physisorption (Xu et al. 2012). The expression of this model is given by:

\[
q_e = K C_e^{1/n}
\]

where \(K\) is Freundlich constant related to adsorption capacity, and \(n\) is an empirical value, which is a function of the degree of heterogeneity of the adsorbent. The intercept of the plot of log \(q_e\) versus log \(C_e\) gives \(K\) and \(n\).

2.8. Adsorption kinetics

Pseudo-first order and pseudo-second-order kinetic models are widely applied to understand the behaviors involved in the uptake of pollutants by adsorbents. The experimental adsorptivity data
were obtained by varying the contact time at five-minute intervals using an initial oil concentration of 300 ppm, WS samples dosage of 5 mg, and shaking speed of 160 oscillations/min and were analyzed by plotting a linear fit. The pseudo-first-order kinetic equation in linear form is given by (Diraki et al. 2018):

\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]  
*(6)*

where \( q_t \) is adsorption capacity at time \( t \) (mg/g), \( k_1 \) is the pseudo-first-order rate constant (min\(^{-1}\)).

The plot of \( \ln(q_e - q_t) \) versus \( t \) was used to determine \( k_1 \).

The pseudo-second-order kinetic equation in linear form is given by:

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  
*(7)*

where \( k_2 \) is the pseudo-second-order rate constant (g/mg min). A linear fit of \( t/q_t \) versus \( t \) was applied to obtain \( k_2 \) and \( q_e \) from intercept and slope, respectively.

### 3. Results and Discussion

#### 3.1. Pre-treatment of pristine WS and PMMA grafting via radical initiated polymerization

The mechanism of grafting with ceric ion (Ce\(^{4+}\)) as initiator involves the formation of an intermediate complex with the cellulosic units and results in a macro-cellulosic short-lived radical on either carbon C\(_2\) or carbon C\(_3\) or the hydroxyl groups bonded to these carbons of cellulose backbone *(Figure 1)* (Tosh and Routray 2014). The polymeric chains will be incorporated onto the cellulose backbone at these active sites resulting in the formation of the graft copolymer. The propagation of the polymeric chain will be initiated by a reaction between the macro-cellulosic radical and the monomer. The reaction terminates when the polymeric radicals react among themselves or react with Ce\(^{3+}\), resulting in the regeneration of active Ce\(^{4+}\) species. However, the fibrous cellulose in the WS cell wall needs to be exposed using a pre-treatment process. Moreover, pre-treatment is also necessary to increase the surface roughness by removing lignin and hemicellulose intercalated between cellulose fibers. Overall, the alkaline treatment solubilizes lignin and subsequently swells the cell wall and cellulose microfibrils (Thomsen et al. 2021). This step is crucial to gain access to cellulose which is present in the crux of the cell wall (Brandt et al. 2013; Williams et al. 2019). In addition to augmenting the grafting of PMMA on cellulose, the chemical treatment also serves the purpose of having extractive-free biomass, which makes sure
that there will be no secondary pollution of water. It also opens the tubular interconnected pore channels, which otherwise will not be accessible to viscous oil during oil adsorption. A simple one-step economical and environmentally benign pre-treatment of WS, using a mixture of 0.5wt% NaOH and 30% H$_2$O$_2$, is shown to be effective in serving all the purposes described above [29]. Figure 1 shows pre-treatment derived degradation of cell walls, exposure of internal cellulose fibers, and extraction of lignin and hemicellulose (Zang et al. 2016).

**Figure 1.** Structure of lignocellulosic WS, the pre-treatment process to expose the embedded fibrous cellulose, and mechanism of graft copolymerization of PMMA on the exposed fibrous cellulose.

### 3.2. Optimization of monomer concentration

The significant parameters that influence the grafting percentage (Gp) include reaction time, initiator concentration, monomer concentration, and reaction temperature. Many researchers have extensively studied the effect of these parameters on the efficiency of CAN-initiated polymerization. Therefore, reaction time, temperature, and initiator concentration were chosen from previous literature (Fakhrul-Razi et al. 2009), and this study focused on the effects of monomer concentration on the grafting percentage of PMMA since the objective was to use a minimum amount of monomer to enhance the cost-efficiency of straw modification. Moreover, monomer concentration is the predominant parameter that defines the graft percentage of CAN
initiated polymerization. The concentration of monomer significantly affects the dilution of macro-
cellulosic radical sites, miscibility of the reagents, viscosity of the reaction medium, and
availability of the monomers in the vicinity of macro-cellulosic radicals. The weight ratio of
WS/MMA varied from 0.75 to 3.65, and the highest graft percentage of 127% was obtained for
the WS/MMA ratio of 1.25. The increase in the monomer amount from 2.4 g of MMA to 4.7 g and
then to 7.5 g increased the graft percentage of PMMA from 103% to 118% and then 127%.
However, a further increase in the monomer concentration up to 12.5 g caused a downfall in the
PMMA graft percentage to 109%. This lowering in the percentage of grafting at high monomer
concentration is presumably associated with the dilution of the WS, increased phase separation
between the solvent water and monomer, or the higher viscosity of the reaction medium that
ultimately slows down the diffusion of the monomer to the active sites. The WS with the highest
PMMA grafting percentage of 127% was used for all characterization and oil adsorption studies.

3.3. Characterisation of adsorbents

3.3.1. Morphology and elemental analysis of pristine, pretreated and WS-g-PMMA

The SEM micrographs (Figure 2) display the distinctive fibrous microstructures and the surface
morphology of the pristine, pretreated, and PMMA grafted wheat straw. At lower magnifications
(Figure 2 top panels), the structure of the pristine, pretreated WS looked similar, but the structure
of WS-g-PMMA was broken to some extent. This indicated that the overall original structure of
wheat straw was not changed dramatically. The micrographs at higher magnifications (Figure 2
middle panels) clearly displayed the differences between the three samples. While the pristine
straw exhibited a homogenous, smooth surface with a hollow tubular structure, the pretreated straw
sample exhibited a loose and fibrous structure with a porous structure opened along the pore walls.
Note that the internal pore walls of the pristine WS are predominantly hydrophilic and used for the
transport of water; these pores are, therefore, not accessible to oil due to limited capillary
penetration and need to be opened from the sides of the pore walls to allow access to oil. The
PMMA grafted WS samples exhibited an undulant coarse surface and a mesh-like texture among
smoother domains of PMMA, indicating the presence of a percolating network. Similar
observations were reported for grafting PMMA on Agave Americana fibers (Singha and Rana
2012). In addition, the magnified SEM image of WS-g-PMMA clearly shows that they are
composed of numerous bridging fibrils which conduct water through the plant body. The microporous structure of WS-g-PMMA is also showcased by the profuse vessel to vessel pitting (Jiang et al. 2018). Smaller sizes of WS-g-PMMA particles, the formation of a percolating network, and exposed vessels, as well as the vessel to vessel pitting, are all beneficial for enhanced oil adsorption. The elemental composition of pristine, pretreated, and WS-g-PMMA is evaluated by EDX analyses (Figure 2 bottom panels). The main elements existing in the pristine WS are carbon (C, 35.2%), oxygen (O, 47.1%), and silicon (Si, 17.7%). Carbon and oxygen originate from basic compositional polymers (i.e., cellulose, hemicellulose, and lignin) of WS as well as the wax and resins of the cell walls. Meanwhile, silicon originates from the abundant silica in the plant cell walls accumulated by the absorption of silicon from the soil (Dodson 2011; Abd-Talib et al. 2018). Silica also contributes to the high percentage oxygen content in the elemental composition of pristine WS. In contrast to the pristine straw, the percentage of silicon is negligible in pretreated straw. This indicated that the alkaline hydrogen peroxide pre-treatment successfully removed the silica from the cell wall, almost completely leaving behind empty cavities, which are essential for higher oil adsorption capacity (Dodson 2011). Moreover, the C/O ratio in the pretreated WS is 1.14, which is almost twice compared to pristine WS (0.75) and very close to the C/O ratio of 1.2 in cellulosic repeating units. Note that the low C/O ratio in pristine WS is related to the high amount of oxygen originating from silica in addition to the oxygen in the basic compositional polymers of WS and cell wall matrix. This means that alkaline hydrogen peroxide pre-treatment effectively removed most of the wax, resins, silica, lignin, and hemicellulose, mostly leaving behind the cellulosic fibrous structure. The removal of these materials is essential for eliminating the materials responsible for secondary pollution, exposing the reactive surface sites for PMMA grafting, and increasing the access for oil adsorption.
Figure 2. SEM micrographs at lower and higher magnifications, and EDX results of pristine, pretreated, and WS-g-PMMA. The hollow tubular structure of the pristine WS and porous structure with broken surface roughness and loose fibers of pretreated WS are easily visible. The WS-g-PMMA sample possessed vessels with numerous micropores.

Meanwhile, the C/O ratio in the WS-g-PMMA was twice that in the pretreated WS, indicating considerable grafting of PMMA onto the fibrous cellulose backbone. The efficient grafting of PMMA is highly essential for the hydrophobization of fibrous cellulose and the increase in oil adsorption capacity. The observation related to the changes in elemental composition upon PMMA grafting is consistent with a previous study in which PMMA grafted rice straw has been used as a roofing material (Mukherjee et al. 2017). The intensity of the C atom bonded to O (C-O, and C=O) over the C atom bonded C (C-C) in the XPS C1s region increased from pristine to pretreated to WS-g-PMMA (Figure 3), indicating the progress of each step of pre-treatment and PMMA grafting. The C-C bonded C arises from alkyl and aryl groups, C-O bonded C arises from the ether, alcoholic, and carbonyl functional groups, and C=O arises from only carbonyl functional groups (Yu et al. 2007). Pre-treatment removes carbon-rich waxes, resins, and lignin, leaving mostly oxygen-rich cellulose in addition to some hemicellulose. Therefore, the intensity of the C-O peak and the corresponding C-O/C-C increases upon pre-treatment. Meanwhile, PMMA grafting
increases the C-O bonded C from its ester carbonyl groups leading to the increase in the intensity of this C-O peak and the corresponding C-O/C-C. The trend of the C=O/C-O is more obvious in realizing the progress of the pre-treatment and the PMMA grafting. The pristine WS contain more carbonyl carbon originating from the waxes, lignin, and hemicellulose. Removal of these constituents reduces the carbonyl C=O bond contents the pretreated WS. Therefore, the C=O/C-O for pretreated WS is lower than that for pristine WS. On the other hand, C=O/C-O increases from pretreated WS to WS-g-PMMA since the ester functional groups of PMMA are adding more C=O bonds.

**Figure 3.** XPS C1s regions, demonstrating the increase in the intensity of the C atom bonded to O (C-O, and C=O) over C atom bonded C (C-C) for pristine to pretreated to WS-g-PMMA. The corresponding table shows the atomic percentage of C in different bonding environments and the ratio of C-O/C-C, C=O/C-C, and C=O/C-O.

| Sample          | C-C (atom%) | C-O (atom%) | C=O (atom%) | C=O/C-C | C=O/C-C | C=O/C-O |
|-----------------|-------------|-------------|-------------|---------|---------|---------|
| Pristine WS     | 48.72       | 39.65       | 11.72       | 0.81    | 0.24    | 0.30    |
| Pretreated WS   | 44.83       | 44.13       | 11.04       | 0.98    | 0.25    | 0.25    |
| WS-g-PMMA       | 37.95       | 44.81       | 17.24       | 1.18    | 0.45    | 0.38    |

3.3.2. surface functional groups of pristine, pretreated and WS-g-PMMA

The success of pre-treatment and subsequent PMMA grafting was evaluated by the simultaneous disappearance of characteristic vibration modes of pristine WS and appearance of characteristic PMMA vibration modes in the FTIR spectrum of pretreated WS and WS-g-PMMA, respectively (**Figure 4**). The carbonyl (C=O) stretching vibration due to the carbonyl groups of wax, hemicellulose, and lignin around 1730 cm\(^{-1}\) in pristine straw is almost absent in pretreated straw. This can be attributed to the extraction of wax, hemicellulose, and lignin during pre-treatment (Lv et al. 2017). A dominant peak at 1035 cm\(^{-1}\) is for the C-O stretching vibration of the C-O-C ether linkage and C-O-H bonds, and the second dominant peak in between 3000-3600 cm\(^{-1}\) is for the O-
H stretching vibrations of the hydroxyl groups of cellulose, hemicellulose, and lignin present in pristine WS. The intensity of these peaks became more pronounced in the FTIR spectrum of pretreated WS, further supporting the inference that pre-treatment removed other species (e.g., lignin and hemicellulose), leaving behind predominantly the cellulose fibrous structure. Note that cellulose units contain more OH functional groups and ether linkages than those present in lignin and hemicellulose. Lastly, the intensity of the hydroxyl group's peak declined significantly after the grafting of PMMA on the pretreated sample due to the hydroxyl groups' participation in radical creation that reacted with the monomer and was subsequently replaced by PMMA. Moreover, the evolution of new prominent peaks centered at 1720 and 1147 cm\(^{-1}\) can be attributed to C=O and C-O stretching vibration modes of the ester groups, respectively, which are characteristic vibration modes of PMMA (Sugumaran et al. 2017; Galhardo et al. 2018) and confirm the success of PMMA grafting.

**Figure 4.** FTIR spectra of pristine WS, pretreated WS, and WS-g-PMMA.

3.3.3. Surface area and porosity of pristine, pretreated and WS-g-PMMA
The surface area of the pristine, pretreated, and WS-g-PMMA was analyzed using Brunauer-Emmett-Teller (BET) theory, and pore size distribution was analyzed with DFT (Density Functional Theory) by outgassing the samples with nitrogen at 150 °C for 2 h (Quantachrome Autosorb iQ). The surface area, pore size, and pore volume of all three samples are presented in Figure 5 and Table 1. The shape of the hysteresis loops in Figure 5 and the pore size (Table 1) for pristine, pretreated, and WS-g-PMMA clearly indicate the presence of mesopores and micropores in all three samples. However, the mesopore distribution predominates in all the samples. The morphology of the materials (Figure 2 middle panels) shows a highly diverse distribution of pores and hence indicates that the materials indeed consist of a complex porous structure. The International Union of Pure and Applied Chemistry (IUPAC) isotherm type IV(a) and (b), therefore, comes into the picture (Thommes et al. 2015). The type (IV) isotherms are usually considered for materials with complex pore systems. The surface area and pore volume of the samples are in the order of pristine WS > pretreated WS < WS-g-PMMA. The reason behind the low surface area and pore volume of pretreated WS and WS-PMMA compared to pristine WS is mainly believed to be due to the kinetic restrictions of the flow of nitrogen into their narrow micropores (< 0.45 nm). The shape of the hysteresis loop for pristine WS (Figure 5d) mostly correlates with type H2(a) hysteresis since the desorption curve is steep (Cychosz and Thommes 2018), the reason being a wide distribution of pore cavity compared with the neck distribution. The structure of the tubular vascular interconnected vessels (Figure 2 middle panel left) with numerous pits at each node in the structure of pristine WS justifies this finding (Liu et al. 2005; Yu et al. 2008). The hysteresis loop shape for pretreated and WS-g-PMMA (Figures 5e and 5f) also indicate type H2(a), but with cavitation (Monson 2012). This indicated that adsorption is accompanied by desorption through cavitation for smaller pore sizes at a certain critical temperature. The pretreated WS and WS-g-PMMA contain numerous micropores along with mesopores in contrast to the pristine WS. Hence, the micron-sized pores are causing cavitation in these samples, leading to lower estimated surface area and pore volume values. Meanwhile, the shape of the DFT (Figure 5d) also indicates that the pristine sample has a larger number of mesopores compared to the pretreated and WS-g-PMMA.

The reason for a higher surface area and pore volume of the pristine WS can also be due to the presence of the epidermis consisting of an increased number of the original mesopores. In this circumstance, the decrease in the surface area and pore volume of pretreated WS and WS-g-PPMA
can be attributed to the defragmentation of the outer layers of wheat straw, including the epidermis and lignin. One important observation is that the surface area and pore volume increased from pretreated WS to WS-g-PMMA. Temperature plays a major role in defining the porous structure of biomass material (Daud et al. 2003; Lee et al. 2014; Quach et al. 2017). Many studies have reported the increase in BET surface area and pore volume at higher reaction temperatures involving steam due to expansion/coalescence of the existing micropores to form macropores and also the simultaneous formation of new pores (Daud et al. 2003; Zhao et al. 2017; Ding et al. 2020). The temperature of the PMMA grafting reaction was 70 °C, and the total residence time of pretreated WS under this temperature was 2.5 h; the prolonged duration under this temperature might have contributed to the formation of new pores and enlargement of the existing ones. The oxidizing environment under CAN and nitric acid might have also contributed to an increase in porosity and surface area. However, nitrogen is sometimes inappropriate for analyzing micropores, especially for those consisting of non-polar surfaces (e.g., PMMA grafted in this study). The interaction of nitrogen with non-polar surface functionalities can lead to inaccurate surface area values as these interactions may shift the pore filling pressure of nitrogen to a very low relative pressure (\(P/P_o = \text{about } 10^{-7}\)). Hence, \(P/P_o\) does not correlate well with the micropore sizes in these cases. Therefore, the surface area value for WS-g-PMMA might be higher than estimated with nitrogen. Even if the surface area and pore volume are higher for pristine WS due to the presence of interconnected tubular pore channels and these channels are accessible to nitrogen gas, viscous hydrophobic oil may not penetrate them due to the restricted capillary penetration and hydrophilicity of the inner pore surface. Therefore, breaking these pores in the pre-treatment and PMMA grafting steps could benefit access to the oil.
Figure 5. Cumulative surface area (a, b, c), and adsorption/desorption curves of nitrogen for pristine, pretreated, and WS-g-PMMA (d, e, f).
Table 1 BET surface area and pore width of pristine, pretreated and WS-g-PMMA

| Sample      | BET surface area (m²/g) | Pore size (nm)       | Pore volume (cc/g) |
|-------------|-------------------------|----------------------|--------------------|
| Pristine    | 3.84                    | 1.6-6.5, 7-20, 26-32 | 1.6 × 10⁻²         |
| Pretreated  | 2.60                    | 1.6-5, 10-24, 26-34 | 8.0 × 10⁻³         |
| WS-g-PMMA   | 2.99                    | 1.6-4, 4-12, 28-32  | 1.6 × 10⁻²         |

3.3.4. Surface wettability of pristine, pretreated and WS-g-PMMA

It is well-known that surface roughness and surface hydrophilicity/hydrophobicity are the main two influential parameters determining surface wettability (Wenzel 1949; Chau et al. 2009). Moreover, surface wettability is a crucial parameter for understanding the level of affinity of the adsorbent to oil or water. Therefore, the surface wettability of pristine WS, pretreated WS, and WS-g-PMMA was evaluated by measuring the water and oil contact angles (Figure 6). Water and oil contact angles for pristine WS were found to be 0° and 79°, respectively. Hydrogen bonding between water molecules and abundant surface hydroxyl functional groups caused full penetration of water droplets into the surface of pristine WS (Xu et al. 2018). On the other hand, the hydrophilic surface hydroxyl groups inhibited the adhesion of oil droplets on the surface of pristine WS. The broken surface porous structures might have resulted in the absorption of both water and oil droplets by the pretreated WS, although the surface was hydrophilic, which is consistent with similar observations reported previously (Xu et al. 2018). In contrast to the pristine and pretreated WS, the water contact angle of WS-g-PMMA was very high (111°). On the other hand, the oil contact angle for WS-g-PMMA was 0°. The very high-water contact angle and zero oil contact angle confirm the high hydrophobicity and oleophilicity of WS-g-PMMA. Therefore, the WS-g-PMMA prepared in this study could be a promising candidate for the adsorptive removal of hydrocarbons from oily wastewater.
Figure 6. (a) Water contact angles of pristine WS, pretreated WS, and WS-g-PMMA in three different time-steps and (b) oil contact angles of all three adsorbents.

3.4. Adsorption of oil from an oil-in-water emulsion

3.4.1. Effect of adsorbent contact time on oil adsorptivity

A set of experiments were conducted to understand the influence of adsorbent contact time on oil adsorption efficiency. The experiments were conducted at a constant shaking speed of 160
oscillations/min, an initial oil concentration of 300 ppm, and an adsorbent dosage of 5 mg at room temperature. The time interval was set to five minutes, and the adsorption experiments were conducted until the final oil concentration in the bulk liquid reached a constant value. A significant amount of oil was adsorbed initially due to the availability of many adsorption sites and eventually reached equilibrium, as presented in Figure 7. In the case of pristine WS, the equilibrium was reached earlier due to the low accessibility of oil to the hydrophilic tubular pores of WS and low hydrophobic interactions between the surface of the straw and oil droplets. The overall duration of the adsorption process for pretreated WS was reasonably higher than the pristine WS due to increased exposure of the porous structure caused by the alkaline hydrogen peroxide pretreatment, even though the surface of this pretreated WS is more hydrophilic than that of pristine WS. Hydrophobic interactions between the WS-g-PMMA surface and the oil molecules, along with smaller sizes of WS-g-PMMA particles, the formation of a percolating network, exposed vessels, and vessel to vessel pitting contributed to high oil adsorption. It increased the oil rejection, oil adsorption capacity, and the overall duration of the adsorption process. The oil removal efficiency of WS-g-PMMA was about 4 times higher than pristine WS and 1.6 times higher than pretreated WS. The oil adsorption capacity increased from 300 mg/g to 700 mg/g upon pre-treatment and from 700 mg/g to 1075 mg/g upon grafting of PMMA. In a similar work by (Mysore et al. 2005), vermiculite hydrophobized by mixing with carnauba wax was analyzed for separating oil and water. The batch study results indicated the adsorption capacity to be 108.4 mg/g, 78.14 mg/g, 86.54 mg/g, and 3.97 mg/g for standard mineral oil, vegetable oil, kutwell oil, and refinery effluent, respectively. In another work (Ibrahim et al. 2009), barley straw was chemically modified using NaOH and cationic surfactant hexadecylpyridinium chloride monohydrate. The maximum adsorption capacities were found to be 613.3 mg/g and 584.2 mg/g for canola oil and standard mineral oil, respectively. WS-g-PMMA has demonstrated an explicitly high adsorption capacity of 1075 mg/g respectively, even in the case of low-density diesel oil.
Figure 7. Effect of contact time on (a) oil removal efficiency and (b) oil adsorption capacity of pristine, pretreated, and WS-g-PMMA for 300ppm initial oil concentration, 5mg adsorbent dosage, and 160 oscillations/min shaking speed.

3.4.2. Effect of initial oil concentration and adsorbent dosage

The effect of different adsorbent dosages and the oil concentration was studied by varying the amount of WS-g-PMMA from 5 mg to 25 mg for initial oil concentrations of 100, 200, and 300 ppm. The contact time and shaking speed were kept constant at 30 minutes and 160 oscillations/min, respectively. As shown in Figure 8a, the adsorptive oil removal efficiency (RE) increased linearly with an increase in adsorbent dosage, and it was higher for 100 ppm oil concentration. The reason behind higher removal efficiencies at the higher adsorbent dosage and lower oil concentrations is the availability of higher adsorption sites for oil accumulation sufficient to accommodate all the oil present in the bulk solution.
In contrast to the increase in oil removal efficiency, the adsorption capacity of WS-g-PMMA decreased with the increase in adsorbent dosage and with the decrease in oil concentration (Figure 8b). The hike in the ratio of adsorption sites to the amount of oil in the bulk liquid declined the total adsorption capacity. The adsorption capacity $q_t$ is measured by dividing the mass of oil adsorbed by the total mass of the adsorbent. Hence, the increase in the amount of adsorbed oil remains lower than the increase in the amount of adsorbent, leading to a decreasing trend in the adsorption capacity. The effect of adsorbent dosage on the removal efficiency and adsorption capacity was compared for pristine, pretreated, and WS-g-PMMA by varying the adsorbent dosage from 5 mg to 15 mg while keeping the oil concentration constant at 300 ppm. The order of oil removal efficiency for the increase in adsorbent dosage was WS-g-PMMA > pretreated WS >
pristine WS (Figure 8 c and d). This indicates that surface modification enabled easy penetration of oil by exposing the pores, as evident from the SEM micrographs. More importantly, it significantly increased the hydrophobicity of the surface, as indicated by the FTIR and contact angle results.

3.4.3. Adsorption isotherm models

After evaluating the influence of adsorbent dosage and oil concentration on oil removal efficiency and adsorption capacity, Langmuir and Freundlich adsorption isotherms were used to understand the oil adsorption mechanism. Figures 9 a and b show the linearized plots for Langmuir and Freundlich isotherms, respectively. The Freundlich isotherm provided a better fit to the experimental $C_e$ and $q_e$ values. This strongly indicates the heterogeneity of adsorption sites as well as the involvement of multilayer adsorption of oil. Therefore, adsorption efficiency will be higher at the initial stages of adsorption since it is based on the direct interaction of adsorption sites with oil. The adsorption efficiency will be reduced exponentially with time since adsorption at these stages predominantly involves the interaction of the adsorbed oil layer with excess oil in the bulk solution. These results are in line with work on adsorption of palm oil mill effluent using sago bark (Wahi et al. 2017), where the experimental values fitted well with Freundlich isotherm, indicating heterogeneous adsorption of oil on the bark material. Diesel oil consisting of linear hydrocarbons of different chain lengths contributed to the multilayer heterogeneous adsorption over the mesoporous structure of WS-g-PMMA (Diraki et al. 2018). The Freundlich parameters $n$ and $K_f$ values being greater than 1, as shown in Figure 9b, strongly suggest a higher adsorption capacity of WS-g-PMMA for diesel oil.
3.4.4. Adsorption kinetics

Large-scale application of any adsorption-based filtration system demands evaluating the adsorption rate and the corresponding adsorption equilibrium time. Pseudo-first order and pseudo-second-order kinetics models are widely applied to determine the adsorption kinetics. As seen in Figure 10 b, the pseudo-second-order equation provided a better fit with the experimental oil adsorption data for all three WS samples featuring an $R^2$ value as high as 0.999. At equilibrium, the oil adsorption capacity ($q_e = 1129$ mg/g, Table 3) is very close to the experimental values (1075 mg/g). The predicted values of $q_e$ from the pseudo-first-order equation, on the other hand, were not even close to the experimental data, even though the $R^2$ values are reasonably acceptable. Based on these observations, it can be concluded that the adsorption process follows a pseudo-second-order rate for all three WS samples. The pseudo-second-order rate implies that the rate of adsorption decreased with time. In a similar work (Lin and Chen 2015) on polyethyleneimine modified rice husk, the pseudo-second-order kinetic equation provided the best fit with $R^2 > 0.998$. In addition, the adsorption capacity of the material for treating soybean oil-based emulsion was found to be 428.1 mg/g and 469.5 mg/g at 20 °C and 40 °C, respectively. The pseudo-second-order rate implies that the rate of adsorption decreased with time. This is also consistent with the better fitting of the adsorption data with Freundlich adsorption isotherm, which generally demonstrates higher initial adsorption due to direct interaction of adsorbent with adsorbate followed by slower adsorption with time due to secondary interaction of the surface adsorbed adsorbate with the
adsorbate in the bulk liquid. The higher hydrophobic interaction between the PMMA grafted on WS and oil molecules contributed to stronger physisorption and significantly improved the oil uptake rate by the WS-g-PMMA sample.

![Figure 10](image)

Figure 10. (a) Pseudo-first order and (b) pseudo-second-order kinetic models for removing emulsified oil using pristine, pretreated, and WS-g-PMMA at ambient temperature and shaking speed of 160 oscillations/min.

Table 3. Pseudo-first-order and pseudo-second-order kinetic model parameters for the removal of emulsified oil using pristine and pretreated WS as well as WS-g-PMMA.

| Sample          | $q_e$ (mg/g) | $k_1$ (g/mg.h) | $R^2$ | $k_2$ (g/mg.h) | $q_e$ (mg/g) | $R^2$ |
|-----------------|--------------|----------------|-------|----------------|--------------|-------|
| WS-g-PMMA       | 645          | 0.0927         | 0.921 | 0.0003         | 1129         | 0.999 |
| Pre-treated WS  | 241          | 0.1467         | 0.924 | 0.0013         | 741          | 0.999 |
| Pristine WS     | 82           | 0.1287         | 0.990 | 0.0028         | 346          | 0.999 |

3.4.5. Comparison of oil absorptivity with literature reported adsorbents

There are several reports on different types of straw-based adsorbents featuring exceptionally high oil adsorption capacity in the range of 17.5-28.8 g/g (Table 4). However, most of these adsorbents have several concerns, such as stability of bonds (e.g., ester and silyloxy) formed between the surface of straw and hydrophobization agents, a large excess of chemical usage including many toxic ones, multistep processing, and/or usage of fluorocarbons as hydrophobization agents. Apart from these concerns, the oil adsorption capacity for these adsorbents is not comparable with the current study since the oil adsorption measurement process for these high adsorption studies was
not for diluted emulsified oil. In many cases, an overestimation of the adsorption capacity is possible. Many of the studies even did not provide the adsorption capacity for raw straw. In some studies, raw straw showed significantly higher adsorption capacity (5 to 8.2 g/g) than obtained in this study (346 mg/g). Even raw barley straw was reported to have extensively higher oil adsorptivity (6.5-12 g/g) (Husseien et al. 2009) than surfactant modified barley straw (613.3 mg/g Table 4). However, when compared to the studies on the systematic kinetic studies for oil adsorption using dilute emulsified oil, the adsorption capacity of WS-g-PMMA is significantly higher than PEI modified rice husk and surfactant modified barley straw. The adsorption capacity of WS-g-PMMA is also higher than activated carbon and graphene nanoplatelets while slightly lower than thermally reduced graphene and graphene oxide. However, carbon-based materials are characterized by high costs and a high carbon footprint.

Table 4. Comparison of oil absorptivity with other modified straw reported in the literature

| Adsorbent | Modification | Oil type | Sorption capacity | Remarks | Reference |
|-----------|--------------|----------|-------------------|---------|-----------|
| Rice straw | Acetylation | Suspended machine oil 20 g in an unknown amount of water and 0.5 straw | 24.0 g/g | 1) Not emulsified oil 2) Ester bonds 3) Large excess chemical usage 4) No raw straw adsorption data | (Sun et al. 2002) |
| Wheat straw | Acetylation | Same as above | 28.8 g/g | Same as above (Sun et al. 2002) | (Sun et al. 2004) |
| Wheat straw | 1) Pre-treatment with Toluene-ethanol refluxing to remove w as and resins 2) Pre-treatment with NaClO to remove lignin 3) Pre-treatment NaOH to remove cellulose and hemicellulose 4) Acetylation | Pure oils 1) Diesel 2) Corn Oil Slick 1) Diesel 2) Corn oil | Pure oil 1) 24.2 g/g 2) 25.5 g/g Oil Slick 1) 22.4 g/g 2) 24.7 g/g | 1) and 2) same as above (Sun et al. 2004) 3) Extreme use of chemicals (including toxic toluene, NaClO₂, DMAc, NBS) in multiple Pre-treatment and acetylation steps 4) Raw straw adsorptivity: diesel oil and diesel oil slick 8.2 and 7.8 g/g, respectively | (Lv et al. 2017) |
| Wheat straw | 1) 3 steps chemical pre-treatment as above 2) Esterification with Palmitic Acid | Pure oil 1) Diesel 2) Peanut 3) Lubricant Oil slick 1) Diesel 2) Peanut 3) Lubricant | Pure oil 1) 24.3 g/g 2) 24.9 g/g 3) 22.7 g/g Oil slick 1) 23.5 g/g 2) 23.7 g/g 3) 21.9 g/g | 1), 2), and 3) are like above (Lv et al. 2017) 4) Raw straw adsorptivity: diesel oil and diesel oil slick 7.1 and 6.2 g/g, respectively | (Tang et al. 2018) |
| Material          | Treatment/Modification                                                                 | Oil Type                  | Adsorption Capacity (g/g) | Comments                                                                                           | Reference             |
|-------------------|----------------------------------------------------------------------------------------|---------------------------|---------------------------|----------------------------------------------------------------------------------------------------|-----------------------|
| Cron straw        | 1) Alkaline H$_2$O$_2$ Pretreatment  
2) Synthesis of ZnO particles  
3) ZnO deposition and HDTMOS functionalization | Pure oil                  | 1) 18  
2) 20.4  
3) 22 | 1) Adsorption is not for emulsified oil  
2) Silyloxy bond with the straw may not be stable for long-term operation.  
3) Large amount of chemical usage.  
4) Raw straw adsorptivity pure diesel oil ca. 5 g/g | (Zang et al. 2016)         |
| Corn straw        | 1) Alkaline H$_2$O$_2$ Pretreatment  
2) Synthesis of SiO$_2$ particles  
3) SiO$_2$ deposition and PTES functionalization | Pure oil                  | 1) 17.5  
2) 20.3  
3) 22.6 | 1), 2), 4) same as above (Zang et al. 2016)  
3) Large amount of chemical use: PTES is used to reduce chemical, but fluorocarbon is discouraged | (Xu et al. 2018)        |
| Corn straw        | 1) Alkaline H$_2$O$_2$ Pretreatment  
2) SiO$_2$ particles growth on WS  
3) Synthesis of ZnO particles  
4) ZnO deposition and OTES functionalization | Pure oil                  | 1) 18.70  
2) 20.05  
3) 22.50 | 1), 2), and 3) same as for (Zang et al. 2016)  
4) Extreme chemical usage  
5) Many steps  
6) All the raw materials are fluorine-free | (Tan et al. 2021)         |
| Rice husk         | Polyethylenimine  
450 ppm Emulsified soybean oil | 428 mg/g                  | 1) Emulsified oil  
2) The chemistry of PEI modification is not clear  
3) Lower adsorptivity  
4) Raw rice husk adsorptivity ca. 100 mg/g | (Lin and Chen 2015)       |
| Barley straw      | 1) Pre-treatment with NaOH  
2) Cationic surfactant CPC adsorption | Emulsified:1) Canola  
2) Mineral | 1) 613.3  
2) 584.2 | 1) Emulsified oil  
2) Physiosorbed surfactant can leach  
3) Lower adsorptivity | (Ibrahim et al. 2009)     |
| Wheat straw       | 1) Alkaline H$_2$O$_2$ Pretreatment  
2) PMMA grafting | 300 ppm emulsified diesel oil | 1129 mg/g                  | 1) Emulsified oil  
2) One-step eco-friendly pre-treatment  
3) Less chemical usage  
4) Water as the solvent  
5) PMMA ecofriendly  
6) PMMA stable  
7) Higher adsorptivity | This study               |
| Activated carbon  | - | 165 ppm oilfield produced water | 334 mg/g                  | 1) Emulsified oil  
2) High carbon footprint  
3) Expensive  
4) Lower adsorptivity | (Okiel et al. 2011)       |
| Thermally reduced graphene | - | 200 ppm Diesel-water emulsion | 1550 mg/g | 1) Emulsified oil  
2) High carbon footprint  
3) Expensive | (Diraki et al. 2018)      |
Graphene nanoplatelets | - | 200 ppm Diesel-water emulsion | 805 mg/g | 1) Emulsified oil 2) High carbon footprint 3) Expensive | (Diraki et al. 2018)

Graphene oxide | - | 200 ppm Diesel-water emulsion | 1335 mg/g | 1) Emulsified oil 2) High carbon footprint 3) Expensive | (Diraki et al. 2019)

4. Conclusion

In this study, a simple radical polymerization was explored to enhance the oil absorptivity of an agricultural by-product, wheat straw (WS). An attempt has been made to utilize it as an economical and eco-friendly adsorbent for separating oil from oil-in-water emulsions. The pristine WS was pretreated with alkaline hydrogen peroxide, and PMMA was grafted subsequently in an aqueous solvent using cerium ammonium nitrate as a redox radical initiator. The alkaline hydrogen peroxide pre-treatment played a crucial role in exposing the mesopores, which are vital for any adsorption process. The SEM micrographs indicated the presence of mesopores. In addition, the PMMA grafting enhanced the surface hydrophobicity, leading to stronger hydrophobic interactions between the oil droplets and the grafted surface moieties. The enhanced open surface porous features and the hydrophobicity of WS-g-PMMA contributed to high oil adhesion as observed by the 0º oil contact angle, which in turn led to an increment in the oil adsorption by 3.3 times. The experimental adsorptivity data fit well with Freundlich isotherm, indicating the heterogeneity of adsorption sites as well as multilayer adsorption of oil. The adsorption kinetics was best represented by the pseudo-second-order kinetic model supporting the Freundlich isotherm model of multilayer formation. The adsorption capacity of WS-g-PMMA was found to be 1129 mg/g, which is reasonably high and demonstrates its potential for economical treatment of oily wastewater since the overall cost-efficiency of waste WS along with a simple chemical modification for grafting PMMA process will allow the use of a large amount of this adsorbent for large scale applications.

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Declaration of interest
The authors declare no competing interests.

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