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Crude Oil Biosorption with *Citrus sinensis* Peels

Citrus sinensis Kabuklarıyla Ham Petrol Biyosorpsiyonu

Nermin Hande Avcıoğlu and Sezen Bilen Özyürek

Department of Biology, Hacettepe University, Ankara, Turkey.

ABSTRACT

Dried *Cydonia oblonga, Persea americana*, *Malus domestica* and *Citrus sinensis* peels were used as low-cost biosorbents in crude oil removal. Among them, *Citrus sinensis* was selected as the most effective biosorbent with a removal rate of 83.81% and the effect of adsorption parameters such as pH (4.0-10.0), adsorbent dose (0.1-0.5 g/50mL) and crude oil concentration (0.25-2.5%) were also investigated. Maximum removal rate of 94.37% (qe=1.81) was found at pH=7.0, 0.25 g/50 mL adsorbent dose and 1% crude oil concentration. And 25.91% removal rate (qe=0.49) was determined at the end of the 6th cycle of re-used peels. The kinetics of this adsorption was described by Pseudo-second order model (R^2=0.8167) and the equilibrium modelling were well fitted with Langmuir isotherm (R^2=0.9403). Characteristic bands of cellulose and hemicellulose in the lignocellulotic structure of dried peels were determined by FTIR. Thermogravimetric profile was resulted as a residual weight of 17.5% even at 1000˚C with high resistance to increasing temperature. Therefore, *C. sinensis* peels, which is a common domestic and an industrial food waste, can be used as a low-cost, easily available, biodegradable and environmentally friendly adsorbent in crude oil removal.

Key Words

Citrus sinensis, crude oil removal, adsorption kinetic and isotherm, physicochemical characterization.

ÖZ

Kurutulmuş *Cydonia oblonga, Persea americana, Malus domestica* ve *Citrus sinensis* kabukları, ham petrolün uzaklaştırılmasında düşük maliyetli biyosorbanlar olarak kullanıldı. Bunlardan *Citrus sinensis*, %83.81'lik giderim oranı ile en etkili biyosorban olarak seçildi ve pH (4.0-10.0), adsorbent dozu (0.1-0.5 g/50 mL) ve ham petrol konsantrasyonu (0.25-2.5%) parametrelerinin adsorpsiyona etkisi araştırıldı. Kurutulmuş *C. sinensis* kabukları kullanılarak ham petrol uzaklaştırma için en yüksek uzaklaştırma oranı (%94.37, qe=1.81), pH=7.0, 0.25 g/50 mL adsorbent dozu ve %1 ham petrol konsantrasyonu olarak bulundu. Kabukların tekrar kullanımı ile 6. döngünün sonunda %25.91 uzaklaştırma oranı (qe=0.49) gözlendi. Bu adsorpsiyonun kinetiği, Pseudo-ikinci derece modeli ile açıklandı (R^2=0.8167) ve denge modelleme Langmuir izotermi ile uyumlu bulundu (R^2=0.9403). Kurutulmuş kabukların lignoselülozik yapısındaki selüloz ve hemiselulozun karakteristik bantları FTIR ile belirlendi. Termogravimetrik profil, 1000˚C'de bile %17.5'lik bir kalıntı ağırlığı ile yüksek sıcaklığa karşı direnç gösterdi. Sonuç olarak, yaygın bir evsel ve endüstriyel gıda atığı olan *C. sinensis* kabuklarının, ham petrol uzaklaştırmada düşük maliyetli, kolayca bulunabilir, biyobozunur ve çevre dostu bir adsorban olarak kullanılabilirliği gösterildi.

Anahtar Kelimeler

Citrus sinensis, ham petrol giderimi, adsorpsiyon kinetiği ve izotermi, fizikokimyasal karakterizasyon.

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Correspondence to: N.H. Avcıoğlu, Department of Biology, Hacettepe University, Ankara, Turkey.

E-Mail: hurkmez@hacettepe.edu.tr

INTRODUCTION

With the rapid development of technology and industrialization, the demand for fossil energy sources is increasing day by day [1]. Petroleum, which is a mixture of polycyclic aromatic hydrocarbons, *n*-alkanes and many other chemicals, causes oil spills in marine and terrestrial ecosystems during its use, refining, extraction and transportation and poses a serious risk to living organisms [2-6]. Since petroleum degradation products have a lethal effect on living organisms even at low concentrations, it is necessary to remove this contamination from the environment as soon as possible. In this context, the use of physical, chemical, physicochemical, and biological methods is quite common to remove this contamination [6, 7]. Among these methods, bioremediation, flotation, coagulation, filtration, thermal desorption, reverse osmosis, and adsorption are mainly used in the treatment of oil spill [8-11].

Sorption is a simple, effective, and low-cost method that is widely used in the rapid removal of waterborne pollutants from the environment. Thus, it becomes possible to remove the waste from the environment without causing secondary pollution by sorption [12-14]. Accordingly, inorganic mineral products, organic synthetic and natural adsorbents are used in adsorption processes [9-11]. Compared to chemical methods, the use of bio-based materials in oil removal is an environmentally friendly and inexpensive approach [1]. Especially, cellulose, hemicellulose, and lignin-rich plant biomass wastes produced by the agricultural industry, algae, bacteria, and fungi are commonly used as biosorbents for the treatment of heavy metals, dyes, and pollutants [15-17].

Compared to traditional water treatment methods, the use of biosorbent is advantageous due to its low cost, readily available, environmentally friendly, and high efficiency [18]. Since the hydrophobicity of the adsorbent, large surface area and porosity are the main requirements for adsorption, sorbents obtained from plant and animal wastes are preferred in treatment [19]. Especially natural organic sorbents are emerging as viable options for oil spill cleanup due to their availability, low cost and environmentally friendly [20]. In the literature, the use of lemon peel [21], *Carica papaya* wood [22], *Artocarpus* genus fruit peels [23], pomegranate peel [24], orange peel [25], dragon fruit peel [18], banana peel [26] and various organic sorbents on petroleum removal have been reported.

In this study, the effect of dried fruit peels (*Cydonia oblonga, Persea americana, Malus domestica* and *Citrus sinensis*) on crude oil sorption was investigated with the aim of low-cost treatment, biodegradability of the adsorbent, and waste utilization. The best conditions for crude oil sorption by the potent waste with the highest sorption capacity were also detected. By determining the re-usability of the potent waste peel in sorption experiments, it will contribute to cost reduction and waste utilization in oil sorption. The characterization of the surface morphology and the existing functional groups and bond types of potent waste peel, and its usability as a treatment agent for crude oil removal were also investigated. Lastly, kinetic and equilibrium modelling was used to clarify the biosorption of crude oil with the potent waste. Thus, it is aimed to evaluate the plant wastes, to reduce the cost of chemical and mechanical treatment, and to realize the treatment by ensuring the reuse of fruit peels.

MATERIALS and METHODS

Adsorbent preparation

Fruit peels (*Cydonia oblonga, Persea americana, Malus domestica* and *Citrus sinensis*) were obtained from a local market in Ankara, Turkey. To use in adsorption experiments, fruit peels were washed with distilled water and dried at 37°C for 7 days in a static incubator. Following, all the peels were cut with a dimension of 1x1 cm and were stored at 4°C for experimental use.

Adsorption studies

To investigate crude oil biosorption, 1% Triton X:100 contained distilled water (pH=7.0) was autoclaved at 121°C for 15 min. Following this, 1% crude oil was added under aseptic conditions. The most effective fruit peel in crude oil adsorption was selected and used in the rest of the experiments. Accordingly, 0.1-0.5 g/50mL adsorbent dose, pH=4.0-10.0, 0.25%-2.5% crude oil concentration and sorption time from 0. min to 480. min were investigated to optimize adsorption process. The adsorption capacity of fruit peels was determined according to Al-Zuhairi et al. [27] as follows;

$$qe = \frac{Ci - Cf}{\mathrm{m}}\ x\ V \qquad (1)$$

(q_e: adsorption capacity (g/g), C_i: initial concentration of crude oil (g/L), C_f: concentration of crude oil in equilibrium (g/L), m: mass of adsorbent (g), V: volume (L))

Crude oil extraction and gravimetric analysis

To determine the crude oil adsorption on the surface of fruit peels, dichloromethane (DCM) (CH_2Cl_2) (1:2) (Sigma-Aldrich, Germany) was used to extract remaining crude oil. Following, DCM was removed from the flasks at 90°C for 1 hour by evaporation (Memmert, Schwabach, Germany). The petroleum removal of fruit peels was calculated as gravimetrically according to Ejimofor et al. [28] as follows;

$$\text{Removal rate (\%)} = \frac{\text{Ci}-\text{Cf}}{\text{Ci}} \text{ x } 100 \qquad (2)$$

C_i: initial concentration of crude oil (g/L), C_f: concentration of crude oil in equilibrium (g/L).

Kinetic studies and Biosorption isotherms

Pseudo-first order and Pseudo-second order kinetic models were used to evaluate the rate and mechanism of crude oil adsorption [15, 24, 27, 29]. Additionally, the biosorption mechanism of crude oil by *C. sinensis* peels was also determined with Langmuir and Freundlich adsorption isotherm models [9, 18, 24, 30].

Characterization studies

The surface morphology of gold coated (Leica ACE 600) potent peel visualized by FIB-SEM (FIB-SEM GAIA3, Tescan, Czech Republic) to observe the adsorption of crude oil. Thermogravimetric analyzes (TGA) was performed by using TA Instruments Q600 SDT system and Fouirer transform infrared (FT-IR) spectrometer was also performed by Thermo Fisher Nicolet is 50 Spectrofotometer with a range of 4000 cm^{-1} to 450 cm^{-1} in transmittance mode in order to analyze the existing functional groups and bond types of dried potent peel before and after adsorption.

RESULTS and DISCUSSION

Nowadays, petroleum which is an important non-renewable energy source is widely used in the production of chemical and synthetic polymers. However, even low concentrations of petroleum, which consists of polycyclic aromatic hydrocarbons, can cause toxic effects on living organisms [5, 7, 31]. Accordingly, the oil film layer formed on the water surface by oil spills prevents dissolution of oxygen and photosynthesis. For this reason, it is of great importance to remove the oil spills as soon as possible by using physical, chemical, phytochemical or biological treatment methods [7]. Non-polar organic pollutants with low solubility cannot be completely removed from the environment by physical and chemical treatment methods [32]. In addition, these pollutants have toxic, mutagenic and carcinogenic effects on microorganisms and living things in the aquatic ecosystem as well as on plant and wildlife and causing defects on fishing, farming, and food industry [4, 5, 9, 10, 31, 33, 34]. Therefore, oil-contaminated areas need to be remediated as soon as possible. Due to the low-cost of non-biodegradable adsorbents used in remediation process, researchers are currently focused on investigating renewable, inexpensive, nontoxic, biodegradable, and hydrophobic adsorbents to use in treatment. In this context, agro-industrial wastes are widely used in adsorption studies [11, 35]. The use of wastes as an adsorbent in crude oil remediation processes has gained importance in recent years due to their biodegradable, environmentally friendly, low energy requirement and low-cost [9, 10, 33, 35, 36].

Adsorption studies

Effect of dried fruit peels on crude oil sorption

In adsorption, the chemicals are adsorbed on the biomaterials biologically, physically, or chemically in adsorption media [17, 37]. The use of these materials in adsorption, which is an energy-free physicochemical process that allows the passive attachment of contaminants to the biomass without the need for any thermochemical effect, makes biosorption advantageous [35, 38]. The main requirement for organic sorbents used in removing oil from polluted environments are biodegradable, easily available, environmentally friendly, reusable and low-cost [34, 35].

In this study, dried peels of *Cydonia oblonga, Persea americana, Malus domestica* and *Citrus sinensis* were used as low-cost adsorbents. Among these fruit peels, *C. sinensis* peels were selected as the most effective adsorbent for crude oil removal with a q_e = 0.40 at a removal rate of 83.81% (Figure 1). *C. sinensis*, which is common in the subtropical region of the world, is an abundantly produced agricultural waste. Studies have shown that this fruit, which has a high content of pectin, cellulose, hemicellulose and lignin, is quite suitable for biosorption [39, 40]. Similarly, banana peel [26], avocado, hami melon, dragon fruit peels [18], orange peel [25] and pomegrate peel [24] were also used in adsorption studies in the literature. Considering the importance of the nontoxic, low-cost, renewable, ecological, and economical, and have a large surface area of sorbents used in biosorption, *C. sinensis* peels used in this study have a higher removal rate than other peels in terms of usability in oil removal [5, 35]. In addition, the use of *C. sinensis* peels in crude oil sorption is very important because agricultural industrial wastes are biodegradable and are defined as good adsorbents [41, 42]. Similar to this study, banana pseudo stem fiber [41], stearic acid grafted mango seed shell [9], banana peel fiber (BPF) [11], stearic acid grafted coconut husk (*Cocos nucifera*) composite [10] and floating pinewood biochar decorated with coconut oil-derived fatty acids [5] were also used in adsorption studies.

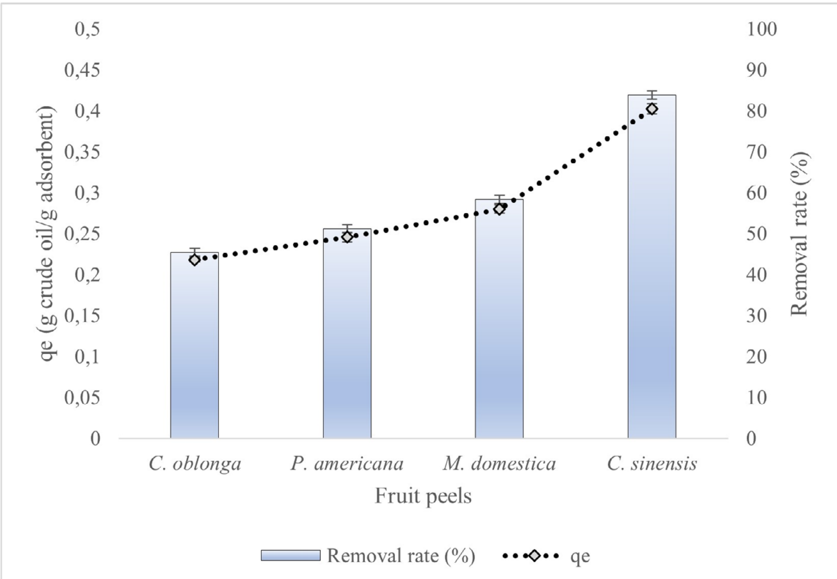

Figure 1. Effect of dried fruit peels on crude oil sorption (Initial crude oil concentration: 1%, Adsorbent dose: 1 g/50 mL, pH=6.0, Agitation speed:150 rpm, Contact time: 24 h and T: 25°C. Each experiment is the mean of three data and the error bars represent the standard deviation).

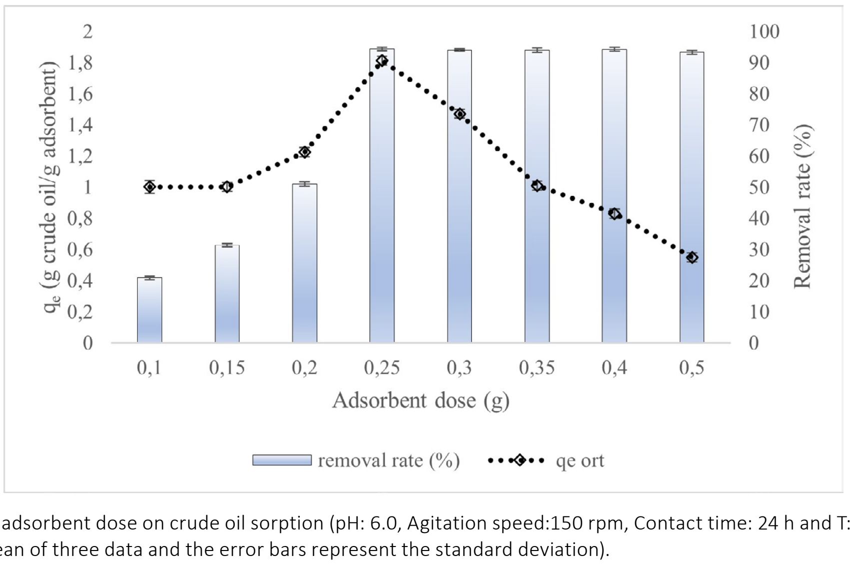

Figure 2. Effect of adsorbent dose on crude oil sorption (pH: 6.0, Agitation speed:150 rpm, Contact time: 24 h and T: 25°C. Each experiment is the mean of three data and the error bars represent the standard deviation).

Optimization of crude oil sorption

Effect of adsorbent dose

The amount of adsorbent is an important parameter that affects the adsorption of oil molecules on the sorbent surface [35]. In the literature, it was found that while the amount of oil adsorbed per unit mass increased depending on the increase in the initial concentration, a decrease was observed in the adsorption rate. This is related to the fact that oil molecules are more easily accessible at low concentrations, and thus the amount of reaching the surface area is quite low [9-11]. Emenike et al. 2022 [35] was concluded that the increase in the adsorbent dose will increase the efficiency of sorption as it will increase the number of functional groups and active sites on the adsorbent surface. In addition, due to the unsaturation of the active sites of the adsorbent, increasing adsorbent dose caused a decrease in the adsorption capacity. Similarly, when the effect of adsorbent dose (0.1-0.5 g/50mL) on crude oil adsorption was examined, the maximum removal rate of 93.33% (q_e=1.79) was obtained with 0.25 g/50mL of *C. sinensis* peels (Figure 2). In another study in which oil adsorption was performed using coconut shell biochar, an increase was observed in the amount of adsorption with the increasing amount of adsorbent, however a decrease in the adsorption capacity was found due to the overlap or accumulation of active sites [35]. Similarly, Mottagi et al. 2021 [1] was stated that the adsorption capacity increased at low adsorbent dose as the oil concentration increased. Rouibah et al. 2023 [43] was stated that the active sites and surface area on the sorbent surface increased due to the increase in biosorbent mass, but the increase in the amount of sorbent did not have an effect on Zn^{+2} removal after 1g/L. Similar to the literature, in this study, the oil sorption increased depending on the increase in the adsorbent dose, but a decrease in the q_e value was observed due to the overlapping of the sorbents above a certain dose and the removal rate remained constant at adsorbent doses > 0.25 g/50 mL (Figure 2).

Effect of pH

Adsorption is directly affected by various parameters such as pH, biomass amount and presence of pollutants in adsorption media [38]. The pH of the environment affects the interaction between the sorbent surface and the pollutant. The increase in pH facilitates the removal of organic pollutants from the environment. This is related to the binding of functional groups on the adsorbent surface with hydroxonium ions at low pH values, which reduces the removal efficiency [35]. In the literature, it has been found that an increase in adsorption is observed in dye removal from polluting environments, since electrostatic attraction will increase in the adsorption regions at low pH values [44]. On the other hand, there was a decrease in the sorption of water-insoluble oil molecules due to the increase in pH, while the decrease in pH value caused protonation in the outer layer of the adsorbent, resulting as an increase in the adsorption of negatively charged petroleum [30]. In the literature, petroleum adsorption was occurred at pH:4.0 with banana peel fiber adsorbent (BPF) [11], pH:3.0 with chitosan-based polyacrylamide [3], pH:5.0 with acetylated *Musa-paradisiaca* peels [30] and pH:4.0 with *Egeria radiate* shell extract (ERSE) [28]. However, when the effect of *C. sinensis* peels used at varying pH values (pH: 4.0 – 10.0) on crude oil adsorption was examined, pH:7.0 was found as the most effective pH value with the maximum removal rate of 94.38% (q_e=1.81) (Figure 3). In the literature, pH:6.8 was found as the optimal pH value for the removal of crude oil with polytetrafluoroethylene membrane [7] and pH:7.32 for micro-sized polyethylene [4]. Al-Zuhairi et al. 2019 [27] was concluded that pH:6.18 is the optimal pH value for oil absorption with papyrus reeds and the increase in pH causes an increase in the adsorption of crude oil. It has been reported that the increase in pH value causes an increase in adsorption by enhancing the electrostatic attraction force in adsorption media. In the literature, it has also been stated that the use of orange peels as an adsorbent is advantageous with their large surface areas and active functional groups. The presence of oxygen groups on the adsorbent surface is very important for the usability of this material as a biosorbent [38].

Effect of crude oil concentration

In this study, when crude oil concentrations ranging from 0.25-2.5% was examined, the maximum removal rate of 94.93% (q_e=1.81) was obtained with 1% oil concentration. As the porous on the adsorbent material decreased more than 1% of oil concentration, there was also a decrease in the removal rate and q_e values (Figure 4). Similarly, when the contaminant concentration of the adsorption was increased from 13 mg/L to 30 mg/L in Zn^{+2} contaminated media, it was observed that the rate of biosorption decreased [43]. Emenike et al. 2022 [35] has been stated that the amount of oil adsorbed depends on the initial crude oil concentration, and the amount of oil that will be adsorbed by the

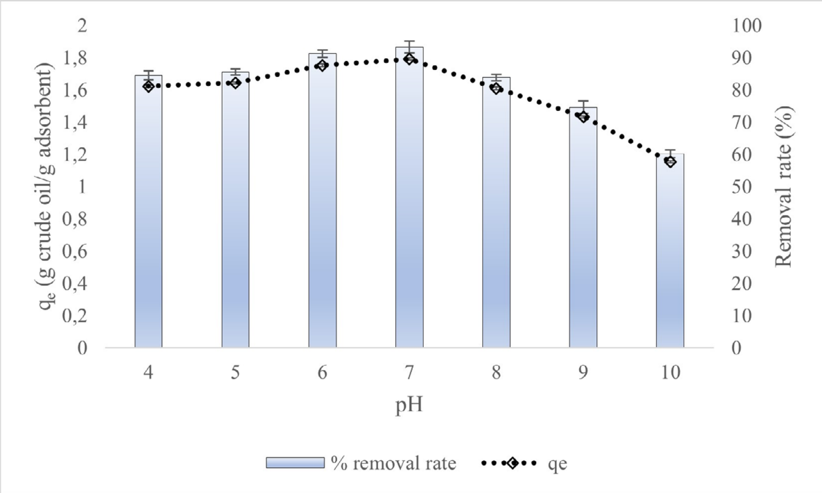

Figure 3. Effect of pH on crude oil sorption (Initial crude oil concentration: 1%, Adsorbent dose: 0.25 g/50 mL, Agitation speed:150 rpm, Contact time: 24 h and T: 25°C. Each experiment is the mean of three data and the error bars represent the standard deviation).

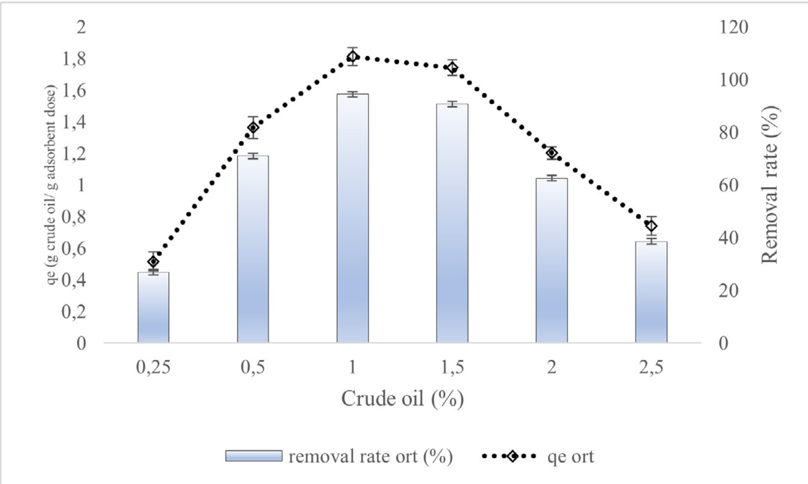

Figure 4. Effect of crude oil concentration on sorption (Adsorbent dose: 0.25 g/50mL, pH: 7.0, Agitation speed:150 rpm, Contact time: 24 h and T: 25°C. Each experiment is the mean of three data and the error bars represent the standard deviation).

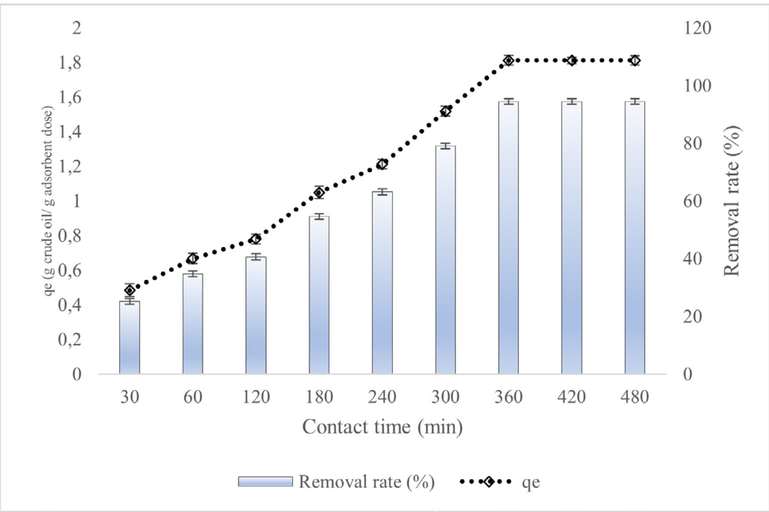

Figure 5. Effect of sorption time on crude oil sorption (Initial crude oil concentration: 1%, Adsorbent dose: 0.25 g/50 mL, pH: 7.0, Agitation speed:150 rpm and T: 25°C. Each experiment is the mean of three data and the error bars represent the standard deviation).

adsorbent in the contaminated environment is certain. As a matter of fact, the presence of empty adsorption sites on the adsorbent surface at the beginning of the adsorption will cause a rapid decrease in the amount of oil. It has been stated that the increase in the amount of crude oil in the crude oil removal using PTFE creates an adsorption repulsive force towards the membrane surface. In addition, it was concluded that the increase in the number of petroleum molecules at high petroleum concentration decreases the distance between each other and enhances the probability of adsorption on the PTFE surface by increasing the repulsive force [7]. Similarly, no increase in adsorption was observed at oil concentrations > 1% in our study (Figure 4).

Effect of sorption time

Not only the initial concentration of crude oil but also contact time are main factors affecting crude oil adsorption and the contact time gives information about the kinetics of adsorption [35, 43]. In this context, in our study, when the oil biosorption with *C. sinensis* peels was examined between 0-480 minutes it was determined that the q_e value and the removal rate were 0.484 and 25.20% in the first 30 minutes, respectively. It was also found that the removal rate (94.375%) and q_e=1.812 increased from the beginning of the adsorption until the 360th minute but then stabilized (Figure 5). Similar to our study, Deniz et al. 2010 [44] found that there was an increase in the biosorption capacity with the increase of the contact time in dye sorption and maximum saturation was reached at 180th min. It has been stated that reaching the maximum adsorption in this process depends on the decrease in the concentration due to the decrease in the ratio of unsaturated regions on the sorbent surface. Similarly, Ali et al. 2021 [33] was observed that increasing contact time caused the active sites on the adsorbent surface to be filled with oil molecules, thus leading to a decrease in the adsorption sites. On the other hand, Saruchi et al. 2016 [45] found that the sorption on the adsorbent surface reached saturation at 60 minutes and the velocity decreased as the gaps on the adsorbent surface were filled. When equilibrium is reached (60. min), there is no empty space on the adsorbent surface. In a different study where grafted natural polysaccharide gum tragacanth was used in oil remediation, it was found that 80th minute was the interval in which adsorbent saturation occurred [29]. In a study in which chitosan-based hydrogel was used in adsorption of crude oil, it was stated that the amount of adsorption increased over time and remained constant when the maximum adsorption was reached (120th minute) [46].

Re-usability of *C. sinensis* waste on crude oil sorption

The re-usability of the sorbent in the removal of oil spills is of great importance in terms of cost reduction, waste disposal and prevention of secondary pollution [5, 33]. When the reuse of AG-CMC-Ag np as a sorbent in oil removal was examined by Ali et al 2021 [33], it was concluded that this sorbent can be used at least 10 times more actively in removal with adsorption-desorption applications, and there was a decrease in its effectiveness after the 10th cycle. In a different study, it has been determined that pristine BC and modified BC maintained their effectiveness in sorption for 5 more cycles [5]. El-Gheriany et. al. 2020 [2] concluded that due to the loss of their oleophilic property during the regeneration phase over time, orange peels can be used for crude oil and diesel removal up to the 5th and 4th cycles, respectively. It has also been observed that peat-derived biochar is 3 cycle more effective in removing crude oil under optimal conditions [6]. An additional 5 cycles of cyclic oil adsorption were observed on CH/PEG/MWCNTs hydrogel. However, a slight decrease in hydrogel capacity was also detected at each cycle [1]. It was determined that the banana peel, which is used as a sorbent in the removal of oil spill, is 20 times more active in bioremoval process. It was also concluded that it had an initial sorption capacity of approximately 90%, and after the 10th cycle it was able to adsorb 50% according to the first sorption degree [26]. Mallampati et al. [18] has also shown that pollutants can be removed for at least 5 more cycles with different fruit peels. It has been concluded that these adsorbents, which are obtained at low cost, are also important adsorbing and concentrating low amounts of pollutants on the surface. A study in which oil removal was performed with pomegranate peels, 76.2% oil removal was observed even in the 6th cycle [24]. In this study, even in the 4th cycle, 55% of crude oil removal was achieved with *C. sinensis* peels. It has also been observed that *C. sinensis* peels had a removal rate of 94.45%, which decreased to 25.91% by the 6th cycle. Accordingly, it was concluded that *C. sinensis* peels, which is low-cost and biodegradable adsorbent, have more than 50% oil adsorption capacity even after 4th cycles (Figure 6).

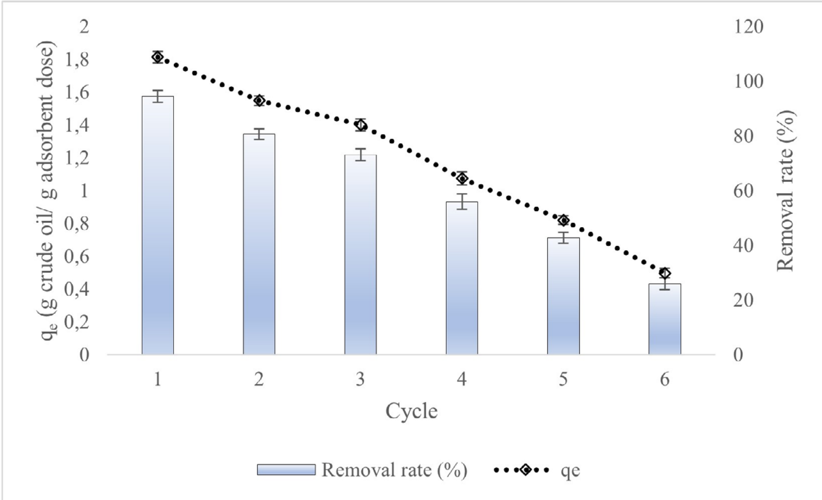

Figure 6. Re-usability of *C. sinensis* waste on crude oil sorption (Initial crude oil concentration: 1%, Adsorbent dose: 0.25 g/50 mL, pH: 7.0, Agitation speed:150 rpm and Contact time: 6 h, T: 25°C. Each experiment is the mean of three data and the error bars represent the standard deviation).

Characterization of *C. sinensis* peels with FT-IR, FIB-SEM and TGA

C. sinensis peels contain sugars as glucose, fructose, galactose, arabinose and galacturonic acid and as well as polysaccharides as cellulose and hemicellulose. The FT-IR spectrum of dried *C. sinensis* peels before and after crude oil adsorption is given in Figure 7a and Figure 7b. The main functional groups in the dried *C. sinensis* peel are expressed by the characteristic peaks of lignocellulosic materials. A slight curve in the region between 3600 and 3000 cm^{-1} is assigned to stretching vibrations of –OH groups present in carbohydrates and phenolic groups in *C. sinensis* peel. The bands at 2916 cm^{-1} and 2849 cm^{-1} are due to the asymmetric and symmetric stretching of C–H groups. The band at 1461 cm^{-1} is attributed to the bending vibrations of CH_2 and CH_3, which related to the basic structure of lignocellulosic material. The bands at 1734 cm^{-1} and 1712 cm^{-1} are corresponded to carbonyl group of esters. The adsorption bands at 1269 cm^{-1} are due to the carbonyl group in the ester bond. The signal at 1022 cm^{-1} is related to the stretching vibrations of C–OH and C–OR groups present in carbohydrates and polysaccharides. These bands correspond the characteristic bands of cellulose and hemicellulose in the lignocellulosic materials such as *C. sinensis* peel (Figure 7a).

As shown in Figure 7b, a curve at 3338 cm^{-1} is due to stretching mode of –OH and –CH groups corresponded to phenolic, alcoholic, and carboxylic acids in the crude oil. Because of the hydrogen-bonded O–H has a broader shape at 3400-3300 cm^{-1} region, the band at 3338 cm^{-1} is attributed to the intermolecular H bonds in the structure of crude oil. While the adsorption peaks at 2893 cm^{-1} related to aliphatic C–H stretching and the band at 1604 cm^{-1} is related to the C=O stretching vibration. Because of crude oil contains sulfur element in its chemical structure, a band at 1032 cm^{-1} is related to the sulfoxide group with alkane substitutions. The adsorption bands mentioned above clearly show the sorption of crude oil on dried *C. sinensis* peel. The FT-IR spectrum of *C. sinensis* peel before and after crude adsorption were interpreted according to similar studies [2, 47-49] (Figure 7a and 7b).

The change in the microstructure of dried *C. sinensis* peels before and after crude oil sorption was shown in Figure 8a and Figure 8b. Peels have an irregularly distributed macro and microporous surface before crude oil adsorption. However, it was observed that the surface was covered with crude oil with intraparticular diffusion allowed the surface to become smoother (Figure 8b). According to the FIB-SEM micrographs, it was revealed that the structure of dried *C. sinensis* peels' surface and its cavities are suitable for crude oil adsorption (Figure 8).

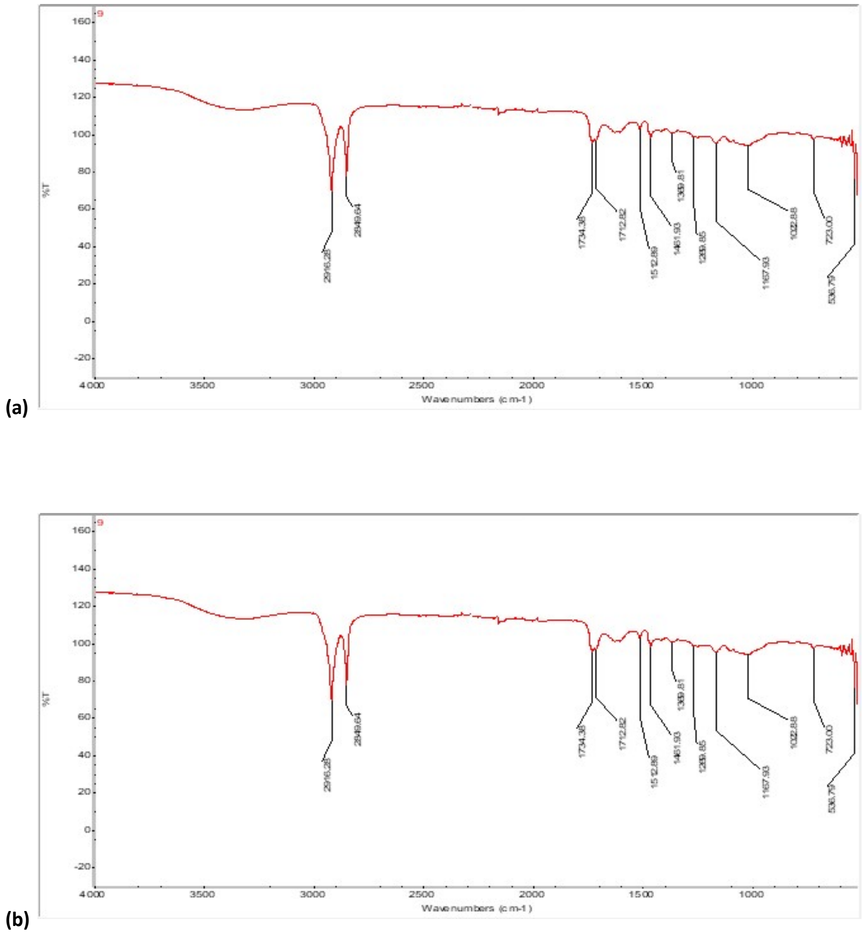

Figure 7. FT-IR analyzes of *C. sinensis* peel (a) untreated, (b) treated with crude oil.

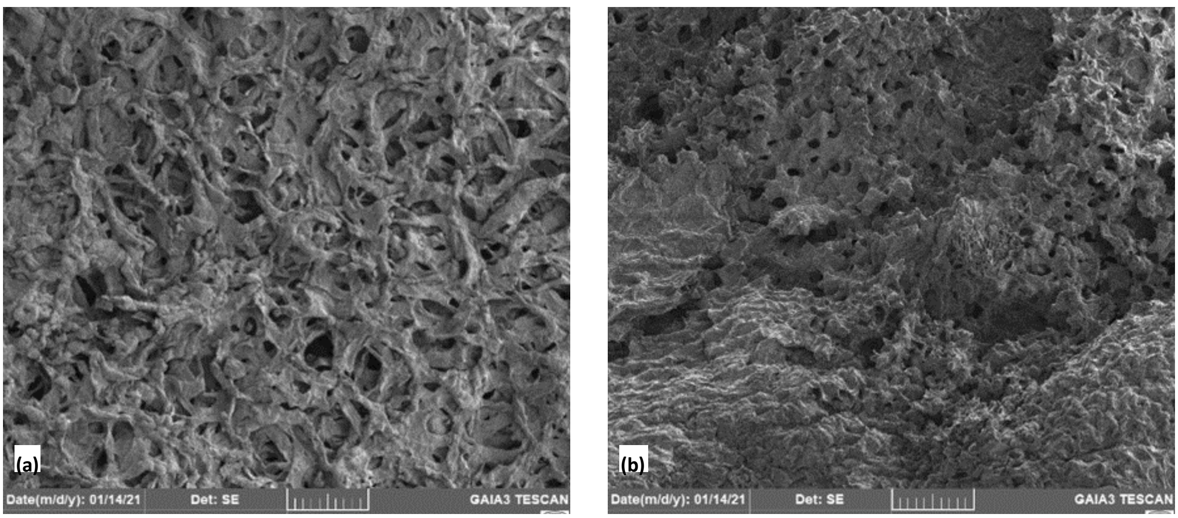

Figure 8. FIB-SEM images of *C. sinensis* peel (a) untreated with crude oil, (b) treated with crude oil.

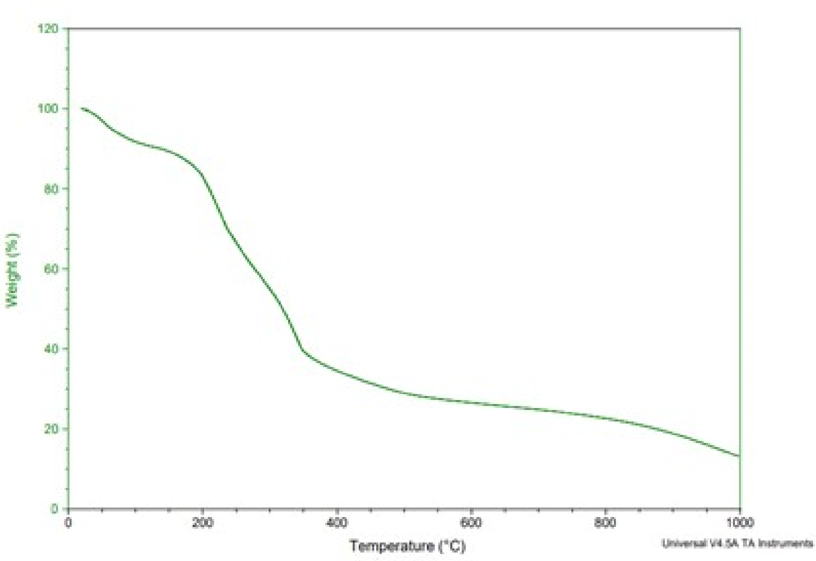

Figure 9. Thermogravimetric analyzes of *C. sinensis* peel.

In this study, degradation profile of the sorbent was investigated with TGA-DTA device by means of the mass loss of *C. sinensis* peel as a function of temperature [9]. Thermokinetic profile of dried *C. sinensis* peels revealed three phases of degradation. The initial weight loss took place at 0 ˚C to 150˚C (~10%) corresponded to the dehydration of weakly bonded water molecules on the peel surface [6, 12]. The second weight loss (~40%) was observed between 150-350˚C and mainly related to the dehydration, decomposition of glucose linkages, cellulosic materials and depolymerization reactions [2, 9, 50]. Lastly, the third weight loss was occurred between 350-1000˚C and even at 1000 ˚C resulting as volatilization [50]. The residual mass was found as 17.5% at 1000˚C (Figure 9). Considering that the adsorption of crude oil is carried out at room temperature, as stated in the literature, the data obtained from the TGA results show that *C. sinensis* peel can be used effectively in crude oil sorption [12].

Kinetic study

To investigate the biosorption kinetics of crude oil with *C. sinensis* peels, pseudo-first order and pseudo-second order kinetic models were tested. As a result, it was observed that pseudo-second order kinetic model with R^2 =0.8167 was well fitted for crude oil adsorption (Table 1). Similar to this study, pseudo-second order kinetic model was well fitted for oil removal with papyrus reeds [27], *Egeria radiate* shell extract [28], micro-sized polyethylene [4] and chitosan [46]. Kinetic model parameters for this research were shown in Table 1.

Table 1. Kinetic model parameters for crude biosorption with dried Citrus sinensis peels (Initial crude oil concentration: 1%, Adsorbent dose: 0.25 g/50mL, pH: 7.0, Agitation speed:150 rpm, Contact time: 6 h and T: 25°C).

Kinetic model	Parameter
Pseudo-first order	K_1- 0.0087
	R^2- 0.7225
Pseudo-second order	K_2- 0.0086
	R^2- 0.8167

Table 2. Parameters of isotherm models of crude oil adsorption on Citrus sinensis peels (Initial crude oil concentration: 1%, Adsorbent dose: 0.25 g/50 mL, pH: 7.0, Agitation speed:150 rpm, Contact time: 6 h and T: 25°C).

Isotherm model	Parameter
Langmuir	$1/q_{max}$- 0.1954
	KL-0.048
	RL-0.1152-0.9216
	R^2- 0.9403
Freundlich	1/n- 0.9405
	K_F-1.3971
	R^2- 0.42

Biosorption isotherm

Langmuir and Freundlich isotherm models were performed to evaluate the interactions between crude oil and *C. sinensis* peel. According to the results obtained from isotherm analysis, Langmuir isotherm was found as well fitted model for crude oil adsorption with a coefficient of 0.9403 (Table 2) meaning as the adsorption was occurred on to a monolayer surface [7]. Also, R_L values (separation factor) were found as 0.1152 - 0.9216 and is proved the favorability of this biosorption process (Table 2). In literature, crude oil removal with chitosan [46], floating pinewood biochar decorated with coconut oil-derived fatty acids [5], *Egeria radiate* shell extract (ERSE) [28] and stearic acid grafted coconut husk (*Cocos nucifera*) [9] are well fitted Langmuir.

CONCLUSION

Rapid remediation of crude oil, which has a toxic effect on living things even at low concentrations, is of great importance for environmental health. Nowadays, researchers are mainly focused on the adsorption techniques using bio-based adsorbents because of their unique properties as environmentally friendliness, biodegradable and low-cost. So, different fruit peels were evaluated in terms of their biosorption capacities and the most effective waste peel in crude oil biosorption was determined. Then, the main parameters affecting the crude oil adsorption with dried *C. sinensis* peels were also detected. Additionally, it was observed that waste of *C. sinensis* peels can be reused at least 6 times and this is advantageous in terms of waste utilization. Adsorption kinetics and isotherms were also studied, and it was found that crude oil adsorption with *C. sinensis* peels were well fitted with pseudo-second order kinetics and Langmuir isotherm. The surface morphology, functional groups and bond types and thermokinetic profile of this biosorbent were clearly emphasized. As a result, it was concluded that this biosorbent, which is low-cost, environmentally friendly and easily available is very effective in the removal process of crude oil with its applicable structure.

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