



Adsorption of Oil from Industrial Wastewater with *Eucalyptus globulus* Labill. Bark: Optimization Study

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Abstract Oily wastewater is one of the most hazardous contaminants that can hurt the ecosystem. There is an urgent need to adopt an efficient, eco-friendly, and low-cost material to replace the old traditional treatment methods of oily wastewater that were very expensive in addition to their relatively low efficiency. *Eucalyptus* bark is considered one of the materials that are rarely used in this field, although it has the characteristics that qualify it to be a distinguished and promising one. The optimum conditions of using *Eucalyptus globulus* Labill. (Blue gum) bark in the removal of oil from prepared aqueous solutions were concluded before applying in the treatment of real oily industrial wastewater from New Borg El-Arab City, Egypt. The sequential optimization adsorption results were as follows: initial oil concentration, 500 mg/l; adsorbent dosage, 0.5 g/l; pH, 3; exposure time, 45 min; temperature, 20 °C; and shaking rate, 300 rpm. The pretreatment of biomass with H_3PO_4 proved it to be superior in the oil removal process where the efficacy reached 450.69 mg/g, while the unmodified form came second where the adsorption efficacy reached 395.86 mg/g, after that the NaOH-modified form came third by efficacy reached 315.85 mg/g. The results of SEM elucidated this order of efficacy according to the porosity of the bark

surface. FTIR analysis indicated that OH, carboxylic C=O, and carboxylic C-O groups are the contributing groups in the oil adsorption process for the three forms of *Eucalyptus* bark. The reusability of *Eucalyptus* bark using n-hexane for one cycle reached 96.34, 97.13, and 95.83% for unmodified, H-modified, and OH-modified forms, respectively, and for five cycles reached 56.29, 58.01, and 55.81% for unmodified, H-modified, and OH-modified forms, respectively. The application of *Eucalyptus* bark in the H-form in the treatment of real oily wastewater was achieved by efficacy ranging between 91.46 and 96.23% which proves the excellence of *Eucalyptus* bark in the treatment of oily wastewater.

Keywords Adsorption · Bark pretreatment · *Eucalyptus globulus* · New Borg El-Arab City · Oily wastewater

1 Introduction

Like everywhere else in the globe, residential area growth has led to an increase in environmental concerns, foremost among them being environmental pollution (Cetin et al., 2022a). Oil is one of many pollutants that can seriously harm the ecological system. Municipal and industrial establishments are often the main producers of pollution (Bozdogan et al., 2019). Huge quantities of oily effluents are produced from various industries, such as the oil and soap

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industries, which must be removed before the water can be reused for other purposes or discharged into the environment. The percentages of oily pollutants must be less than the permissible stipulated standard limits when liquid wastes are disposed of in the environment because of the harmful effects they can cause on aquatic organisms and human health. Also, the ecosystem is greatly impacted by the alteration in soil quality and vegetation cover brought on by soil contamination with such wastewater (Cetin et al., 2022b and Cetin et al., 2022c). As well as, the drainage system may clog when there is a high level of oil and grease present, which may result in an overflow. Using detergents causes an oil emulsion to occur because they contain surfactants with two ends: a hydrophilic end that clings to water molecules and a hydrophobic end that clings to oil particles. However, the removal of emulsified oil is more difficult due to its stability in the aqueous phase (Hamid et al., 2016, Martini et al., 2020 and Jaber & Alward, 2019).

There are several popular methods for removing oily materials from waterways such as membrane filtration, advanced oxidation, and biological treatment. However, these methods have several disadvantages such as high operating and maintenance costs, toxic sludge generation, and complex procedures. In comparison, adsorption is an effective and economical method (Chai et al., 2015). The process of transferring a molecule from a fluid bulk to a solid surface is known as adsorption. Many factors affect the adsorption process of pollutants (adsorbate) onto biomass (adsorbent) such as pH, contact time, temperature, solid:liquid ratio, and adsorbate concentration. Optimization is using a factor in the greatest or most efficient way possible. The optimization may be reached via two methods; the first is the sequential method where the concluded optimum result of the experiment is applied in the subsequent experiment to reach to the maximum efficacy at the last experiment. The second method is the cumulative method, where all experiments are performed at the same time to obtain the optimum results for each, and an additional last experiment is performed under all the concluded optimum conditions to detect the maximum efficacy.

An important factor in the selection and design of an adsorption process is the adsorbent's cost. In general, adsorbent can be assumed to be "low cost" if it requires little processing and is abundant in nature, or waste material either from industry or agricultural

by-products with almost no economic value. Plant barks are among the foremost widely applied low-cost biomass materials within the study of pollutant removal from aqueous media or wastewater (Ighalo & Adeniyi, 2020). *Eucalyptus* bark has the potential to replace expensive commercial adsorbents at a lower cost because it is readily available, non-hazardous, and reasonably priced, as well as it was found to be an effective sorbent for the removal of some pollutants (Afroze et al., 2016, Ghodbane & Hamdaoui, 2008 and Saliba et al., 2002).

Eucalyptus globulus (also called the blue gum) is a tall, broadleaf, evergreen shrub, known as one of three globally major fast-growing tree species. It is belonging to the Myrtaceae family, well known and widely grown as ornamental and windshield plant. Different parts of this plant are nutritionally very important and therapeutically highly valuable, as the essential oil (EGEO) is extracted from its leaves, buds, branches, and fruits, and exhibits numerous biological properties, such as wound healing, anti-diabetic, antibacterial, anti-inflammatory, and antioxidant. *Eucalyptus* is primarily indigenous to Tunisia and Australia, but it has also been observed in Africa (including Egypt) and the tropical to temperate southern regions of the USA. Bark of *E. globulus* is classified as a by-product and it is currently used as fuel (Liu & Li, 2010, Assaggaf et al., 2022, Hayat et al., 2015, El-Kadi et al., 2000 and Mota et al., 2013). In developed countries, *Eucalyptus* is utilized in the pulp and paper industries as the main fiber resource, in addition to essential oil production, manufactured wood products, and green chemical feedstocks (Seng Hua et al., 2024).

However, the biomass of *Eucalyptus* is efficiently applied to remove several heavy metals and dyes from wastewater and aqueous solutions (Anastopoulos et al., 2022, Zafar et al., 2022, Alshiteewi, 2023 and Samimi, 2024); there are few studies on using this efficient biomass in the adsorption of oily wastewater. This made the goal of the research to deepen the study in removing this pollutant that is difficult to get rid of with this biomass that has not been adequately studied. The exhausted *Eucalyptus* biomass after biosorption processes can be composted and used as a good substrate in greenhouse experiments (de Carvalho et al., 1991).

The objectives of the study were firstly, determining the optimum conditions to adsorb oil from

aqueous solutions via batch sequential method using the bark of *Eucalyptus globulus* trees in its raw form, acidic modified with phosphoric acid and alkali modified with sodium hydroxide; secondly, evaluation the feasibility of the optimum condition application in the treatment of real oily wastewater collected from oil and soap factories in the new Borg El Arab City, Egypt.

2 Material and Methods

2.1 Preparation of *Eucalyptus* Bark Biomass

Eucalyptus globulus Labill. bark was obtained from the silviculture area in Borg El-Arab region in August 2021. The bark was washed thoroughly with distilled water until the clear color of the leachate was obtained, oven-dried at 40 °C for 24 h, crushed, and sieved through a 2-mm sieve.

Acid-modified biomass (H-modified) was prepared according to Patnukao and Pavasant (2008), and *Eucalyptus* bark was impregnated by a ratio (1:1, w:v) into a solution of H_3PO_4 (A.R grade, 85 wt% in H_2O) from Sigma-Aldrich Chemical Company, Germany. The mixture was stirred manually for 3 min at room temperature, and washed by hot distilled water until the pH of the leachate was raised to 7; finally, the product was dried at 105 °C for 4 h.

Alkali-modified biomass (OH-modified) was prepared according to Afroze et al. (2016), and *Eucalyptus* bark was contacted by a ratio (1:10, w:v) with 0.1 M NaOH (ACS reagent, $\geq 97.0\%$, pellets) from Sigma-Aldrich Chemical Company, Germany. The mixture was stirred with a magnetic stirrer for 12 h, filtered, and rinsed with distilled water until the pH of the leachate was reduced to 7; finally, the product was dried at 90 °C for 12 h.

2.2 Adsorption Experiments (Batch Procedures)

An immiscible oil/water mixture (IOWM) was prepared with the desired concentration via the addition of the required weight of commercial food oil to the specific volume of distilled water (w:v), stirred at 200 rpm for about 5 min, then used immediately for batch procedures. A specific weight of bark biomass was shaken with a desired volume of IOWM. The

detailed experimental conditions were shown below each represented data.

Oil concentration was determined gravimetrically according to EPA Method, 1664 (2010) using n-hexane as extractable material (for analysis EMSURE ACS, from Sigma-Aldrich Chemical Company, Germany).

For desorption experiments, the *Eucalyptus* bark was oil-loaded under the concluded optimum conditions and then conducted with 0.1 M solution of three types of eluents: NaHCO_3 , CH_3COOH , and n-hexane. Conditions of adsorption, desorption, and resorption were mentioned in the remarks of each figure.

2.3 Examination of *Eucalyptus* Bark Surface by Scanning Electron Microscopy

The dried *Eucalyptus* bark samples (unmodified, modified, and oil-loaded biomasses) were coated using a gold sputter coater (SPI-Module) that was examined by SEM (JSM-5500 LV, JEOL, Japan) under an accelerating voltage of 18 kV.

2.4 Determination of Functional Groups onto *Eucalyptus* Bark Biomass by Fourier Transform Infrared

Dried *Eucalyptus* bark samples (unmodified, modified, and oil-loaded biomasses) were finely powdered, pressed into KBr pellets, and analyzed by FTIR Spectrophotometer (8201 DC, Shimadzu, Japan) along wavenumber range $400\text{--}4000\text{ cm}^{-1}$.

2.5 Application of Biomasses in the Treatment of Real Oily Wastewater

Ten wastewater samples were collected from oil and soap factories in industrial New Borg El-Arab City, in May 2022. *Eucalyptus* biomasses were conducted to treat oily wastewater samples under the elicited optimum conditions from the batch experiments.

2.6 Calculations and Data Evaluation

2.6.1 Adsorption Equations

The amount of adsorbed oil on adsorbents was calculated according to Ighalo and Adeniyi (2020) and Afroze et al. (2016) via the equation:

$$q = [(C_i - C_f)V]/M$$

where q is the amount of adsorbed oil onto the unit amount of adsorbent (mg/g), C_i is the initial oil concentration (mg/l), C_f is the final oil concentration (mg/l), V is the volume of solution (l), and M is the adsorbent mass (g).

2.6.2 Desorption and Resorption Equations

The amount of desorbed oil from *Eucalyptus* biomasses using NaHCO_3 , CH_3COOH , and n-hexane as eluents was expressed according to Bulgariu and Bulgariu (2014) and Kanwal et al. (2013) via the equation:

$$\text{Desorption \%} = (q_{\text{desorbed}}/q_{\text{adsorbed}}) \times 100$$

The amount of resorbed oil on *Eucalyptus* biomasses was expressed according to Aboulsoud (2008) via the equation:

$$\text{Resorption \%} = (q_{\text{resorbed}}/q_{\text{adsorbed}}) \times 100$$

2.6.3 Real Wastewater Treatment Equation

The amount of removed oil from wastewater was calculated according to Shaaban et al. (2017) via the equation:

$$\text{Removal efficacy (\%)} = [(C_i - C_f)/C_i] \times 100$$

where C_i is the initial oil concentration before treatment, and C_f is the final oil concentration after treatment.

2.6.4 Statistical Analysis

A triplicate of each experiment was subjected to MSTAT-C. Duncan's test was used to analyze data via an analysis of variance (ANOVA) (Waller & Duncan, 1969). At 0.05 significance probability level, means with different alphabetical letters differ significantly.

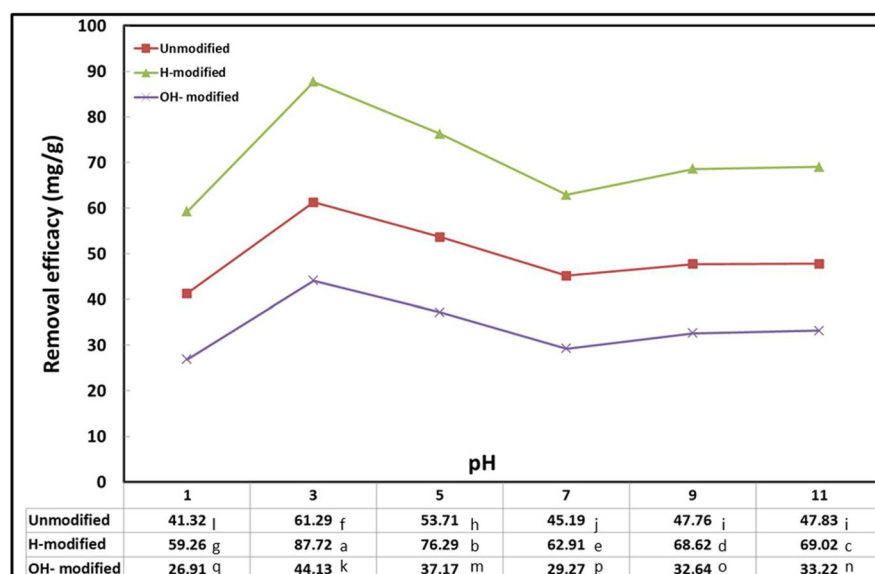
3 Results and Discussion

3.1 Effect of pH

Because variations in pH cause differences in ionization degree and the surface characteristics of the adsorbent, the efficacy of the adsorption process is influenced by pH (Jaber & Alwared, 2019). While maintaining the other parameters constant, pH in the range of 1 to 11 was investigated and the results are shown in Fig. 1.

All *Eucalyptus* bark forms followed the same behavior against pH change. Oil removal efficacy increased from 1 to 3; afterward, the efficacy decreased from pH 5 to 7 to give the lowest significant

Fig. 1 Interaction effect of *Eucalyptus* bark forms with pH (conditions: room temperature, initial oil concentration, 1 g/l; exposure time, 120 min; adsorbent dosage, 10 g/l; shaking rate, 200 rpm)



one. The removal efficacy slightly increased again from pH 9 to 11. The influence of acidic pH media can support de-emulsification and the formation of larger oil droplets, which increased oil adsorption onto the sorbent surface. Conversely, in alkaline media, the saponification process took precedence, where the oil undergoes hydrolysis to produce glycerol and fatty acid salts (soap), which is more soluble in water than in n-hexane. This is evident in the change of water clearance and subsequently resulted in the detection of less oil in the solvent and lower oil removal on the adsorbent. The destabilization of organic sorbent materials in a neutral pH media can be linked to the least significant oil removal efficacy at neutral pH than in acidic or alkaline solutions (Martini et al., 2020 and Ahmad et al., 2005). As concluded from this experiment, an optimum pH of 3 was applied in the subsequent experiments.

3.2 Effect of Exposure Time

One of the most crucial factors for the effective utilization of the *Eucalyptus* bark in a practical application is exposure time. Under constant parameters, different time intervals were conducted and results are shown in Fig. 2. Adsorption occurred in two phases for all bark forms, a primary rapid phase where the oil removal efficacy was greatly increased at a unit time, this phase is observed from 1 to 30 min. It was followed by a secondary slow phase, where the

removal efficacy was regressed to give the equilibrium at 45 min and no tangible increase was observed afterward. The abundance of vacant available binding sites on the adsorbent surface, which makes oil particles and bark more likely to interact, contributed to the rapid initial phase. Due to the hindrance effect between oil particles and each other as well as the limited surface area available for the capture of adsorbate after the equilibrium point, removal efficacy tended to level off (Anifah et al., 2022 and Hamid et al., 2016). As concluded from this experiment, an optimum exposure time of 45 min was applied in the subsequent experiments.

3.3 Effect of Adsorbent Dosage

The assessment of the optimal adsorbent quantity is one of the key elements from an economic perspective. Because it offers the binding sites for oil adsorption, the dosage of the adsorbent has a significant impact on the efficacy of the adsorption process (Jaber & Alward, 2019 and Badawy et al., 2020). To study this parameter, the results were expressed as mg/g and % to detect the highest removal efficacy as well as the saturation level of the adsorbent, respectively (Fig. 3).

While keeping the IOWM volume constant, the *Eucalyptus* bark dosage was inversely proportional to removal efficacy calculated as mg/g while it was directly proportional to removal efficacy calculated

Fig. 2 Interaction effect of *Eucalyptus* bark forms with exposure time (conditions: room temperature, initial oil concentration, 1 g/l; pH, 3; adsorbent dosage, 10 g/l; shaking rate, 200 rpm)

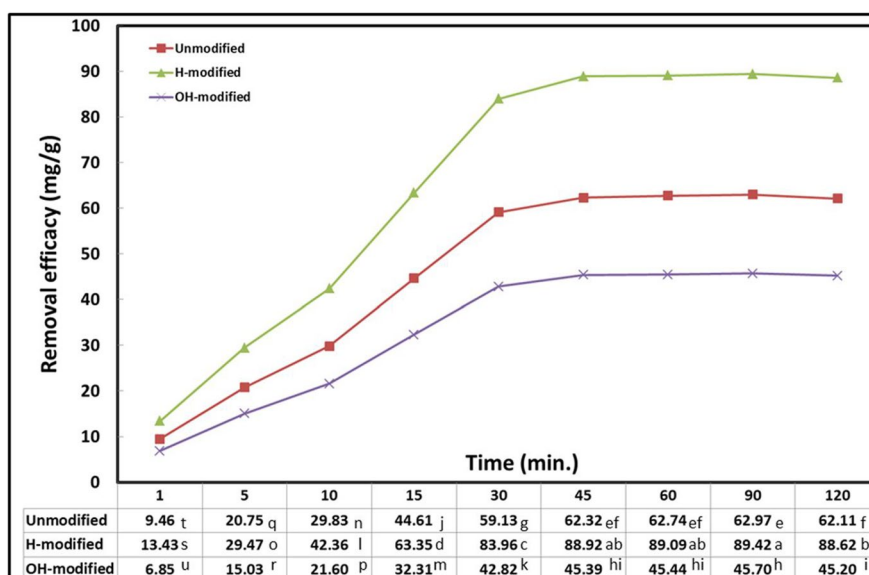
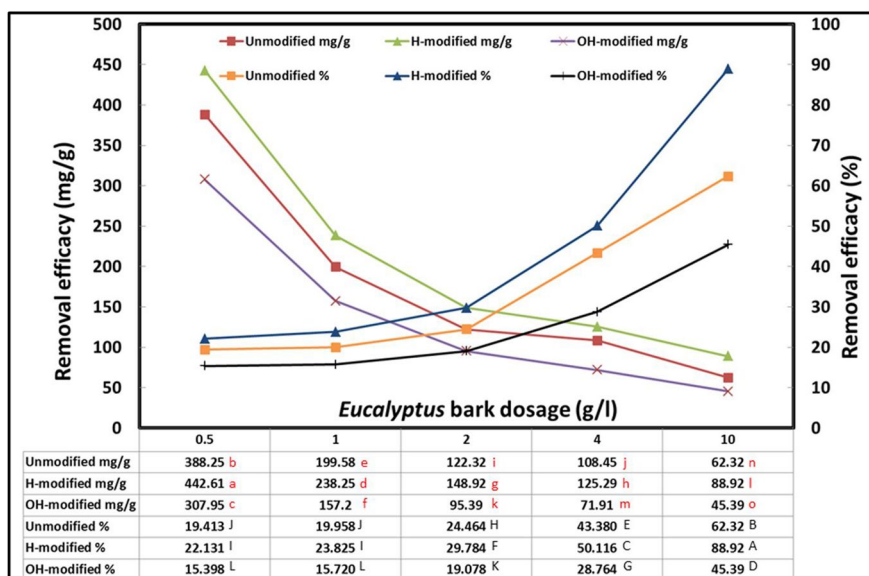


Fig. 3 Interaction effect of *Eucalyptus* bark forms with *Eucalyptus* bark dosage (conditions: room temperature, initial oil concentration, 1 g/l; pH, 3; exposure time, 45 min; shaking rate, 200 rpm). “Remarks: The results expressed in mg/g are referred to by the lowercase statistical letters, while the results expressed in percent are referred to by the uppercase statistical letters”



as % to a certain level where the equilibrium was attained. Decreasing the amount of adsorbent from 10 to 0.5 g was associated with increasing the amount of oil adsorbed per unit mass of *Eucalyptus* bark from 62.32 to 388.25 mg/g for the unmodified form, from 88.92 to 442.61 mg/g for the H-modified form, and from 45.39 to 307.95 mg/g for OH-modified form. On the other hand, this decrease from 10 to 1 g was associated with decreasing the adsorbed % of oil particles from 62.32 to 19.95% for unmodified form, from 88.92 to 23.82% for H-modified form, and from 45.39 to 15.72% for OH-modified form. After that, the decrease was leveled off by decreasing bark dosage to 0.5 g/l and no significant decrease was observed indicating saturation of adsorbent at this ratio. Calculating the efficacy as mg/g referred to the amount of oil adsorbed on the unit mass of *Eucalyptus* bark, so as the bark dosage increased (as the denominator) while the volume was constant (as the numerator) containing a constant number of oil molecules, caused each unit mass to adsorb fewer oil particles. On the other hand, calculating the efficacy as % refers to the saturation of adsorbent binding sites, as an increase in the *Eucalyptus* bark dosage increases the oil adsorption due to an increased surface area and consequently the number of available binding sites (Ingole et al., 2014, Anifah et al., 2022 and Afroze, et al., 2016). As concluded from this experiment, an optimum adsorbent dosage of 0.5 g/l was applied in the subsequent experiments.

3.4 Effect of Initial Adsorbate Concentration

This factor represents the change of adsorbate molecules' number (concentration) while the volume is constant. Conversely, the adsorbent dosage as a factor represents the change in adsorbate volume while the concentration is constant. The initial concentration of adsorbate has a significant impact on the adsorption process, which is crucial for the development of water treatment technology (Afroze, et al., 2016). Different oil concentrations were tested with constant parameters, and the results are shown in Fig. 4. The higher initial oil concentration enhanced the adsorption efficacy until equilibrium was attained at 500 mg/l, at which point there was no significant increase. This is because the solid surfaces of the particles had reached their capacity before adding additional oil content (Jaber & Alwared, 2019). The highest significant efficacies were as follows: 444.13, 389.87, and 308.59 mg/g for H-modified, unmodified, and OH-modified forms, respectively. As concluded from this experiment, an optimum initial oil concentration of 500 mg/l was applied in the subsequent experiments.

3.5 Effect of Temperature

In the range of 20–60 °C, the effect of temperature on the oil adsorption process was investigated, and the results are shown in Fig. 5. Slight decline in oil adsorption was witnessed by temperature elevation

Fig. 4 Interaction effect of *Eucalyptus* bark forms with oil concentration (conditions: room temperature, adsorbent dosage, 0.5 g/l; pH, 3; exposure time, 45 min; shaking rate, 200 rpm)

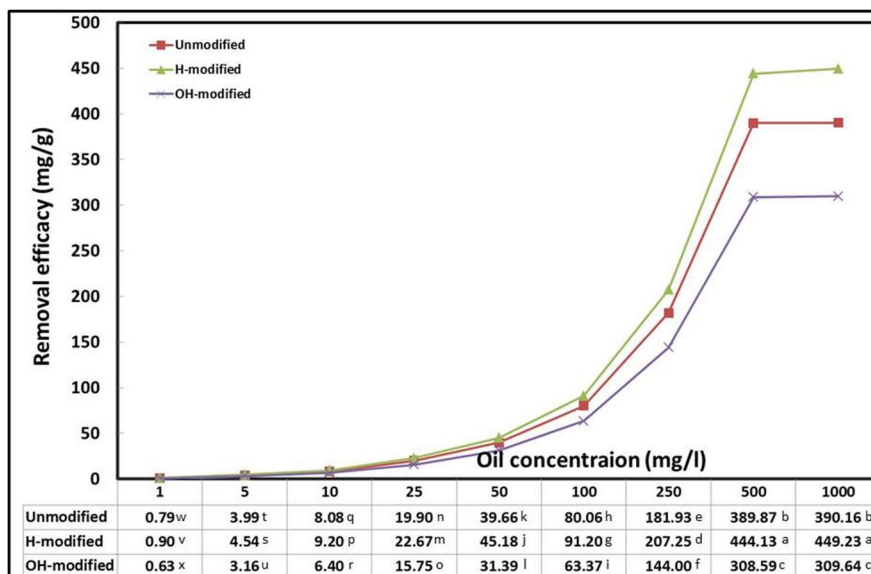
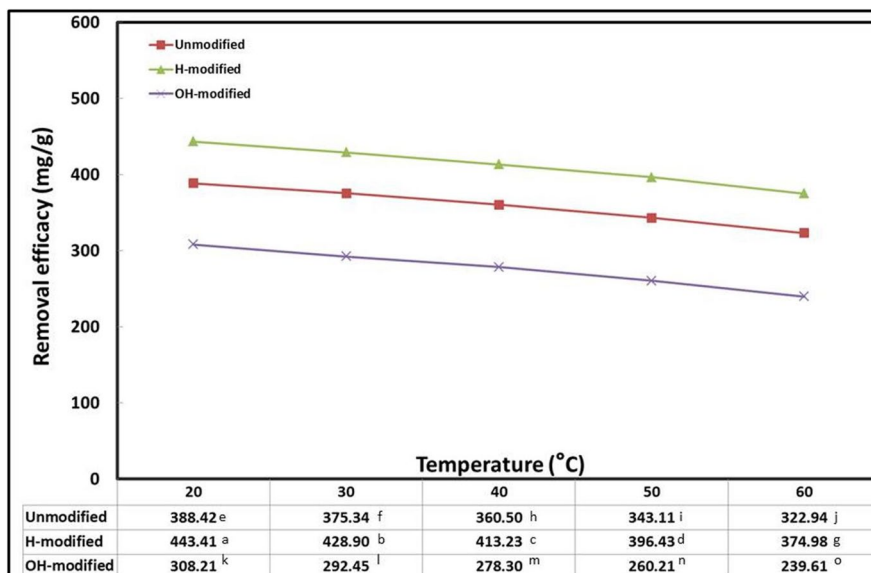


Fig. 5 Interaction effect of *Eucalyptus* bark forms with temperature (conditions: initial oil concentration, 500 mg/l; adsorbent dosage, 0.5 g/l; pH, 3; exposure time, 45 min; shaking rate, 200 rpm)



from 20 to 40 °C, and the oil adsorption keeps on diminishing discernibly by temperature elevation to 60 °C. This decreasing trend in oil adsorption can be attributed to several factors, including the lower viscosity of IOWM solution, the increase in the random motion of oil molecules suspended in water that is known as Brownian motion, which reduces their entrapment on the sorbent surface, and the increased energy required to attach oil particles. The decrease in adsorption efficacy by increasing temperature means *Eucalyptus* bark particles acted as exothermic

adsorbent (Wahi et al., 2014, Alaa El-Din et al., 2018, Jaber & Alwared, 2019 and Martini et al., 2020). As concluded from this experiment, an optimum initial oil concentration of 20 °C was applied in the subsequent experiments.

3.6 Effect of Shaking Rate

Because it affects the likelihood of binding to sorbent binding sites and controls the mobility of sorbate ions, the shaking rate can promote the sorption

process (Badawy et al., 2020). As shown in Fig. 6, the adsorption efficacy was directly proportional to the shaking rate. The highest significant adsorption efficacy was attained at the highest shaking rate (300 rpm). Higher stirring speed acts to increase the mass transfer rate and mobility of adsorbent particles and conversely acts to decrease the surface layer resistance, thus acts to increase the adsorption efficacy of the oil (Lin & Liu, 2000, Garba et al., 2016, and Ahmad et al., 2005). As concluded from this experiment, an optimum shaking rate of 300 rpm was applied in the subsequent experiments.

3.7 Effect of Modification Agent

The results of the aforementioned experiments proved that the H-form of *Eucalyptus* bark is a portentous biological tool able to adsorb oil substances by efficacy reached 450.69 mg/g under the optimum conditions of initial oil concentration, 500 mg/l; adsorbent dosage, 0.5 g/l; pH, 3; exposure time, 45 min; temperature, 20 °C; and shaking rate, 300 rpm. The unmodified form comes second where the adsorption efficacy reached 395.86 mg/g, after that the OH-modified form comes third by efficacy reaching 315.85 mg/g.

H_3PO_4 is a dependable and effective dehydrating agent that may encourage more cross-linked structure development and enhance the fibrous structure of raw organic materials, which stimulates the creation of pores and consequently expand the biomass structure

which is essential for adsorption capacity. Moreover, functional surface group dissociation in an acidic medium contributes to an increase in charge densities. Oppositely, NaOH promotes the saponification of oil particles which decreases the oil adsorption on the bark surface (Daaou & Bendedouch, 2012, Yorgun & Yıldız, 2015, Ahmad et al., 2005 and Souza et al., 2016).

3.8 Reusability of Adsorbent

The adsorbent should be able to perform a large number of cycles of adsorption, desorption, and resorption to make the process more cost-effective and to secure the safe disposal of sorbent after exhaustion. The adsorbent mass and desorbent solution can both be reused, which makes it possible to use them in continuous systems in industrial processes (Shaaban et al., 2017).

Three types of eluents (0.1 M) are examined as alkali, acid, and solvent those are $NaHCO_3$, CH_3COOH , and n-hexane, respectively. The adsorption and resorption processes were conducted under the previously concluded optimum conditions. The highest significant desorption and resorption efficacies were achieved in case of n-hexane followed by $NaHCO_3$ then CH_3COOH (Fig. 7). This result can be attributed to the type of eluent, as n-hexane is an organic solvent can extract the oil from *Eucalyptus* bark surface, while $NaHCO_3$ as an alkali acts to

Fig. 6 Interaction effect of *Eucalyptus* bark forms with shaking rate (conditions: initial oil concentration, 500 mg/l; adsorbent dosage, 0.5 g/l; pH, 3; exposure time, 45 min; temperature, 20 °C)

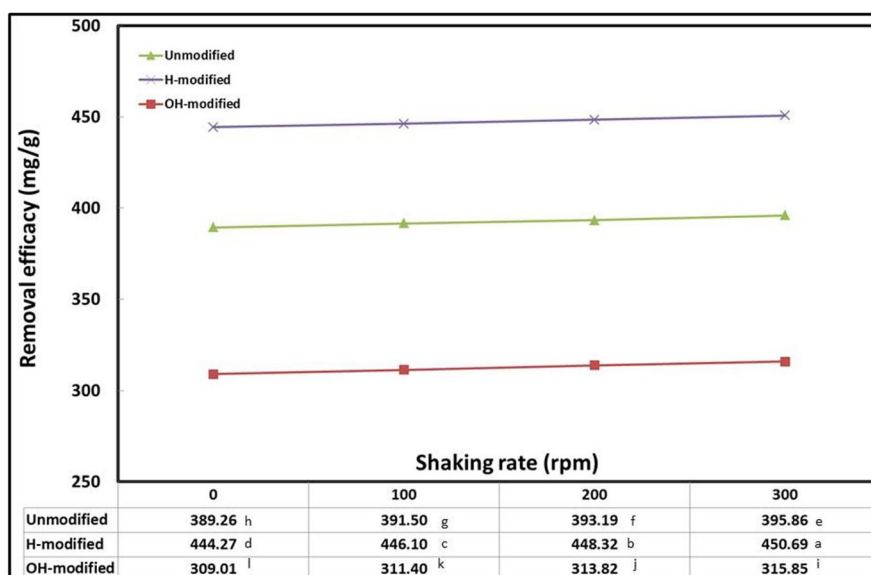
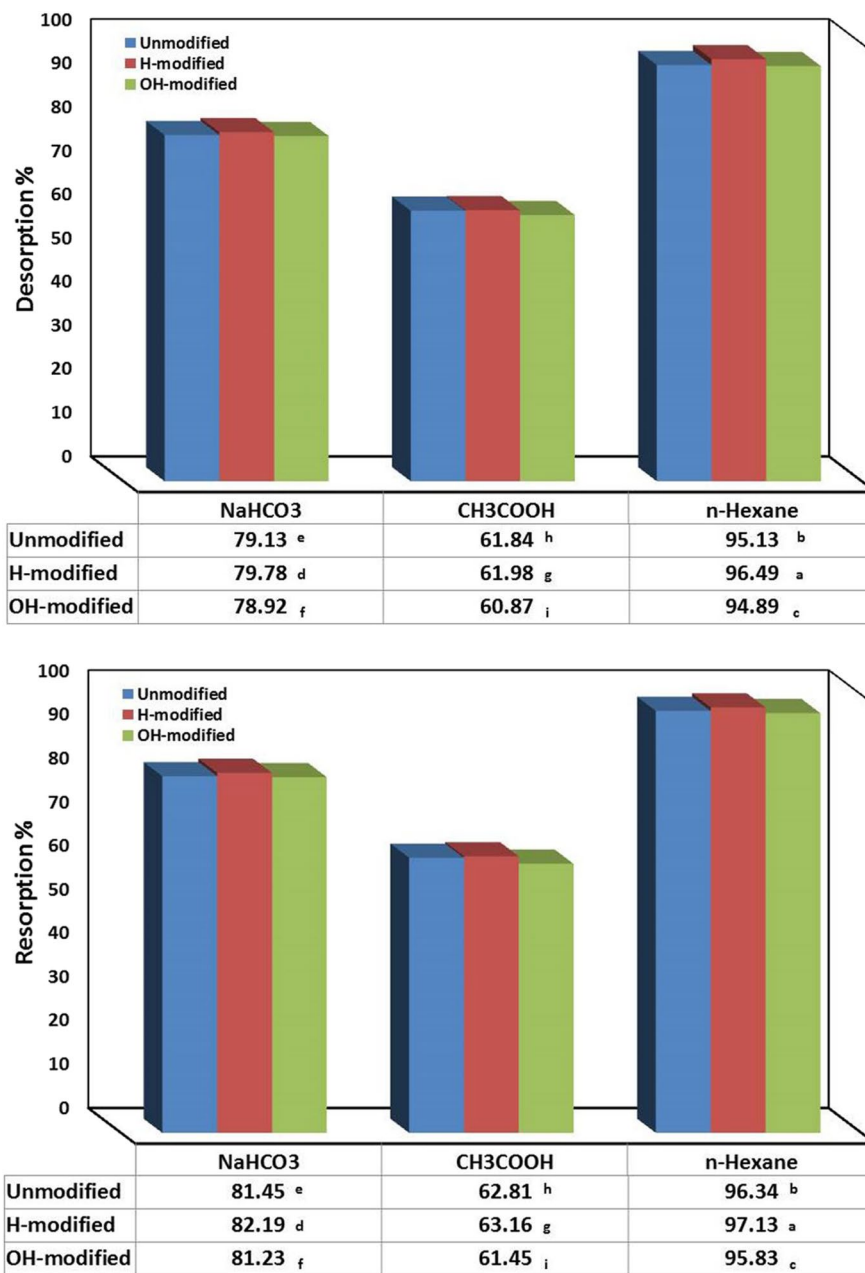


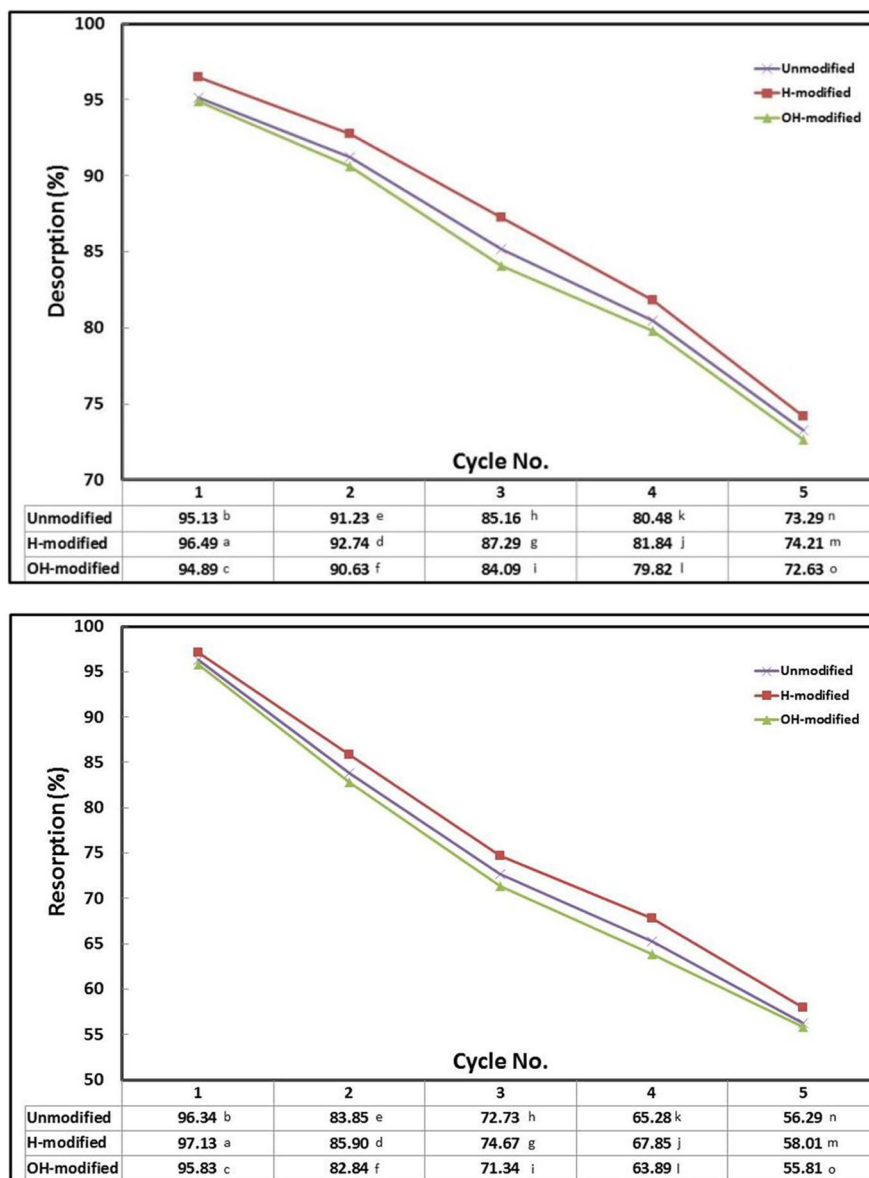
Fig. 7 Desorption and resorption efficacies of oil onto *Eucalyptus* bark forms for one cycle. (Conditions of adsorption and resorption: initial oil concentration, 500 mg/l; adsorbent dosage, 0.5 g/l; pH, 3; exposure time, 45 min; temperature, 20 °C; shaking rate, 300 rpm). (Conditions of desorption: eluent concentration, 0.1 M; adsorbent dosage, 1 g/100 ml; exposure time, 45 min; temperature, 20 °C; shaking rate, 300 rpm)



enhance saponification process where the oil undergoes hydrolysis to produce glycerol and fatty acid salts (soap) and these compounds cannot be separated from the eluent, conversely CH₃COOH as an acid support de-emulsification and the formation of larger oil droplets that makes its elution from bark surface is more difficult (Ahmad et al., 2005 and Martini et al., 2020).

The reusability of *Eucalyptus* bark biomass was examined by using 0.1 M n-hexane for five cycles of desorption and resorption (Fig. 8). Both the desorption and resorption efficacies decreased with increasing cycle numbers. A potential reason can be credited to the unfavorable impact of the eluent on the biomass binding sites. Additionally, in each cycle, the accumulation of remaining oil molecules within the

Fig. 8 Desorption and resorption efficacies of oil onto *Eucalyptus* bark forms for five cycles using n-hexane. (Conditions of adsorption and resorption: initial oil concentration, 500 mg/l; adsorbent dosage, 0.5 g/l; pH, 3; exposure time, 45 min; temperature, 20 °C; shaking rate, 300 rpm). (Conditions of desorption: eluent concentration, 0.1 M; adsorbent dosage, 1 g/100 ml; exposure time, 45 min; temperature, 20 °C; shaking rate, 300 rpm)



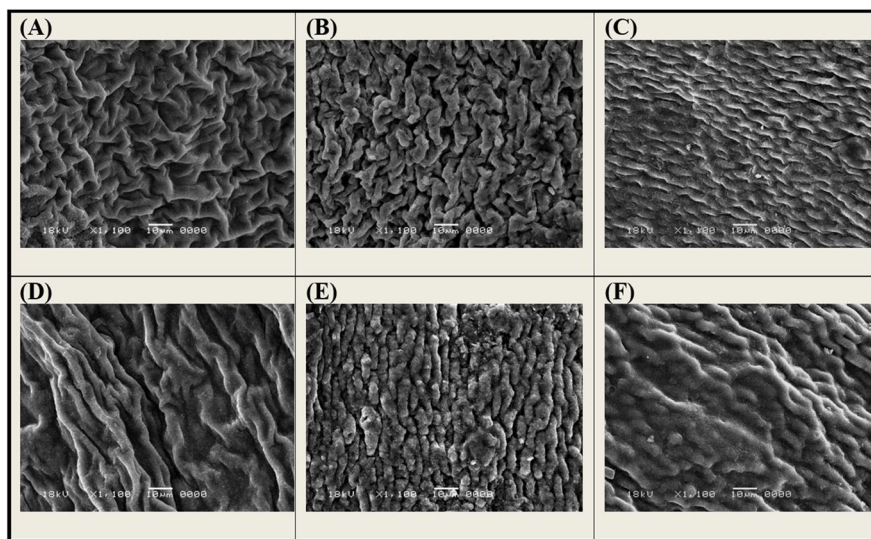
biomass reduces the efficacy of subsequent resorption (Tüzün et al., 2005).

3.9 Examination of *Eucalyptus* Bark Surface by Scanning Electron Microscopy (SEM)

SEM was used to study the morphology of *Eucalyptus* bark biomass and micrographs presented in Fig. 9. The naturally unmodified biomass contains plenty of pores that are required for oil trapped in the interior surface of the biomass (Martini et al., 2020). The biomass surface was changed due to H_3PO_4 and

NaOH modification as well as oil adsorption on these three forms. The H-modified form has a more porous and irregular structure than the unmodified one. Meanwhile, the OH-modified form surface appears smoother and fewer pores are observed. The porous and wrinkled structures provide a more specific surface area available for oil adsorption (Afroze et al., 2016). This finding may interpret the superior efficacy of the H-modified form more than the unmodified and the OH-modified form comes third. Oil adsorption onto *Eucalyptus* forms causes some morphological changes such as a thick cell wall, surface

Fig. 9 The SEM micrographs (at $\times 1100$ magnification) of the surfaces of *Eucalyptus* bark forms before and after oil adsorption; **A** unmodified form, **B** H-modified form, **C** OH-modified form, **D** unmodified oil-loaded form, **E** H-modified oil-loaded form, **F** OH-modified oil-loaded form. (Oil adsorption conditions: initial oil concentration, 500 mg/l; adsorbent dosage, 0.5 g/l; pH, 3; exposure time, 45 min; temperature, 20 °C; shaking rate, 300 rpm)



lumps appearing and oil seeming to cover the texture; this may be attributed to the strong affinity and cross-linking between the oil particles and the active groups in the matrix of the cell wall (Mansour et al., 2017).

3.9.1 Determination of Functional Groups onto *Eucalyptus* Bark Biomass by Fourier Transform Infrared

Different forms of *Eucalyptus* bark under investigation are subjected to FTIR analysis to identify the various groups involved in the oil adsorption process (Table 1). The transmittance bands were referred to according to Liu (2021). The unmodified form was considered as control. Several peaks were observed demonstrating that the surface of *Eucalyptus* bark is made up of a variety of functional groups. Only the

peaks of contributed groups were focused on and discussed. The peaks were corresponding to the hydroxyl group (OH) at 3313.5 cm^{-1} , C=O in the carboxyl group at 1619.5 cm^{-1} , C-O in the carboxyl group at 1415.9 cm^{-1} , nitro group (N=O) at 1316.9 cm^{-1} , and C-O in the alcoholic group at 1032.3 cm^{-1} .

The H-modified form exhibited band shifts to higher wavenumber for carboxylic C=O and alcoholic C-O groups; meanwhile, band shifts to lower wavenumber were detected for OH, carboxylic C-O, and N=O groups. A newly developed broadband at $1100\text{--}1300\text{ cm}^{-1}$ for phosphorus compounds due to H_3PO_4 treatment was detected (Puziy et al., 2002 and Yakout & El-Deen, 2016).

The OH-modified form exhibited shifts to higher wavenumber for N=O and alcoholic C-O groups; similar results were detected by Afroze et al. (2016). Oppositely, a band shift to a lower wavenumber was

Table 1 FTIR frequencies for *Eucalyptus* bark forms before and after oil adsorption

<i>Eucalyptus</i> bark forms	Wavenumber (cm^{-1})					
	OH	C=O carboxylic	C-O carboxylic	N=O	C-O alcoholic	P
Unmodified	3313.5	1619.5	1415.9	1316.9	1032.3	-
H-modified	3150.3	1710.3	1216.3	1218.1	1124.5	1100–1300
OH-modified	3315.8	1610.3	1416.9	1421.4	1154.7	-
Unmodified oil-loaded	3332.4	1634.8	1407.5	1317.3	1034.2	-
H-modified oil-loaded	3173.9	1727.6	1208.4	1219.5	1123.6	1100–1300
OH-modified oil-loaded	3337.1	1627.1	1409.1	1422.7	1155.4	-

Oil adsorption conditions: initial oil concentration, 500 mg/l; adsorbent dosage, 0.5 g/l; pH, 3; exposure time, 45 min; temperature, 20 °C; shaking rate, 300 rpm

detected for the carboxylic C=O group. No change was detected in bands corresponding to OH and carboxylic C-O groups.

Regarding the oil-loaded forms, band shifts to higher wavenumbers were exhibited for OH and carboxylic C=O groups; conversely, band shifts to lower wavenumbers were exhibited for the carboxylic C-O group. No change was detected in bands of N=O, alcoholic C-O, and P.

Hence, OH, carboxylic C=O and carboxylic C-O groups are the contributing ones in the oil adsorption process for the three forms of *Eucalyptus* bark under study.

3.9.2 Comparative Evaluation of *Eucalyptus* Bark Maximum Oil Removal Efficacy with Other Sorbent Tools

The H-form of *Eucalyptus* bark in the current study was superior to many other sorbent materials in the removal of oily substances, where its removal efficacy reached 450.69 mg/g. For example, Moi et al. (2020) used the corn cob carbon to remove the emulsified oil from wastewater and achieved an efficacy of 17.1 mg/g. A relatively higher efficacy was recorded by Anifah et al. (2022) where the sewage sludge was used to prepare an activated carbon that was able to remove oil and grease from restaurant wastewater by efficacy reached 63.75 mg/g. Recently, Alatabe et al. (2023) used the sedge cane grass for oil adsorption from wastewater; the maximum removal efficacy was 137.40 mg/g.

3.9.3 Treatment of Real Oily Industrial Wastewater from New Borg El-Arab City

Depending on oil concentrations, five of the ten collected wastewater samples from New Borg El-Arab City were chosen to be treated using the H-form of *Eucalyptus* bark under the optimum extrapolated conditions. According to the Egyptian Environment Law No. 4 of 1994 (amended in Law No. 9 of 2009), the quality of wastewater samples before and after treatment was evaluated, where oil and grease concentration must be less than 15 mg/l (Table 2). As expected, the wastewater of oil factories contains higher oil concentrations than soap ones. Oil concentrations ranged between 18.37 and 41.42 mg/l. The removal efficacy ranged between 91.46 and 96.23% which proves the

Table 2 Oil concentrations in wastewater of New Borg El-Arab City before and after treatment using *Eucalyptus* bark H-form

Sample No	Factory activity	Oil concentration (mg/l)		Removal efficacy (%)
		Before	After	
1	Oil	33.40	1.26	96.23
2	Oil	25.87	2.21	91.46
3	Oil	41.42	3.12	92.47
4	Soap	18.37	0.92	94.99
5	Soap	21.81	1.35	93.81

Adsorption conditions: adsorbent dosage, 0.5 g/l; pH, 3; exposure time, 45 min; temperature, 20 °C; shaking rate, 300 rpm

excellence of *Eucalyptus* bark in the treatment of oily wastewater.

4 Conclusions

As a specialized study that does not have many references and it has not been studied in depth before, the *Eucalyptus* bark biomass demonstrated promising findings in the treatment of oily wastewater. Moreover, it is a naturalistic, cheap, obtainable, reusable, and environmentally consonant tool. The optimization results were as follows: initial oil concentration, 500 mg/l; adsorbent dosage, 0.5 g/l; pH, 3; exposure time, 45 min; temperature, 20 °C; and shaking rate: 300 rpm. *Eucalyptus* bark biomass's ability to be reused ensures environmental preservation when disposed of after use. Pretreatment of biomass with H₃PO₄ showed higher significant results, while the raw biomass can be used also with reasonable efficacy in case of the requirements of saving time and cost. *Eucalyptus* bark surface is rich in many functional groups that make it a potential tool for other pollutant removal.

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Data Availability Datasets generated during the current study are available from the corresponding author on reasonable request.

Declarations

Competing Interests The author declares no competing interests.

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