

Development of newspaper/polystyrene composite adsorbent for oil spills removal

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ABSTRACT

In the present study, the adsorption equilibrium, kinetics, and thermodynamic studies of crude oil spills on waste newspapers (WNP), waste polystyrene (WPS) and their composites (WNP/WPS composites) were investigated using a batch mode under various parameters. Characteristics of the prepared low-cost sorbents were established using contact angle measurement, scanning electron microscopy and Fourier-transform infrared spectroscopy. The influence of contact time, initial oil film thickness, oil type, temperature, salinity, agitation rate, reusability, and adsorbent dosage on crude oil adsorption was investigated. The oil sorption rate was investigated by two kinetic models specifically the pseudo-first and the pseudo-second-order. However, the sorption mechanism of spilled oil was distinguished by the Elovich, Boyd, and the intraparticle diffusion kinetic. The rate kinetics of oil adsorption on adsorbents is better explained by second-order kinetics. The equilibrium data were found to fit adequately with the Langmuir with maximum monolayer sorption capacities 16.66, 14.28, and 20 g/g for WNP, WPS, and WNP/WPS composites, respectively. The eco-friendly characters of the recyclable waste materials with moderate crude oil sorption capacities proved the potential applicability of these sorbents as oleophilic-base sorbents for crude oil spill removal.

Keywords: Oil spill; Newspaper; Polystyrene; Kinetics; Isotherms

1. Introduction

Since the days of the industrial rampage, the growth of mankind has depended on the usage of fuels. From that time on, reconnaissance, manufacture, refining, and carriage of such fuels expanded throughout the world at a fast tread, without considering their true influence on the ambiance and on human verdure. Fuels utilization has also become one of the main purposes for a significant decline in biodiversity, due to pollution of surface waters,

underground waters, and soils, and to changes in life rotation within the affected zones [1].

Crude oil is a blend of gaseous, liquid, and solid hydrocarbon compounds that take place in sedimentary crag deposits throughout the world and includes slight quantities of nitrogen-, oxygen-, and sulfur-containing compounds, as well as that trace amounts of metallic constituents [2]. Oil puts out saltwater (the ocean) and commonly floats on freshwater (rivers and lakes). Very heavy oil can seldom

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submerge in freshwater and usually, oil stretches out speedily across the water surface to shape a thin layer that we call an oil slick. As the oil keeps spreading, the stratum becomes thinner and thinner, eventually becoming a very thin layer called a sheen, which often looks like a rainbow [3].

When the oil is spilt into the water, it leads up to various processes which are famed as weathering processes such as evaporation, dissolution, oxidation, emulsification, sedimentation, spreading, dispersion and lastly biodegradation. The evaporation process modifies the physical features of the oil and leads up to a variation of its density and pour point due to the forfeit of volatile components. In addition, emulsification influences oil composition and breeds a reduction in oil density and a rise in pour point. Spreading occurs at varying averages according to the oil characteristics as light oil spreads quicker than heavy oil. Through all factors affecting spreading, water temperature and wind speed have an intensive effect on pollutants. All these processes aid in the choice of a convenient method for oil spill remediation [4]. These processes are affected successively, by factors including the composition of the dropped oil, the period of weathering, the kind of oil being weathered, temperature, and wave behavior [5].

The environmental catastrophes produced from oil spills have made a great requirement for coast effective cleanup ways. Actually, several ways used for containing and cleaning up oil spills in watery environments can be classified into three main groups. The first group includes physical (mechanical) methods, such as booms and skimmers, which are used to stop the spread of oil, condense it into one zone, and eject it from the water [6].

These processes ease oil reclamation from the spill site. The plurality of boom layouts takes place into two categories: curtain booms and fence booms. Booms are arranged in U (most common), V and J shapes [7]. Skimmers are typically related to the settling tanks, and there are many factors on which prosperity of skimming depends like type and thickness of oil spill, the location of spill and weather conditions [8].

The second group is a chemical step such as dispersion, *in-situ* burning and using various solidifiers. And lastly, the third one counts biological handling (bioremediation) of oil and it can be used instead of mechanical methods, especially in zones where untreated oil may arrive shorelines and sensitive habitats where a cleanup becomes tricky and environmentally damaging [6].

The option of cleaning way is relying on the kind of oil, the nature of the surface on which it spills, the soil and subsoil conditions, and the prevailing weather conditions. In most cases, two or more ways are combined to fulfill an efficient clean-up [6].

Adsorption is rated the most preferred method for oil spill clean-up, in order to it is a simple method, environmentally-friendly and of low cost. In recent years, the attention of many researchers is drawn to use agricultural wastes or by-products materials. It offers many benefits, including being a low-cost standby material and the capability to biodegrade [9,10]. It is substantial to note that cleaning-up with a sorbent is one of the most efficient technologies among all oil removal techniques that give good results in oil removal from polluted water [11]. Table 1 shows the

classification of sorbents such as inorganic minerals, organic synthetic and organic vegetables [12,13].

Sorbents can strip oil from produced water by using an appropriate way without oil draining out as it can gather and convert liquids to the semi-solid or solid phase. With regards to the benefits of the sorbent material produced from wastes, besides being of low cost, it is high oil sorption, with low water pickup, high buoyancy and good reusability [14,15].

Cellulose, the most plentiful organic polymer, is considered an almost unlimited bioresource and can be derivatized to produce various valuable products [16]. Waste newspaper (WNP), one of the cellulosic materials, consists of nearly 61% cellulose and 16% hemicellulose and other inorganic fillers (e.g., printing inks and other process associate materials [17]. The greater cellulose content in the WNP than other ligno-cellulosic materials indicated that it is an alternate source for cellulose-related production [18].

The focus of the present work is to assess the ability of waste newspapers, waste polystyrene and their composites as recycled sorbents, of low cost and usually obtainable waste material for oil spill removal water across different factors. The influence of variable parameters, such as surface properties, oil type, oil film thickness, sorption time, temperature, salinity and the morphology of sorbents are also studied.

2. Materials and methods

2.1. Materials

Waste newspapers (WNP) and waste polystyrene foam (WPS) were collected by the authors. n-hexane and tetrahydrofuran (THF) supplied by Sigma-Aldrich Chemicals Ltd., (Germany). Local sodium chloride and ethanol absolute perused from Adwick, Egypt. Crude oil supplied from Belayim Petroleum Company (Egypt) with density 0.92 g/cm^3 and viscosity 489 (poise).

2.2. Formulation of newspaper/polystyrene wastes composite

Waste polystyrene is dissolved in tetrahydrofuran (THF) to form a solution with different concentrations by being stirred for a suitable period of time (1/2 h). Waste newspapers (powder form) are dipped in the prepared coating solution and stirred at room temperature for 2 h, then washed using ethanol and dried in an incubator for 15 min. Prepared composites were tested for oil sorption capacity and characterized.

2.3. Characterization

The characteristics of the WNP, WPS, and WNP/WPS composite were investigated by Fourier-transform infrared spectroscopy (FTIR; Shimadzu FTIR-8400S, Japan). In addition, an investigation of the morphological properties was carried out using scanning electron microscopy (SEM, Joel JSM-6360LA, Japan). The oleophilic and hydrophobic characters for sorbents may be easily considered using contact angle measurement (Raméhart Instrument Co. Model 500-F1, UK). The contact angle is defined as the

Table 1
Types of oil spill sorbents

Categories	Inorganic mineral	Organic synthetic	Organic vegetable
Sorbent types	Glass-Wool-Sand-Graphite-Silica-Zeolites	Polypropylene-Polyurethane	Cotton fiber-Straw-Feathers-Sawdust-Wood fiber

angle between the solid surface and a tangent, drawn on the drop surface, passing through the triple-point atmosphere/liquid (crude oil and distilled water)/solid.

2.4. Kinetic studies

In order to investigate the mechanism of the sorption kinetics of crude oil on the sorbents, the parameters of the sorption were determined using the pseudo-first-order, pseudo-second-order, Elovich, Boyd and the intraparticle diffusion models [19–26]. In order to describe the equilibrium and the kinetics of the oil sorption process onto the sorbents, the batch technique was employed to monitor the effect of the contact time (5–120 min), the initial crude oil volume (5–45 mL), the adsorbent dose (0.1–1 g), sorbent dimensions (sheet) = 3 cm² × 3 cm², and the reaction temperature (25°C–45°C). A constant weight of the sorbent (0.2 g) was spread over the surface of a 250 mL beaker holding 100 mL of artificial seawater composed from distilled water contains 3.5% NaCl. The sorbent materials were shaken with polluted seawater at 105 rpm.

2.4.1. Pseudo-first-order

Lagergren presented a first-order rate equation to describe the kinetics of liquid-solid phase adsorption, which is believed to be the earliest model, pertaining to the adsorption rate, based on the adsorption capacity. The pseudo-first-order equation takes the following form:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{1}$$

where q_e and q_t are respectively the sorption capacities at equilibrium and at time t . K_1 is the rate constant of pseudo-first-order sorption kinetics [26].

2.4.2. Pseudo-second-order

The main assumptions for the pseudo-second-order were that may be chemical adsorption, involving valent forces through sharing or the exchange of electrons. If the rate of sorption is considered to be a second-order mechanism, the chemisorption kinetic rate equation can be given as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

where q_e and q_t are the sorption capacities at equilibrium and at time t , respectively and K_2 is the rate constant of pseudo-second-order sorption [26].

The initial adsorption rate, h (mol/g min) is expressed as:

$$h = K_2 q_e^2 \tag{3}$$

2.4.3. Intraparticle diffusion

The adsorption process requires a multi-step approach involving the transport of solute molecules from the aqueous phase to the surface of the solid particles, followed by diffusion of the solute molecules into the interior of the pores, which is likely to be a slow process [27]. The rate parameter of the intraparticle diffusion model can be written as:

$$q_t = K_s t^{0.5} + C \tag{4}$$

where q_t is the sorption capacity at time t . Also, K_s is the rate constant of sorption kinetics in the intraparticle diffusion model and C is the intercept [26].

2.4.4. Elovich equation

The Elovich equation is given as follows:

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \tag{5}$$

The integration of the rate equation with the same boundary conditions as the pseudo-first- and second-order equations becomes the Elovich equation.

$$q_t = \beta \ln(\alpha\beta) + \beta \ln t \tag{6}$$

where α is the initial adsorption rate (g/g min) and β is related to the extent of surface coverage, the activation energy for chemisorptions (g/g) [28].

2.4.5. Boyd model

The model of Boyd is widely used for studying the mechanism of adsorption. Boyd model determines whether the main resistance to mass transfer is in the thin film (boundary layer) surrounding the adsorbent particle, or in the resistance to diffusion inside the pores. This model is expressed as [29]:

$$F = 1 - \frac{6}{\pi} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 B_t) \tag{7}$$

where F is the fractional attainment of equilibrium, at different times, t , and B_t is a function of F .

$$F = \frac{q_t}{q_e} \quad (8)$$

where q_e is the amount of adsorbate adsorbed at infinite time (g/g) and q_t represents the amount of oil adsorbed at any time t (min), F represents the fraction of solute adsorbed at any time t , and B_i is a mathematical function of F .

$$B_i = \left(\sqrt{\pi} - \sqrt{\pi - \left(\frac{\pi^2 F}{3} \right)} \right)^2 \quad \text{For } F < 0.85 \quad (9)$$

$$B_i = -0.4977 - \ln(1 - F) \quad \text{For } F > 0.85 \quad (10)$$

The values of B_i for each fraction adsorbed proposed. The linearity test of B_i vs. time were used to distinguish between the film- and particle-diffusion controlled adsorption.

If the plot is a straight line passing through the origin, the adsorption rate was governed by the particle diffusion; otherwise, it was governed by the film diffusion [30].

2.5. Adsorption isotherms

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage and the possibility of interaction between the adsorbate species. Adsorption data are usually described by adsorption isotherms, such as Langmuir, Freundlich, and Temkin isotherms [31].

2.5.1. Langmuir isotherm

The Langmuir model is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane [31]. The Langmuir isotherm is given by:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (11)$$

where C_e is the equilibrium oil concentration (g/L), q_e the amount of oil adsorbed per unit mass of adsorbent (g/g), q_m and K_L are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively [32].

The essential characteristics and the feasibility of a Langmuir isotherm can be expressed regarding a dimensionless constant separation factor R_L as follows [33]:

$$R_L = \frac{1}{1 + K_L C_0} \quad (12)$$

where C_0 (g/L) is the initial crude oil concentration. R_L values specify the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable if $R_L > 1$.

2.5.2. Freundlich isotherm

The Freundlich expression is based on an exponential relationship and is generally applicable to a heterogeneous surface energy distribution [32]. The equation is shown:

$$\log q_e = \log K_f + \left(\frac{1}{n} \right) \log C_e \quad (13)$$

where C_e is the equilibrium oil concentration (g/L), q_e the amount of oil adsorbed per unit mass of adsorbent (g/g), K_f and n are the Freundlich constants, the characteristics of the system. K_f and n are the indicators of the adsorption capacity and adsorption intensity, respectively [31].

2.5.3. Temkin isotherm

This isotherm contains a factor that explicitly taking into account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that the heat of adsorption (a function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. The Temkin isotherm has been used in the following form:

$$q_e = B \ln K_T + B \ln C_e \quad (14)$$

where C_e is the equilibrium oil concentration (g/L), q_e the amount of oil adsorbed per unit mass of adsorbent (g/g), and T is the temperature (K). K_T is Temkin isotherm maximum binding constant (L/g) and B (J/mol) is the heat of adsorption [34].

3. Results and discussion

3.1. Formulation of newspaper/polystyrene wastes composite

The Formulation conditions of the newspaper/polystyrene wastes composite including the WPS/WNP ratio (g/g), the formulation time and temperature have been studied. The WPS/WNP ratio has been varied from 0.25 to 4.0 g. The oil sorption capacity of the obtained composite formulations varied from 17.0 to 15.0 g/g. Varying the formulation time from 2 to 4 h shows no impact on the oil sorption capacity of the obtained composites formula. On the other hand, elevating of the formulation conditions has a negative impact on the oil sorption capacity which reduced from 17.0 g/g at 25°C to 15.0 g/g at 45°C.

3.2. Characterization of prepared chitosan derivatives

3.2.1. Scanning electron microscopy

The SEM images of WNP powder, WPS powder, and WNP/WPS composite powder are shown in Figs. 1–3 at different magnifications. It was found for WNP powder,

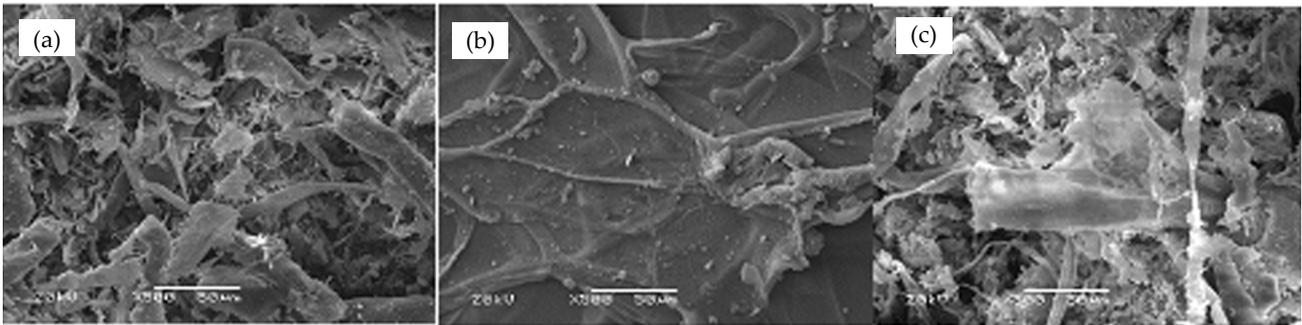


Fig. 1. SEM micrograph of (a) WNP powder, (b) WPS powder, and (c) WNP/WPS composite powder at X500.

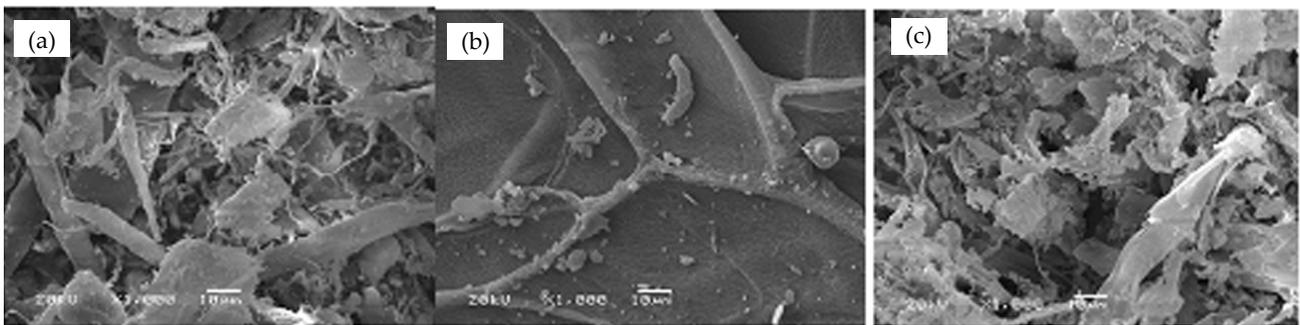


Fig. 2. SEM micrograph of (a) WNP powder, (b) WPS powder, and (c) WNP/WPS composite powder at X1000.

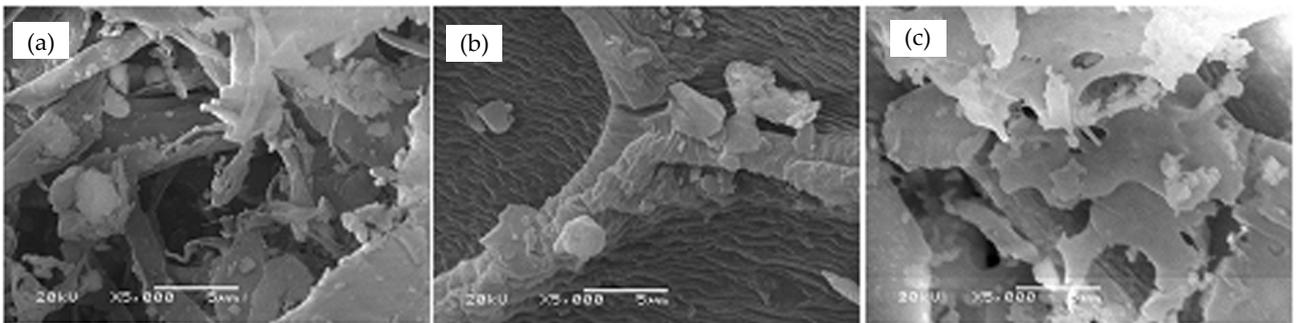


Fig. 3. SEM micrograph of (a) WNP powder, (b) WPS powder, and (c) WNP/WPS composite powder at X5000.

WPS powder, and WNP/WPS composite powder that there is a combination of small and large particle size, heterogeneous rough, an irregular morphology and porous surfaces with crater-like pores. These pores can make oil entrance into the internal of the material easier and helped in the sorption process. The pictures illustrate that the increase in the exfoliated percentage on the surface of WNP/WPS composite powder besides the increase in the surface roughness.

3.2.2. Contact angle measurement

Figs. 4 and 5 indicate that the hydrophobic and oleophilic properties of the WNP/WPS composite powder are actually improved compared to parent waste materials due to the presence of a cover of WPS which seems more hydrophobic than WNP. For example, in the case of testing material for water contact θ value for WNP powder is

61.45°, WPS powder is 111.89°, and WNP/WPS composite powder is 113.15°. While using crude oil will result in different contact angle values as WNP powder is 50.65°, WPS powder is 72.99°, WNP/WPS composite powder is 68.9°. It can be noticed that all adsorbent materials are oleophilic and modified coated composites are hydrophobic.

3.2.3. FTIR spectroscopy

FTIR spectra of WNP/WPS composite powder and WNP/WPS composite sheet are shown in Fig. 6a and b. The resultant peaks at $2,912\text{ cm}^{-1}$ could be related to the presence of CH_2 bond rocking, while the band of $1,477\text{ cm}^{-1}$ could be attributed to the aromatic ring, and various substitution of the benzene ring of polystyrene component between 900 and 700 cm^{-1} for both powder and sheet composites with some shifts owing to the presence of impurities.

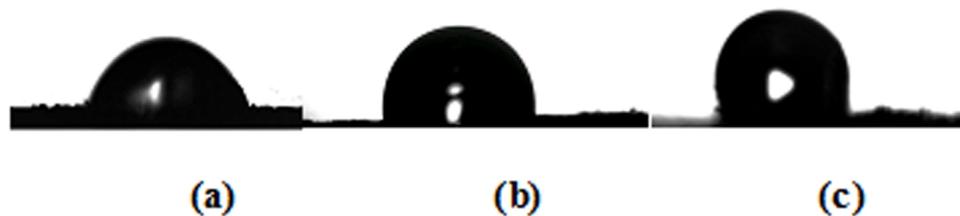


Fig. 4. Contact angle images for (a) WNP powder, (b) WPS powder, and (c) WNP/WPS composite powder using water droplets.

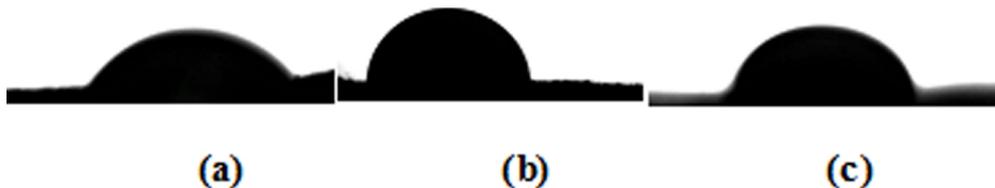


Fig. 5. Contact angle images for (a) WNP powder, (b) WPS powder, and (c) WNP/WPS composite powder using crude oil droplets.

3.3. Batch adsorption experiments

3.3.1. Effect of the contact time

The effect of contact time on the crude oil sorption capacities of waste newspapers, waste polystyrene and their composite were investigated at different contact times; Fig. 7. It is clear that the sorption capacity reaches a maximum value of 14.2 g/g, 14.81 g/g after 15 min for WNP powder and WPS powder. While 17.46 g/g after 20 min was obtained for WNP/WPS composite powder. It was clarified that the initial oil adsorption rates are very fast so that the floating oil spills will be absorbed quickly by the prepared sorbents in several minutes upon the adjunct to the artificial seawater due to the availability of a large number of vacant surface localities for adsorption during the initial stage. The interaction of Van der Waals forces and the hydrophobic interaction enable the diffusion of extra oil to the interior free sites. These results are in agreement with other authors developing nanoporous polystyrene fibers as an adsorbent for oil spill clean-up, as it can be obviously observed that the oil sorption capacities increase as the contact time increases. The observation shows that the oil sorption process by PS fibrous mats is a gradual process [35]. Also, the results are in agreement with others who studied sorption by thermally treated rice husks [36], acetylated rice husks [37], and modified lingo-cellulosic *Delonix regia* pods [38].

Furthermore, it was clear from the previous results that the WNP/WPS composite powder has the highest oil sorption capacity. These results could be attributed to the generated hydrophobic-oleophilic characters resultant from the coating of WNP with hydrophobic WPS. Therefore, increasing the interactions of Van der Waals forces as well as the hydrophobic interactions, and as a result, enables the diffusion of extra oil to the interior free sites.

3.3.2. Effect of the sorption temperature

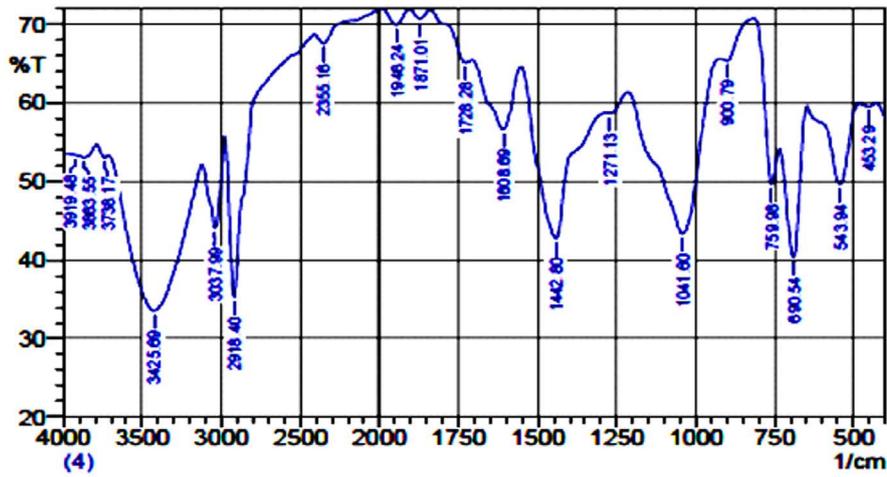
It is comprehensible from Fig. 8 that waste newspapers, waste polystyrene and their composite tend to sorb

slightly more crude oil with elevating temperature. These results show that sorption of oil does not depend strongly on temperature owing to the extremely high viscosity of crude oil, as it may make the diffusion of oil harder. These results are in agreement with authors who studied sorption by human hair [39] and hard coal [40]. Other authors, where, they studied oil sorption by using polymer nanofibers, indicated that oil with high viscosity can result in two opposing effects, either increasing or decreasing oil sorption. The increased sorption happened due to the adherence of the oil to the fiber's surface whereas the decreased sorption occurred when oil is inhibited from penetrating the interior of the fiber [41].

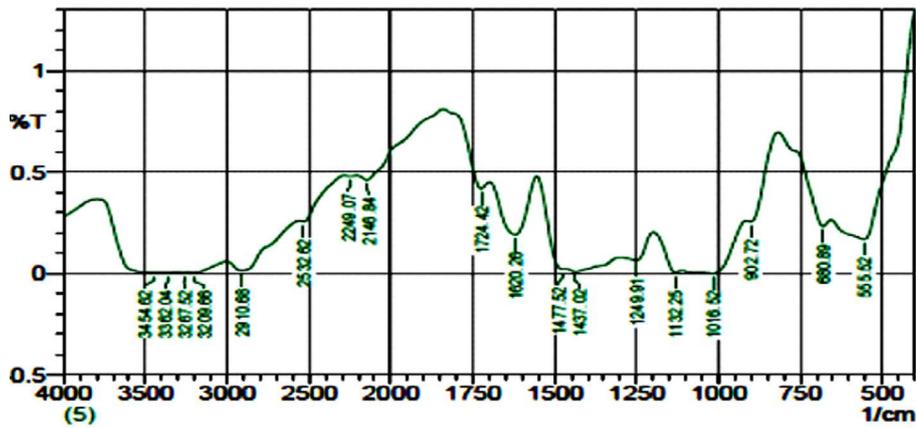
3.3.3. Effect of the oil film thickness

Different oil film thickness was experimented to study the effect of the amount of oil on the sorption capacity of WNP powder, WPS powder, and WNP/WPS composite powder. Fig. 9 investigates the impact of increase the crude oil film thickness on the sorption capacity. The slight increment of sorption capacity (6%) for both WNP powder and WPS powder has been duplicated in the case of WNP/WPS composite powder (12%) with the increase of the oil film thickness from 1 mm to 3 mm where maximum values reached. Further increase of oil thickness up to 10 mm has no significant effect. This could be explained by the saturation of the sorbent sites. In general, increasing the oil thickness provides an important driving force to overcome all resistances of the oil between the aqueous and solid phases, thus increasing the uptake. In addition, increasing the initial oil concentration increases the number of collisions between oil and the adsorbent, which enhances the sorption capacity [42].

The obtained results are in agreement with another study that explained the profile of crude oil sorption by corn stalk and cotton based on the chemical composition and surface properties of the fibers as well as the concentration, specific gravity and temperature of the crude oil [43].



(a)



(b)

Fig. 6. FTIR spectra of (a) WNP/WPS composite powder and (b) WNP/WPS composite sheet.

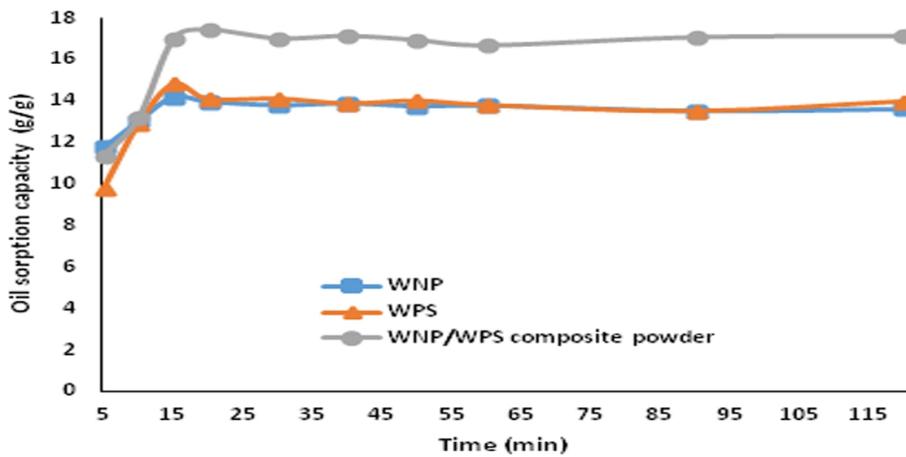


Fig. 7. Effect of the sorption time on the crude oil sorption capacity; 0.2 g sorbent, 3 mm oil film thickness, 100 mL 3.5% NaCl, 150 rpm, and room temperature.

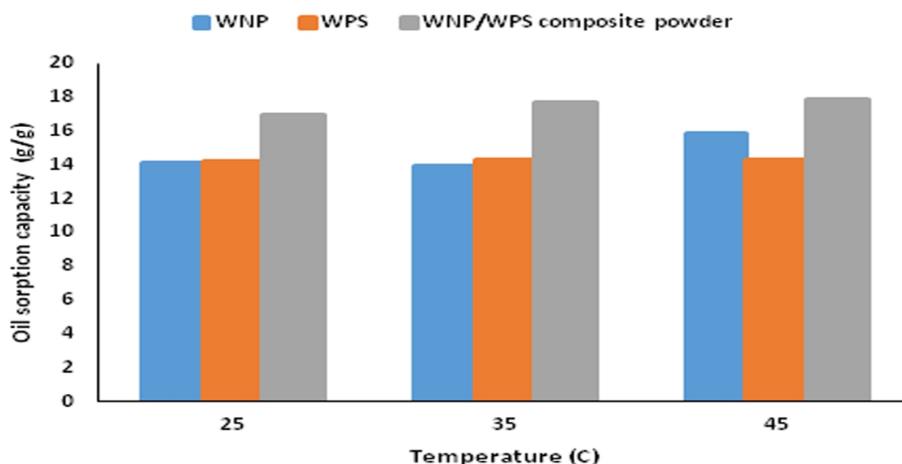


Fig. 8. Effect of the temperature on the crude oil sorption capacity; 0.2 g sorbent, 3 mm oil film thickness, 100 mL 3.5% NaCl, 150 rpm, and 120 min.

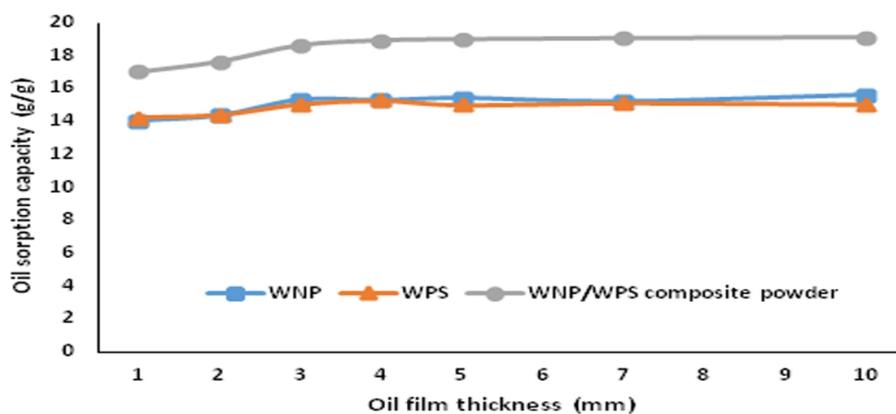


Fig. 9. Effect of the oil film thickness on the crude oil sorption capacity; 0.2 g sorbent, 100 mL 3.5% NaCl, 150 rpm, room temperature, and 120 min.

3.3.4. Effect of the medium salinity

The effect of the medium salinity (NaCl concentration) on the sorption capacity of crude oil was studied as it is important to know the behavior of the sorbents in seawater. The experiment was conducted using aqueous solution of NaCl; 0.5%, 1.5%, 2.5%, 3.5%, 4.5% and 5.5% (w/v). The obtained results indicate that the change in water salinity has no noticeable impact on the sorption capacity of the heavy crude oil.

3.3.5. Effect of the sorbent dose

The sorbent dose is an important factor in large-scale industrial application for the selection of suitable sorbent for the removal of a desired crude oil spills. The consequence of sorbent dose on the sorption capacity of oil on WNP, WPS and their composite forms were experimented with using fixed film thickness of crude oil (5 mL). Fig. 10 discusses that there is a progressive increment of the sorption capacity with the initial increase of sorbent dose.

Where, maximum oil sorption capacity of WNP powder (14.91 g/g) and WPS powder (14.41 g/g) obtained using 0.3 g sorbent dose, while the WNP/WPS composite powder has maximum sorption capacity (17.76 g/g) using 0.2 g sorbent dose. These results may be due to increasing the exposed sites available for the adsorption process per unit gram of sorbent and its composites [44]. It is strongly observed that after a certain increase of sorbent dose, there is an exponential decrease in the oil sorption capacity. The logical reason is that the amount of oil is fixed each run and the sorbent dose increase progressively. Since the oil sorption capacity is the ratio between the weight of the adsorbed oil to the weight of adsorbent material, thus raising the weight of adsorbent and remaining oil adsorbed static will decrease the oil sorption capacity each time. The gained results are agreed with the obtained results by other researchers. They studied the availability of barley straw for crude oil sorption which indicates that increasing the sorbent dose; removes a large amount of oil. Thus, the interface between oil and water nearly disappeared allowing sorbent to absorb a high value of water [45].

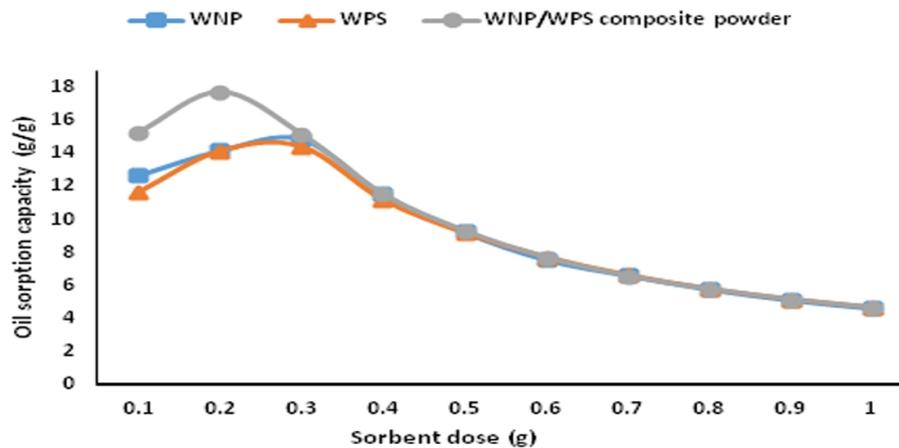


Fig. 10. Effect of the sorbent dose on the crude oil sorption capacity; 3 mm oil film thickness, 100 mL 3.5% NaCl, 150 rpm, room temperature, and 120 min.

3.3.6. Effect of the agitation rate

The effect of stirring (agitation) speed on the sorption capacity was investigated and illustrated in Fig. 11. The experiments were carried out at 0–250 rpm to simulate weather and wave conditions in the seawater. Fig. 11 demonstrated that increasing the agitation rate up to 100–150 rpm has a positive effect on the sorption capacity of oil on WNP, WPS, and their composite. Increasing the agitation speed could increase the dispersion of oil into the sorbents and increase the exposed surface of the sorbent to the oil spills. Furthermore, these results can be associated with the fact that the increase of the agitation speed enhance the turbulence and result in a decrease in the boundary oil layer thickness around the sorbent composites [46]. However, with further increase of the agitation speed up to 250 rpm, the sorption capacity reaches a plateau. This indicates that a shaking rate in the range of 50–150 rpm is sufficient to assure that all the surface binding sites are made readily available for the oil removal process [47].

3.4. Reusability

Evaluation of the reusability of the developed sorbents towards the removal of the heavy crude oil is investigated in Fig. 12 under fixed conditions for 7 successive cycles. It can be seen that the capacity of the sorbents linearly decline and lost around 50% of their values after 5 cycles only. The WNP powder and WPS powder can be reused for a maximum of 5 cycles, while WNP/WPS composite powder can be reused for 4 cycles. Furthermore, the oil sorption capacity is getting decreased as the number of sorption cycles increases. After the 7th cycle, the WNP powder, WPS powder, and WNP/WPS composite powder sorbents lost 72.0%, 80.0% and 91.0% of their sorption capacity. That behavior might be due to the remaining oil in the sorbent structure with the increase in the number of sorption cycles. Also, maybe owing to the deterioration of the sorbent structure during the washing process. The obtained results are in agreement with previously published results by other authors' study which investigate the crude oil sorption by

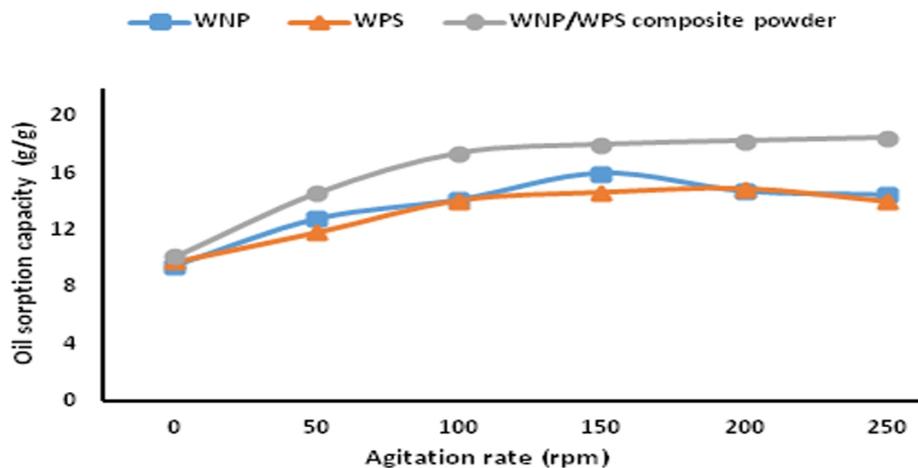


Fig. 11. Effect of the agitation rate on the crude oil sorption capacity; 0.2 g sorbent, 3 mm oil film thickness, 100 mL 3.5% NaCl, room temperature, and 120 min.

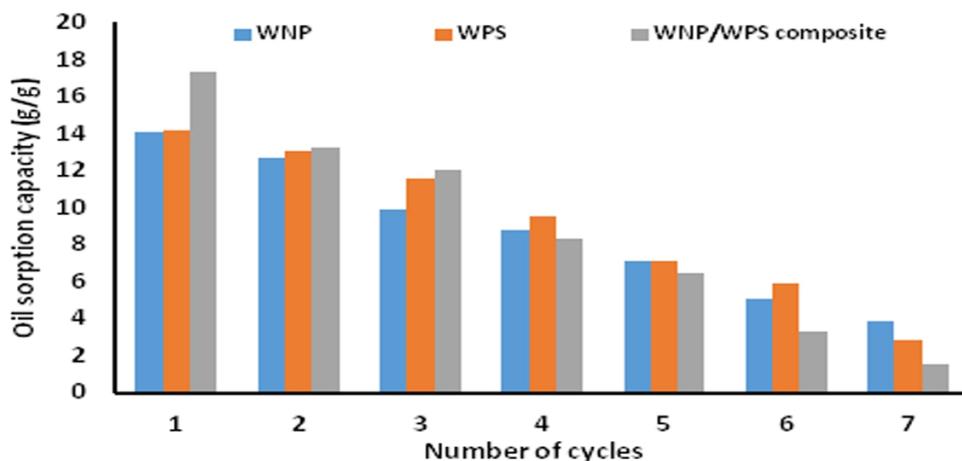


Fig. 12. Reusability of the WNP, WPS, and WNP/WPS composite powders; 0.2 g sorbent, 3 mm oil film thickness, 100 mL 3.5% NaCl, room temperature, 150 rpm, and 120 min.

cattail fibers and polyurethane sponges. They found that the decreased oil sorption capacity was considered to be a consequence of the irreversible deformation of sorbent by pressing [48,49]. Also, these results are in agreement with another author who studied the sorption by pomelo peel modified with acetic anhydride and styrene. The results reported that hexane extraction did not affect the chemical composition and stability of the fiber [50].

3.5. Kinetic studies

3.5.1. Pseudo-first-order

The linear plots of $\ln(q_e - q_t)$ vs. t , illustrated in Fig. 13; allows the calculation of the pseudo-first-order parameters K_1 and $q_{e,cal}$ from the slope and the intercept. The values of these parameters are listed in Table 2, along with the corresponding R^2 values.

It can be seen that the correlation coefficients R^2 for all sorbents were poor where it varied from 0.0452 to 0.6834.

It was deduced that the $q_{e,cal}$ values of the pseudo-first-order kinetic model are not close to the $q_{e,exp}$ values, so this model is not proper for depicting the kinetic adsorption mode in consistent with other publications which studied the kinetics of oil sorption by using super-hydrophobic kapok fiber [51], the hydrogel of chitosan-based [52] and banana pseudostem fibers [53].

Table 2

Pseudo-first-order kinetic parameters for WNP powder, WPS powder, and WNP/WPS composite powder sorbents

Sorbent type	R^2	K_1 (min^{-1})	$q_{e,cal}$ (g/g)	$q_{e,exp}$ (g/g)
WNP powder	0.370	0.014	1.785	13.05
WPS powder	0.142	0.006	1.274	13.72
WNP/WPS composite powder	0.055	0.009	0.812	17.05

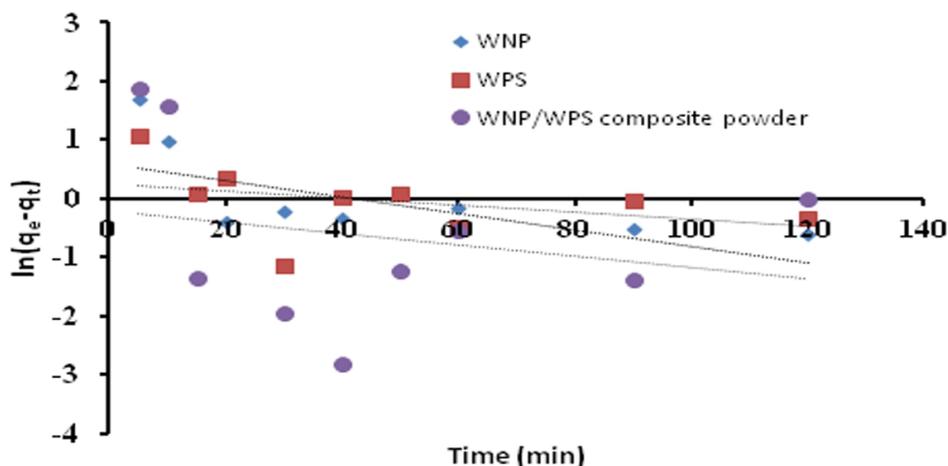


Fig. 13. Pseudo-first-order model for heavy oil adsorption by WNP powder, WPS powder, and WNP/WPS composite powder sorbents.

Table 3

Pseudo-second-order kinetic parameters for WNP powder, WPS powder, and WNP/WPS composite powder sorbents

Adsorbent type	R^2	K_2 (g/g min)	$q_{e,cal}$ (g/g)	$q_{e,exp}$ (g/g)	h (mol/g min)
WNP powder	0.999	0.0468	12.72	13.05	7.970
WPS powder	0.999	0.134	12.87	13.72	25.223
WNP/WPS composite powder	0.997	0.076	16.55	17.05	22.093

3.5.2. Pseudo-second-order

Fig. 14 illustrates the linear plot of the pseudo-second-order equation. It was clear that the correlation coefficient, R^2 of the pseudo-second-order adsorption model (Table 3), is closer to 1 indicating that the pseudo-second-order model predominates the oil adsorption process. Comparing the values of $q_{e,cal}$ obtained from the slope of the linear plot with that obtained from the experimental data ($q_{e,exp}$) illustrate that the two values are very close. Therefore, this sorption system fitted the pseudo-second-order model well. As well, the initial sorption rate (h) of WNP/WPS composite powder was faster than its counterpart of the WNP and slightly lower than that of the WPS powder. In general, the composite formation of WNP and WPS results in a noteworthy enhancement of the oil sorption rate as it increased from 7.97 to 22.093 (mol/g min). From our knowledge, the pseudo-first-order model and pseudo-second-order model are based on the hypothesis of physisorption and chemisorption process. Thus, these results imply that the chemisorption mechanism plays a vital role in the adsorption process [54], so it can be concluded that the adsorption process of spilt oil molecules onto the prepared sorbents are the chemisorption. This investigation agrees with other publications [51,52].

3.5.3. Intraparticle diffusion

The pseudo-first and the pseudo-second-order equations are based on the adsorption capacity. They only predict the behavior over the whole range of studies

supporting the validity that the chemisorption is the rate control. Thus, these findings remain uncertain about the adsorption mechanism. Therefore, the intraparticle diffusion model was integrated. Fig. 15 illustrates a plot of q_t against $t^{0.5}$ for the sorption of crude oil for the sorbents. It is evident from the plots that there are two separate stages; the first linear portion (Stage I) and the second curved path followed by a plateau (Stage II). In Stage I, oil was rapidly up taken by adsorbents. This is attributed to the immediate utilization of the most readily available adsorbing sites on the adsorbent surfaces; the instantaneous adsorption is very fast owing to the strong interaction between the oil molecules and the external surface of the sorbents. In Stage II, very slow diffusion of adsorbate from the surface site into the inner pores is observed. In this stage, the diffusion through the small pores is followed by the establishment of final equilibrium during the intraparticle diffusion. The sorption started to slow down and became stagnant as the adsorbate molecules occupied all the active sites of the adsorbent, and the maximum adsorption was reached. Thus, the initial portion of oil adsorption by adsorbents may be governed by the initial intraparticle transport of oil which is controlled by the surface diffusion process and the later part is controlled by pore diffusion [55].

Table 4 lists the intraparticle diffusion constants, K_s and C as well as the corresponding correlation coefficient, R^2 for the second stage. Ultimately, it is noticed that R^2 values are not high. The non-zero intercepts of the plots elucidate that the intraparticle diffusion is engaged in the adsorption

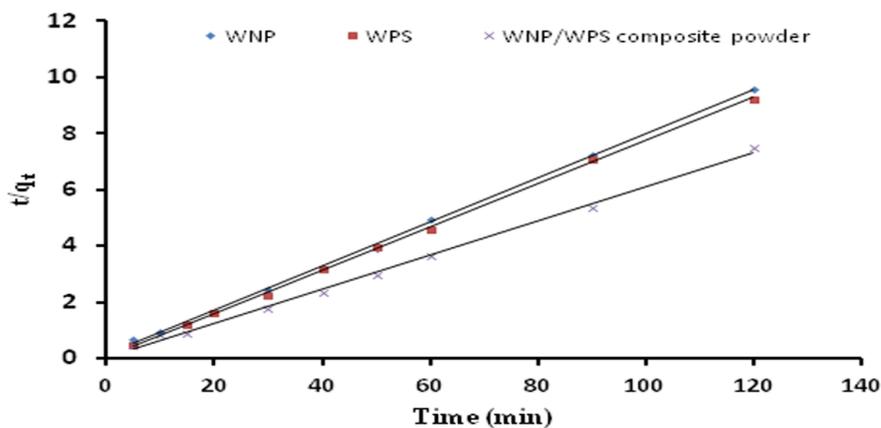


Fig. 14. Pseudo-second-order model for heavy oil adsorption by WNP powder, WPS powder, and WNP/WPS composite powder sorbents.

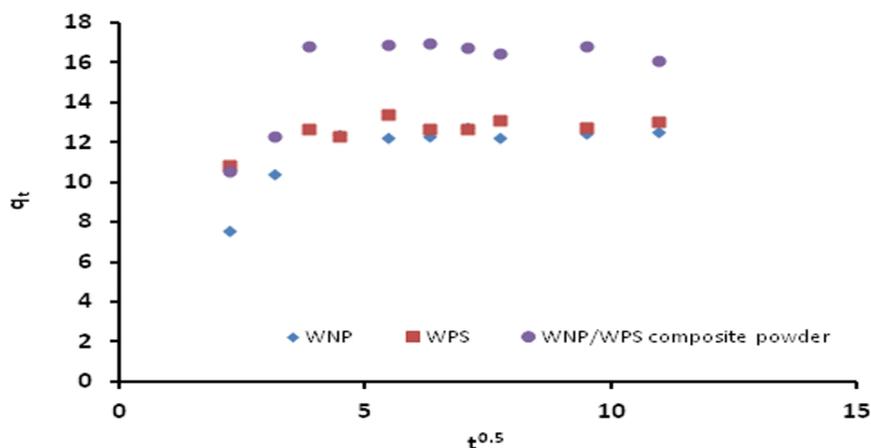


Fig. 15. Intraparticle diffusion model for heavy oil adsorption by WNP powder, WPS powder, and WNP/WPS composite powder adsorbents.

Table 4

Intraparticle diffusion kinetic parameters for WNP powder, WPS powder, and WNP/WPS composite powder adsorbents

Adsorbent type	R^2	K_s (g/g min)	C (g/g)
WNP powder	0.4971	0.412	9.042
WPS powder	0.3865	0.164	11.549
Coated WNP powder	0.4033	0.520	12.256

process, but it is not the individual rate-controlling step for the adsorption of oil.

3.5.4. Elovich model

Elovich model is used widely in describing the kinetics of chemisorption. The probability that the oil adsorption was taking place in the water/oil/adsorbents system, and comprising the contribution of other forces, besides the regular Van der Waals forces, has been assessed by concerning the Elovich model. It assumes that the actual adsorbent surfaces are energetically-heterogeneous. The Elovich equalization does not submit any particular mechanism for the adsorbate-adsorbent reactions [56]. The Elovich parameters which determined from the slope and the intercept of the linearization of the Elovich equation (Fig. 16) are tabularized in Table 5. The value of β is revealing the number of available adsorptive sites, whereas α is the adsorption quantity. It was declared that the correlation coefficients R^2 are not very good as they are less than 0.8 for all the sorbents, so sorption kinetics of all sorbents are not fitted with the Elovich equation.

3.5.5. Boyd model

The model of Boyd is widely used for studying the mechanism of adsorption. Boyd model determines whether the main resistance to mass transfer is in the thin film (boundary layer) surrounding the adsorbent particle, or in the resistance to diffusion inside the pores. If the plot is a straight line passing through the origin, the adsorption

Table 5

Elovich kinetic parameters for WNP powder, WPS powder, and WNP/WPS composite powder adsorbents

Adsorbent type	R^2	β (g/g)	α (g/g min)
WNP powder	0.707	1.3606	119.014
WPS powder	0.5794	0.5657	226.8
WNP/WPS composite powder	0.5798	1.7508	128.5

rate was governed by particle diffusion; otherwise, it was governed by the film diffusion [30].

Fig. 17 shows the Boyd plot for the heavy crude oil adsorption. It was observed from the plots that the film-diffusion is the rate-controlling mechanism. Further, $\log(1-F)$ vs. time was plotted to reconfirm the above observation. The deviation from the origin and linearity for all plots shown in Fig. 18, support the fact that the adsorption of crude oil onto sorbents occurs via the internal transport mechanism. Similar observations were also founded by another study [57].

3.6. Adsorption isotherms

3.6.1. Langmuir isotherm

The Langmuir isotherm declares that the adsorbents with the highest possible q_{\max} and a high value of K_L are the most desirable. The linear plot of C_e/q_e vs. C_e which has a slope of $1/q_{\max}$ and intercept of $1/q_{\max} K_L$ is described in Fig. 19. From the regression correlation coefficient (R^2) values which regarded as a measure of the goodness of fit of the experimental data on the isotherm's model (Table 6), it explains that the Langmuir can represent well the adsorption of oil onto the surface of all sorbents. Also, the high monolayer coverage of oil on the outer surface of sorbents occurs uniformly on the reactive sites via the strong electrostatic attraction between oil molecules and adsorbent [58]. In this study, all R_L values described in Table 7 are fall between zero and one, showing

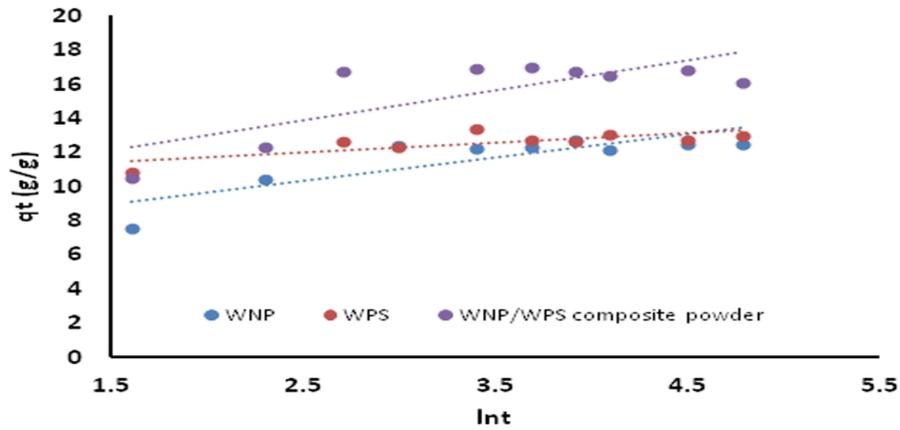


Fig. 16. Elovich model for heavy oil adsorption by WNP powder, WPS powder, and WNP/WPS composite powder adsorbents.

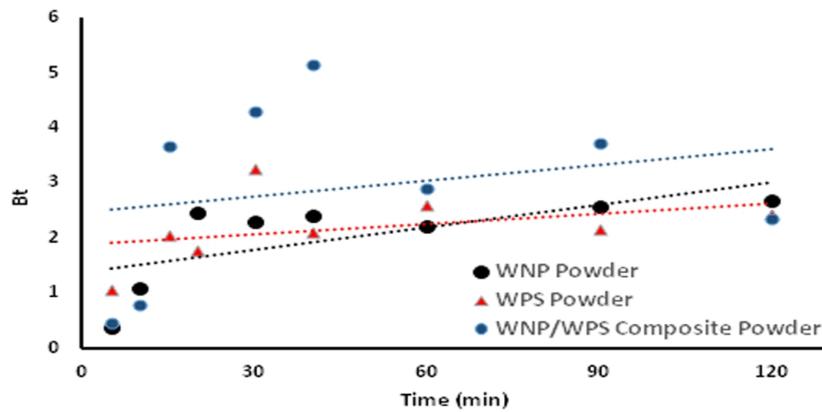


Fig. 17. Boyd model for heavy oil adsorption by WNP powder, WPS powder, and WNP/WPS composite powder adsorbents.

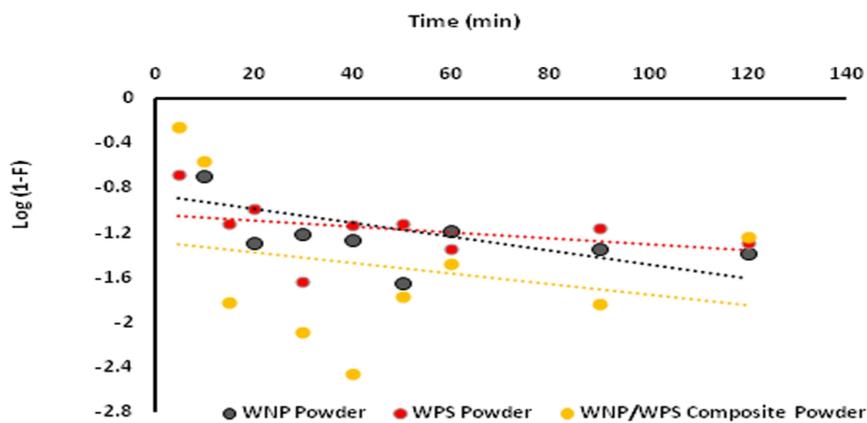


Fig. 18. Confirmation of the Boyd model for heavy oil adsorption by WNP powder, WPS powder, and WNP/WPS composite powder adsorbents.

that the oil sorption process is favorable at the experimental conditions. The low values of R_L could explain the high adsorption of the spilled oil from the artificial seawater [59].

3.6.2. Freundlich isotherm

The Freundlich constants K_f and n are obtained from the respective slope and intercept of the plot $\ln q_e$ vs. $\ln C_e$ as shown in Fig. 20. The K_f constant is concerned with

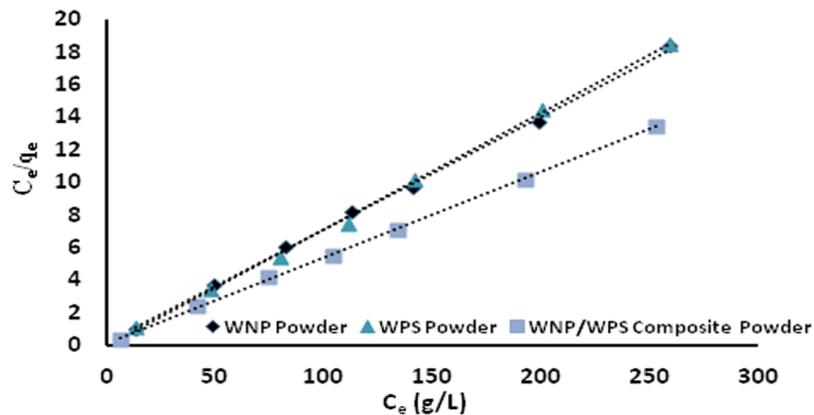


Fig. 19. Langmuir isotherm for heavy oil adsorption by WNP powder, WPS powder, and WNP/WPS composite powder adsorbents.

Table 6

Langmuir isotherm parameters for heavy oil adsorption by WNP powder, WPS powder, and WNP/WPS composite powder adsorbents

Adsorbent type	R ²	q _m (g/g)	K _L (L/g)
WNP powder	0.998	14.285	0.348
WPS powder	0.998	14.285	0.560
Coated WNP powder	0.999	20.000	0.511

the ability of the adsorbent to adsorb, and n constant is concerned with the tendency of the adsorbate to be adsorbed. Smaller values of $1/n$ indicate the stronger interaction between the adsorbent and crude oil spill [47]. The parameters of the Freundlich isotherm are shown in Table 8. It is found that the Freundlich isotherm model does not perfectly fit well according to the correlation coefficient R^2 at different oil concentration as represented in Table 8 which ranged from 0.5 to 0.9. The slope $1/n$ measures the surface heterogeneity which becomes more predominant as $1/n$ gets closer to zero. When the values for $1/n$ are below 1 it confirms a standard Freundlich isotherm, while values above 1 are indicative of the cooperative sorption [60].

3.6.3. Temkin isotherm

The plot of q_e against $\ln C_e$ shown in Fig. 21 representing the Temkin model and provides a straight line with a slope of B which is positive for all sorbents. When the intercept value is larger, this means that the adsorbent/adsorbate interaction is also larger. The parameters of this model, as well as the corresponding R^2 values, are listed in Table 9. It is found that the Temkin isotherm model does not fit well according to the values of correlation coefficient (R^2) at different oil concentrations. These results are in agreement with authors who studied the adsorption isotherm on oil sorption by using hen feathers [61], banana peel [62], and acetylated lignocelluloses' biomass [63].

4. Comparative study

The attained maximum monolayer sorption capacity for the sorption of crude oil onto the waste newspaper powder, waste polystyrene powder (WPS), and WNP/WPS composite powder sorbents have been compared with the q_{max} for other listed sorbents (Table 10). It was obvious that the developed WNP/WPS composite powder apparently exhibits higher performance than other sorbents earlier reported. However, this comparison is unfair owing to the diversity of the operating conditions.

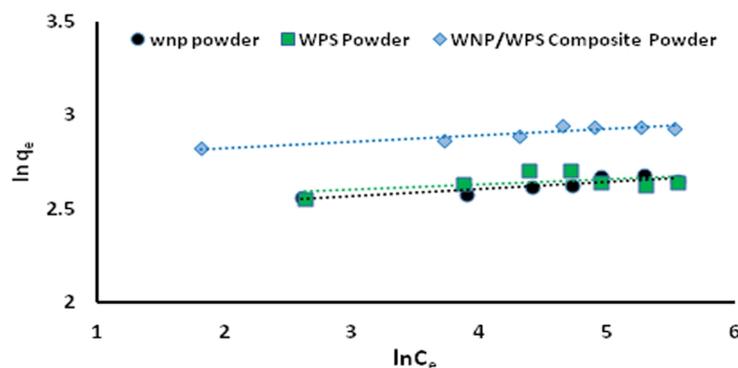


Fig. 20. Freundlich isotherm for heavy crude oil adsorption by WNP powder, WPS powder, and coated WNP/WPS composite powder adsorbents.

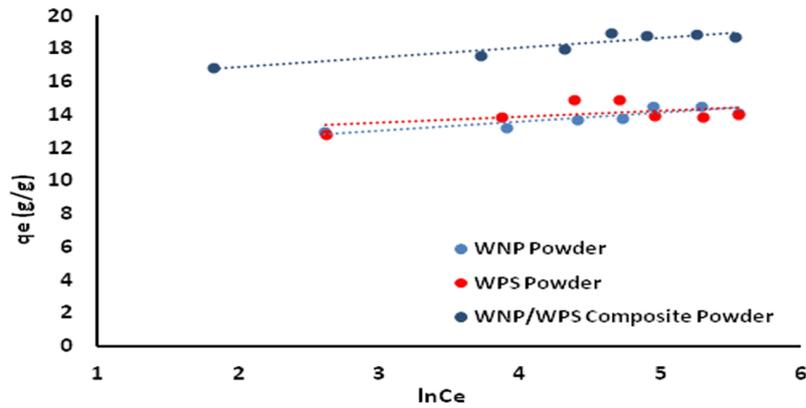


Fig. 21. Temkin isotherm for heavy oil adsorption by WNP powder, WPS powder, and WNP/WPS composite powder adsorbents.

Table 7
Dimensionless constant separation factor R_L for the adsorption of crude oil

Initial concentration (g/L)	WNP powder	WPS powder	WNP/WPS composite powder
38.457	0.069	0.044	0.048
73.805	0.037	0.023	0.025
106.618	0.026	0.016	0.018
136.564	0.02	0.012	0.014
164.549	0.017	0.01	0.011
221.212	0.012	0.008	0.008
278.819	0.01	0.006	0.006

Table 8
Freundlich isotherm parameters for heavy oil adsorption by WNP powder, WPS powder, and WNP/WPS composite powder adsorbents

Adsorbent type	R^2	$1/n$	K_f (g/g)
WNP powder	0.774	0.039	8.864
WPS powder	0.295	0.027	10.228
WNP/WPS composite powder	0.874	0.033	12.507

5. Collected oil spills management

The overall management approaches when dealing with the collected oil spills is the same as any type of waste and can be concluded in the following reduce, reuse, and recycle.

- Reduce the amount of oily waste collected. In this regard, our developed adsorbent has high selectivity towards the oil that has been detected,
- Reuse of the collected oil spills through a refinery or recycling plant,
- As the last solution when the collected oil spills cannot be reused or reprocessed, comes up the land filling in designed sites or going to use as a source of fuel in the cement and steel factories.

Table 9
Temkin isotherm parameters for heavy oil adsorption by WNP powder, WPS powder, and coated WNP powder adsorbents

Adsorbent type	R^2	B (J/mol)	K_T (L/g)
WNP powder	0.763	0.5345	58.209
WPS powder	0.275	0.3764	89.455
WNP/WPS composite powder	0.866	0.6022	70.729

Table 10
Comparison of the maximum sorption capacity for the crude oil by various sorbents

Adsorbent	Sorption capacity	Reference
Chitosan flakes	0.38 g/g	[58]
Chitosan powder	0.28 g/g	[58]
Chitosan-based polyacrylamide hydrogel	2.30 g/g	[59]
Chitosan (prawn shells)	18.52 g/g	[60]
Acetylated corncobs	0.08 mg/g	[61]
Lauric acidmodified oil palm leaves	1.20 mg/g	[50]
Carbonized rice husks	6.00 g/g	[50]
Cellulose aerogel functionalized with methyltrimethoxysilane	24.40 g/g	[62]
Butyl rubber	25.0 g/g	[63]
Nonwoven polypropylene	15.00 g/g	[63]
BuAc-cellulose graft copolymer	13.80 g/g	[54]
Waste newspaper powder (WNP)	14.28 g/g	This study
Waste polystyrene powder (WPS)	14.28 g/g	This study
WNP/WPS composite powder	20.00 g/g	This study

6. Conclusion

Waste newspapers powder, waste polystyrene powder, and their developed composite powder have been characterized and tested for the removal of heavy crude oil spills from oil-saline water solution. The sorbents show fast equilibrium reach after 15–20 min. The environmental

temperature up to 45°C, oil film thickness up to 10 mm, and salinity up to 5% was found of neglectable effect on the sorption capacity. On the other hand, the stirring rate was found to strongly affect the sorption capacity and reach a maximum at 250 rpm. The optimum sorbent dose for having maximum sorption capacity was found 0.3 g for the WNP and WPS powders. The WNP/WPS composite powder show maximum sorption capacity at 0.2 g. Equilibrium data are well fitted with the Langmuir isotherm indicating the high monolayer coverage of oil on the outer surface of sorbents occurs uniformly on the reactive sites via the strong electrostatic attraction between oil molecules and adsorbent. The maximum adsorption capacity is obtained as 20 g/g for WNP/WPS composite powder with the application of Langmuir isotherm. The rate kinetics of oil adsorption on sorbents is better explained by pseudo-second-order kinetics. These results imply that the chemisorption mechanism plays a vital role in the adsorption process. The non-zero intercepts of the plots elucidate that the intraparticle diffusion is engaged in the adsorption process, but it is not the individual rate-controlling step for the adsorption of oil. The Boyd plot for the heavy crude oil adsorption indicates that the film-diffusion is the rate controlling mechanism. Further, this observation reconfirmed by plotting $\log(1-F)$ vs. time. The deviation from the origin and linearity for all plots support the fact that the adsorption of crude oil onto sorbents occurs via the internal transport mechanism. Finally, the sorbents show moderate reusability where can be reused for five successive cycles before losing 50% of their sorption capacity.

In conclusion, the fast equilibrium, the neglectable effect of the environmental temperature and salinity and oil film thickness, in addition to the strong positive effect of stirring rate on the sorption capacity, reusability, and the low cost and the effectiveness of the sorbents recommend them for applying in the oil spills removal.

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