

**Egyptian Journal of Chemistry** 

http://ejchem.journals.ekb.eg/



# Biosorption of Oil From Wastewaters By A New Modified Chitosan/Cellulose@Agarose Composite



Mustafa A. Ghazal<sup>b</sup>; Manal G. Mahmoud<sup>b</sup>\*; Ismail Abed<sup>a</sup>; Ehsan Abu El-khir<sup>b</sup>;

Mamdouh A. Fahmy<sup>b</sup>;Laila A. Mohamed<sup>b</sup> and Alaa E. Ali<sup>a</sup>

a Chemistry department, Faculty of Science, Damanhour university, Damanhour, Egypt b Marine Chemistry lab., National Institute of Oceanography and Fisheries, Cairo, Egypt

#### Abstract

A new chitosan/cellulose@agarose composite (CS/CA@AG) was synthesized and thoroughly characterized using FTIR, TGA, XRD, SEM, and BET techniques for efficiently removing oil from wastewater through adsorptive processes. The study investigated at how the adsorption process is affected by a number of variables, such as contact time, pH, initial concentration of oil, dose of adsorbent, agitation rate, and temperature. Kinetic, equilibrium, and thermodynamic models were analyzed. Maximum oil adsorption occurred at pH 8, and for the kinetic data, the pseudo-second-order model provided the best description. The equilibrium data fit to both the Langmuir and Freundlich models, with a maximum adsorption capacity of 7142.86 mg/g. These results indicate that the biocomposite represents a promising, eco-friendly, and economically viable method of oil removal from wastewater.

Keywords: Modified Chitosan; Bioadsorbent; Oil Remediation; Kinetic and Equilibrium Model.

# 1. Introduction

In recent years, managing water pollution and ensuring access to clean water have emerged as critical environmental challenges [1-5]. Oil production, a vital component of numerous global industries [6] has led to significant environmental concerns due to oil spills. These spills often result from routine shipping operations, industrial runoff, or improper disposal practices, leading to serious ecological, economic, and social consequences [7]. Consequently, developing effective methods to remove oil spills from water surfaces has become an urgent priority for protecting marine environments [8]. Egyptian Environmental Law 4 regulates the management of hazardous substances and wastes. According to Egyptian Environmental Law 4/94, discharge into the marine environment within 500 meters or more of the coastline. Additionally, it prohibits discharge into fishing grounds, bathing areas, and nature reserves, where the maximum permitted oil and grease discharge is 15 mg/L [9]. Several treatment technologies have been employed to remove oil contaminants, including membrane filtration, oxidation, chemical flocculation, and biological treatments [10-12]. Among these, adsorption has proven to be a crucial method for addressing oil spills. Effective removal of hydrocarbons from soil and surface water is essential to prevent groundwater contamination and mitigate environmental damage. Any residual crude oil in the soil can serve as a persistent source of pollution.

Utilizing sustainable materials, such as natural polymers, offers significant advantages due to their high adsorption capacity, biodegradability, and cost-effectiveness. Cellulose, chitosan, and agarose are well-known biopolymers, with chitosan and cellulose being the most abundant on Earth [13,14]. These materials are natural, renewable, environmentally friendly, non-toxic, biodegradable, and biocompatible. Combining chitosan, cellulose, and agarose can produce biocomposites with enhanced properties, including bioactivity and high mechanical strength, attributed to particular the interactions between the polymers.

The principal aim of this investigation is to achieve a novel biosorbent for oil remediation in wastewater by blending chitosan with cellulose acetate and agarose (CS/CA@AG). FTIR, TGA, XRD, SEM, and BET techniques were employed to thoroughly describe the biosorbent, and batch experiments were used to examine the variables that affect oil adsorption, including pH, contact time, initial concentration of oil, and temperature. The adsorption process was evaluated using kinetic and isotherm models. Additionally, real wastewater applications were explored, including diesel engine oil, bilge tank oil collected from Petroleum Marine Services Company, and crude oil samples from Arab Petroleum Pipelines Co. in Alexandria, Egypt.

## 2. Materials and Methods

#### 2.1.Chemicals and Reagents

Chitosan High Molecular weight, deacetylation: 82.4%, (Alpha Chemika Co., India), Cellulose Acetate (VWR Chemicals BDH PROLABO®, England), Agarose (Vivantis Inc., USA), Dichloro methane HPLC Grade (ADVENT CHEMBIO PVT. LTD®, India), sodium sulphate anhydrous (HIMDIA, India). Glacial acetic acid (Loba Chemie Pvt. Ltd, Mumbai, India). Egypt KU Crude oil (density= 0.8752 g/mol) was obtained from SUMED Co. (Egypt). High Performance Gasoline Engine Oil (MISR SUPER 10000) (SAE viscosity grade: 20W / 50 & performance level: API SJ

\*Corresponding author e-mail: <u>manalgom@yahoo.com</u> (Manal G. Mahmoud)

Receive Date: 01 December 2024, Revise Date: 18 December 2024, Accept Date: 24 December 2024

DOI: 10.21608/ejchem.2024.340850.10915

<sup>©2024</sup> National Information and Documentation Center (NIDOC)

/ CF) obtained from MISR Petroleum CO. Cairo, Egypt. Additional chemical materials of analytical grade were employed in this study.

# 2.2. Preparation of composite (chitosan, cellulose acetate and agarose (CS/CA@AG)

1.0% weight/volume chitosan (CS) solution was prepared by dissolving 1.0 g of CS in 100 ml of 2% acetic acid with stirring continuously at 55°C. Subsequently, 10.0% cellulose acetate (CA) solution was prepared by dissolving 1.0 g of CA in 10.0 ml of glacial acetic acid. The CA solution was then slowly added dropwise to the CS solution with vigorous stirring at 55°C for 30 minutes. In parallel, 1.0% agarose (AG) solution was created by dissolving 1.0 g of AG in 100 ml of distilled water. The AG solution was then added dropwise to the CS/CA mixture solution with stirring continuously at 60°C for 4 hours. Distilled water was utilized to repeatedly wash the resultant homogenous CS/CA@AG mixture solution till the pH was neutral. Subsequently, the solution was spread on a clean, flat glass surface and airdried in a fume hood at room temperature for 48 hours to form the CS/CA@AG film, which was stored in a clear glass container for future use.

#### 2.3. Batch adsorption experiment

Crude oil adsorption on the composites is influenced by a number of factors. To increase the adsorption effectiveness of each composite, the adsorption process was optimised by adjusting factors such pH, time of contact, initial crude oil concentration, temperature, dose, and agitation rate. The optimization experiments were conducted sequentially as per the details in Table (1), while maintaining other parameters constant.

For the batch adsorption experiments, a reaction mixture was prepared by adding 0.030 g of the CS/CA@AG composite to 50 ml of 400 ppm crude oil at pH 8 in a digital laboratory orbital shaker (Unimax 1010). The composite films were removed, and any non-adsorbed residual oil was transferred to a separating funnel. Dichloromethane (DCM) solvent was gradually added to extract the oil, with this extraction process being repeated three times using the same volume of DCM to enhance extraction efficiency.

 Table 1: Variable range for batch experiments of crude
 oil adsorption on the CS/CA@AG composite

Adsorption parameters	Ranges
pH	1 - 12
Contact time (min) at oil	
concentration :	
200 mg/L	10 - 120
400 mg/L	10 - 120
800 mg/L	10 - 120
Effect of initial crude oil	100 5000
concentration (mg/L)	100 - 3000
Adsorbent dose (g/l) at	
oil concentration:	
400 mg/L	0.20 - 2.00
1200 mg/L	0.10 - 4.00
Agitation rate (rpm)	80 - 300
Temperature (°C)	20 - 65

The combined extracted oil was filtered over anhydrous sodium sulfate. Subsequently, the oil dissolved in DCM was collected and made up to a total volume of 50 ml. The concentration of the extracted oil was recorded using a

Egypt. J. Chem. 67, SI: M. R. Mahran (2024)

UV/visible spectrophotometer at a wavelength of 450 nm. Equation (1) was used to determine the percentage of crude oil removal as follows:

$$%Removal = \frac{C_{\circ} - C}{C_{\circ}} \times 100 \quad (1)$$

Where,  $C_o$  represents the initial oil concentration and C represents the oil concentration at time (t) and both in mg/l. Computing the adsorption capacity q (mg/g) at time (t) was by applying the mass balance equation (2):

$$q = \frac{(C_o - C)V}{m}$$
(2)

Where, V is the volume of the solution given by liters and m is the mass in g.

#### 3. Results and Discussion

# 3.1. Synthesis and characterization 3.1.1. FT-IR spectra

The FT-IR spectra of the composite films comprising chitosan, cellulose, and agarose displayed distinct peaks indicative of their molecular characteristics (Figure 1). A broad absorption band observed between 3580 and 3120 cm<sup>-1</sup> is attributable to the stretching vibrations of –OH and –NH groups [15,16]. Peaks at 2931 and 2131 cm<sup>-1</sup> correspond to C–H stretching vibrations. The spectrum also reveals a strong peak at 1742 cm<sup>-1</sup>, which relates to carbonyl groups (C=O). Additionally, a shoulder peak at 1160 cm<sup>-1</sup> is attributed to CH<sub>2</sub> rocking vibrations. Medium peaks at 1384 and 1160 cm<sup>-1</sup> arise from CH<sub>2</sub> wagging vibrations and CCN asymmetric stretching, respectively [17].



Figure1: FTIR spectrum of CS/CA@AG composite

#### 3.1.2. The X-ray diffraction

The recorded XRD diffraction was applied for investigation of the physical properties, composition and structure. The XRD profile of the CS/CA@AG biopolymer showed a broad peak at approximately  $2\theta$  of  $21^{\circ}$  in Figure 2, indicating low crystallinity and the existence of an amorphous phase in the biopolymers. The XRD peaks at  $2\theta$  of  $17.5^{\circ}$ ,  $22.9^{\circ}$  and  $32.5^{\circ}$  designated the crystalline plane of cellulose. Additionally, when AG was added to CS, the peak intensity that corresponded to pure chitosan decreased.

### 3.1.3. Thermal Analysis (TGA and DTA)

The thermal decomposition behavior of the CS/CA@AG composite is depicted in Figure 3, which showcases the overlapping features of cellulose, chitosan, and agarose. The initial stage, occurring from ambient temperature to 200 °C, is attributed to moisture evaporation. The thermogravimetric

(TG) curves reveal a decomposition temperature around 283°C associated with chitosan, while broader decomposition occurs between 290 394°C. and corresponding to cellulose and agarose. The final stage, above 500°C, is associated with the decomposition of lignin and other organic materials. The differential thermal analysis (DTA) curve (Figure 4) shows an exothermic peak at 48-63°C, attributed to the expulsion of water molecules from the polymeric matrix. A broad exothermic peak between 100 and 600°C corresponds to the successive decomposition of the main hydrocarbon chains within the polymeric composite.



Figure 2: X-ray diffraction analysis of CS/CA@AG



Figure 3: TGA Thermogram of Composite CS/CA@AG.



CS/CA@AG

Table2: Surface area parameters for CS/CA@AG composite

#### BET BJH Langmuir Mean pore monolayer volume Mesopore Adsorbent diameter Mesopore radius Total pore $SSA m^2 g^{-1}$ volume cm<sup>3</sup> STP g<sup>-1</sup> volume cm<sup>3</sup>g<sup>-1</sup> (nm)nm $cm^3 g^{-1}$ CS/CA@AG 5.7473 0.1853 0.1916 25.015 29.624 1.66

#### Egypt. J. Chem. 67, SI: M. R. Mahran (2024)

#### 3.1.4. Scanning electron microscopy (SEM)

The images of SEM for the CS/CA@AG composite before and after the oil adsorption process are presented in Figure 5a&b. The adsorbent exhibits heterogeneity characterized by rough, irregular surfaces and pronounced pores, including hollow tubes that improve the area of contact and facilitate oil molecule adsorption. After oil adsorption, the adsorbent surfaces appeared more coarse and sticky (Figure 5b).



Figiure 5: SEM surface images of CS/CA@AG before (a) and after (b) oil adsorption

### 3.1.5. Surface area and porosity BET

The N<sub>2</sub> adsorption-desorption isotherms at 77 K for the CS/CA@AG biopolymer are shown in Figure 6a. The N<sub>2</sub> adsorption-desorption isotherm conforms to a type IV classification, indicating the presence of a mesoporous structure [18]. According to IUPAC classification, the pore diameter ranges from 2 to 50 nm. A summary of the computed parameters, such BET surface area, total pore volume, and average pore diameter provides in Table 2. The experimentally determined pore diameter was 29.62 nm. The BJH plot (Figure 6b) demonstrates that the average pore diameter is 1.66 nm while the BET plot (Figure 6c) and its linear fit yield a specific surface area (SSA) of 25.01 m<sup>2</sup>/g. The total pore volume was measured at 0.185 cm<sup>3</sup>/g, with a mesoporous volume of 0.191 cm<sup>3</sup>/g.



Figure 6: (a) Adsorption desorption isotherm (AD), (b) BJH isotherm and (c) BET isotherm for CS/CA@AG composite.

#### 3.1.6. Contact angle

The contact angle of the CS/CA@AG biopolymer was  $101.10^{\circ}$  (Figure 7). The increase in contact angle suggests enhanced hydrophobicity, likely due to the presence of agarose within the composite.



Figure 7: Contact angel of CS/CA@AG composites.

# **3.2.** Factors affecting adsorption process *3.2.1. The effect of pH*

The pH of the reaction medium is a critical parameter influencing the process of adsorption. The impact of initial solution pH on oil removal was evaluated over a range of pH values (1–12) (Figure 8). The CS/CA@AG composite achieved a maximum removal efficiency of 91.89% with an adsorption capacity of 641.01 mg/g at pH 8.0. A diminished in the effectiveness of oil removal was noted below pH 8, likely due to competition between proton ions (H<sup>+</sup>) and oil molecule [19]. Notably, oil adsorption efficiency declined slightly beyond pH 8.0, attributed to increased stability of oil emulsions, which reduced the contact area between the adsorbent and oil droplets.



Figure 8: Effect of pH on removal of crude oil (%) and adsorption capacity of crude oil (mg/g) by CS/CA@AG composite.

#### 3.2.2. Effect of contact time

Equilibrium time is a vital consideration in designing costeffective wastewater treatment systems [20,21]. The influence of contact time (10 to 120 min) at varying crude oil concentrations (200, 300, 400, and 800 mg/L) on the adsorption process was examined for the CS/CA@AG composite (Figure 9). The optimal contact time removal of crude oil and adsorption capacity was determined to be 50 minutes for concentrations of 200, 300, and 400 ppm, yielding maximum crude oil removal percentages of 98.40%, 97.84%, and 91.90%, respectively, with corresponding adsorption capacities of 315.38, 464.12, and 641.03 mg/g. For an 800 mg/L concentration, the optimal contact time extended to 90 minutes, resulting in 91.93% removal efficiency as a maximum and an adsorption capacity of 1242.32 mg/g. In general, oil adsorption occurred rapidly during the initial phase, reaching equilibrium as available surface sites decreased.



Figure 9: Effect of contact time on removal of crude oil (%) and adsorption capacity of crude oil (mg/g) by CS/CA@AG composite.

# 3.2.3. The effect of initial oil concentration

The impact of initial oil concentrations was assessed across a concentration range of 100 to 5000 mg/L. As shown in Figure 10, the capacity of adsorption of the CS/CA@AG composite increased from 196.15 mg/g at an initial crude oil concentration of 100 mg/L to 2354.36 mg/g at 1600 mg/L,

and to 7327.03 mg/g at maximum concentration of 5000 mg/L. The concentration range of 100–300 mg/L exhibited the highest removal efficiency (98%). However, as oil concentration increased, the removal percentage decreased. This enhanced adsorption capacity at higher initial concentrations can be due to increased contact between the

accessible active sites on the adsorbent and the adsorbate. A higher initial concentration also generates a driving force that overcomes resistance of mass transfer among the adsorbent and the bulk liquid [22]. At elevated oil concentrations, increased surface coverage can lead to saturation, which may reduce overall removal efficiency [13].

3.2.4. The effect of temperature on adsorption equilibrium The influence of temperature on adsorption of oil onto CS/CA@AG composite were conducted at various temperatures ranging between (20 - 65 °C) as presented in Figure (11). The data revealed that the removal % of oil increase from (90.24 to 96.67%) with rising the temperature from 20 to 55 °C which highlights an endothermic adsorption. beyond 55 °C, a decrease in removal % was observed revealing an exothermic adsorption. The decline in the surface tension of water and crude oil is what causes the

increase in oil removal efficiency up to 55°C., Additionally, when the oil's viscosity decreases, the CS/CA@AG composite's oil uptake improves. [23,24]. In the liquid phase, the adsorbate molecules move at random Brownian motion, and effective collisions cause them to become adsorbed when they come into contact with the sorbent. In fact, increasing the temperature causes the molecules to move faster. The oil molecules become unstable due to the rise in Brownian motion, which also intensifies the contact between the oil particles and the sorbent. Therefore, the effectiveness of oil removal increases with temperature [24]. The increase in oil removal efficiency with rising the temperature indicated that the crude oil adsorption process onto the sorbent is endothermic. The loss of some organic compounds through vaporization may explain the lower adsorption efficiency at higher temperatures



Figure 10: Effect of initial conc. on removal of crude oil (%) and adsorption capacity of crude oil (mg/g) by CS/CA@AG composite.



Figure 11: Effect of temperature on removal of crude oil (%) and adsorption capacity of crude oil (mg/g) by CS/CA@AG composite.

# 3.2.5 The Effect of agitation rate

The agitation rate significantly influences adsorption by enhancing contact between the composite surface and crude oil, thereby reducing mass transfer limitations [14]. The removal percentage of crude oil by the CS/CA@AG composite increased from 75.72% to 99.43% as the agitation rate was raised from 80 to 250 rpm (Figure 12). However, a further increase in agitation speed to 300 rpm caused the removal efficiency diminishing to 90.42%, likely due to the composite spending more time in contact with water rather than crude oil.



Figure 12: Agitation speed effect on removal of crude oil (%) and adsorption capacity of crude oil (mg/g) by CS/CA@AG composite.

Egypt. J. Chem. 67, SI: M. R. Mahran (2024)

# 3.2.6. The Effect of the dosage for the adsorbent

An essential factor for the process of adsorption is the adsorbent dose [25], as increasing the adsorbent weight enhances the availability of adsorption sites, which positively impacts crude oil removal efficiency [23]. The effect of CS/CA@AG composite dosage on crude oil removal was evaluated by changing the dose of composite from 0.20 to 2.0 g/L at an oil concentration of 400 mg/L, and from 0.20 to 4.0 g/L at 1200 mg/L, while maintaining other conditions constant (150 rpm, pH 8.0, contact time of 50 minutes, at 25 °C). As shown in Figure 13 a&b, the percentage removal of crude oil increased rapidly from 86.38% to 99.98% as the adsorbent dose rose from 0.20 to 1.0 g/L when the oil concentration reached 400 mg/L. The removal percentage then increased more gradually to 99.98% as the dose was

raised from 1.0 to 2.0 g/L. Similarly, at 1200 mg/L crude oil concentration, the removal percentage increased from 80.56% to 99.99% as the dosage of CS/CA@AG increased from 0.20 to 1.60 g/L, and then rose more slowly to 99.99% as the dosage increased from 1.60 to 4.00 g/L. This behavior may be due to limitations in the transport of crude oil particles to the composite surface and underutilization of the adsorption capacity of the adsorbent [24], where the oil sorption capacity of CS/CA@AG decreased from 776.92 to 201.92 mg/g and from 1511.54 to 241.35 mg/g at 400 and 1200 mg/L, respectively (Figure 14). These findings align with other studies indicating that unsaturated sites remain available during the sorption process [26–29].



Figure 13: (a) Effect of adsorbent dosage (g/l) on removal (%) and adsorption capacity (mg/g) of 400 mg/L crude oil by CS/CA@AG composite and (b) for 1200 mg/L crude oil

# 3.3. Adsorption Kinetic Modeling

Adsorption kinetics depends on the interactions between the adsorbent and adsorbate, as well as the conditions under which the adsorption occurs. This study used a variety of kinetic models, such as pseudo-first-order and pseudo-second-order models, to assess the viability of using the CS/CA@AG biopolymer to treat oil spills. The linear equations of the kinetic models, along with their calculated parameters, are display in Table 3 & Table S1 and Figures 14 and 15.

The pseudo-second-order model clearly matches the CS/CA@AG composite, evidenced by  $R^2$  values that are close to 1. The computed adsorption capacity values (qe) align closely with the experimental data, where the experimental qe values were 464.12, 641.03, and 1242.32 mg/g, while the calculated qe values were 476.19, 662.25, and 1265.82 mg/g, resulting in  $\Delta$ q values of 12.07, 21.22, and 23.50 mg/g for crude oil concentrations of 200, 400, and 800 mg/L, respectively. Additionally, the pseudo-second-order rate constant (k<sub>2</sub>) values were 0.000565, 0.000479, and 0.000388 for crude oil concentrations of 200, 400, and 800 mg/L, respectively. The initial sorption rate (h) was observed to be higher at elevated concentrations, with values of

128.21, 210.08, and 621.12 mg  $g^{-1}$  min<sup>-1</sup> for crude oil concentrations of 200, 400, and 800 mg/L, respectively.



Figure 14: Pseudo-first-order kinetic model plot for the adsorption of the crude oil onto CS/CA@AG composite at different crude oil concentrations

Pseudo-first-order parameters						
[Crude Oil] (mg/L)	qe exp. (mg/g)	qe Calc. (mg/g)	$\Delta q$ (mg/g)	(m	$K_1$ in <sup>-1</sup> )	$\mathbf{R}^2$
200	464.12	538.83	74.71	0.1	1064	0.901
400	641.03	529.64	111.39	0.0	)937	0.726
800	1242.32	548.78	693.54	0.0	0781	0.801
Pseudo-second-order parameters						
[Crude Oil] (mg/L)	qe exp. (mg/g)	qe Calc. (mg/g)	$\Delta q$ (mg/g)	$K_2 (min^{-1})$	$\frac{K_2 qe^2}{(mg/(g min))}$	$\mathbf{R}^2$
200	464.12	476.19	12.07	0.000565	128.21	0.998
400	641.03	662.25	21.22	0.000479	210.08	0.999
800	1242.32	1265.82	23.50	0.000388	621.12	0.999

Table 3: The Adsorption kinetic parameters of pseudo-first order and pseudo-second order kinetic models for crude oil removal by CS/CA@AG composite at different crude oil concentrations



Figure 15: Pseudo-second-order kinetic model plot for the adsorption of the crude oil onto CS/CA@AG composite at different crude oil concentrations

#### 3.4. Oil adsorption isotherms

The oil adsorption process onto the CS/CA@AG composite was assessed using the Freundlich and Langmuir isotherm models. These models assess the homogeneity or heterogeneity of the biosorbent's surface characteristics and describe the interactions between the adsorbent and adsorbate ions, providing essential physicochemical data regarding the adsorption process [30]. Table 4 and Table S2 display the linear equations for these isotherm models, while the corresponding results are illustrated in Figures 16 and 17.

 Table 4: Langmuir and Freundlich isotherm equilibrium

 parameters for crude oil adsorption using CS/CA@AG

Langmuir Isotherm model parameters						
Composite	q <sub>m</sub> (mg/g)	K <sub>L</sub> (l/mg)	R <sub>L</sub> range	$\mathbb{R}^2$		
CS/CA@AG	7142.86	0.0027	0.125-0.758	0.972		
Freundlich Isotherm model parameters						
Composite	Composite Kf (mg/g)		n	$R^2$		
CS/CA@AG	201.33	0.473	2.116	0.995		



Figure 16: Langmuir isotherm model for crude oil adsorption by CS/CA@AG.



Figure 17: Freundlich isotherm model for crude oil adsorption by CS/CA@AG.

# 3.4.1. Langmuir isotherm model

For the CS/CA@AG composite, the linear plot of Ce/qe against Ce was used for estimating the maximum adsorption capacity (Qmax) and the Langmuir constant (KL).The calculated parameters are summarized in Table 4 and depicted in Figure 16. The model of Langmuir Isotherm demonstrated a strong correlation with the equilibrium data ( $R^2 = 0.972$ ), yielding a Qmax value of 7142.86 mg/g. The dimensionless separation factor (RL) indicated that the suitability of CS/CA@AG for oil treatment decreases with increasing initial oil concentration, with values ranging between 0 < RL < 1, suggesting its effectiveness for treating oily wastewater.

# 3.4.2. Freundlich isotherm model

The linear plot of Freundlich equation  $\log(qt)$  against  $\log(Kf)$  (Figure 17) was used to calculate the values of (1/n) and Kf.

The value of 1/n for the CS/CA@AG composite was found to be 2.11, indicating that the biosorbent has heterogeneous surfaces and confirming its favourability for oil adsorption.

### 3.5. Thermodynamic studies

Thermodynamic studies were conducted to assess the adsorption reaction's spontaneity and randomness. For the purpose to assess the temperature dependency of the adsorption process, the adsorption of crude oil onto the CS/CA@AG composite was investigated by computing a number of thermodynamic parameters, such as Gibbs free energy ( $\Delta$ G°), enthalpy ( $\Delta$ H°), and entropy ( $\Delta$ S°).

The Gibbs free energy can be expressed using the van't Hoff equation:

$$\Delta G = -RT \ln K_d \tag{4}$$

Where Kd can be calculated by the subsequent equation:  $K_d = qe/Ce$  (5)

The Enthalpy ( $\Delta$ H) and Entropy ( $\Delta$ S) are computed using the equation that follows:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$
(6)  

$$\ln K_{d} = -\Delta H^{\circ}/RT + \Delta S^{\circ}/R$$
(7)

Where, Ce (mg l<sup>-1</sup>) is the crude oil equilibrium concentration in the solution, qe (mg g<sup>-1</sup>), is the amount of oil adsorbed on the adsorbent at equilibrium, R (8.314 J. mol.<sup>-1</sup> K<sup>-1</sup>) is the universal gas constant, T (K) is the absolute temperature, and K<sub>d</sub> is the distribution coefficient. Linear plot of ln K<sub>d</sub> vs 1/T for adsorption, the slope and intercept are equal to ( $-\Delta$ H° / R) and ( $\Delta$ S°/R), respectively. The slope and intercept of the line derived from the plot (Figures 18) can be used to estimate the values of  $\Delta$ H° and  $\Delta$ S°. Additionally, Table (5) compiles the obtained thermodynamic parameters. The spontaneous nature and capability of adsorption through physical force is revealed by the negative value of  $\Delta$ G° [31, 32].



Figure 18: Van't Hoff plot for oil removal using CS/CA@AG composite at different solution temperatures.

Thermodynamic studies of crude oil adsorption onto composites were conducted over a temperature range of 293 to 323 K. The negative  $\Delta G^{\circ}$  values for the CS/CA@AG composite ranged from -6.662 to -8.809 kJ/mol, confirming the spontaneity of the process. Conversely, a positive  $\Delta H^{\circ}$  revealed an endothermic adsorption process. Additionally, as shown in Table 5, the CS/CA@AG composite's  $\Delta S^{\circ}$  value was 71.349 J/mol K, indicating a rise in randomness at the adsorbent/adsorbate interface through the crude oil adsorption process.

Table 5: Thermodynamic parameters for the adsorption of crude oil onto CS/CA@AG composite.

T (K)	q <sub>e</sub> (mg/g)	ln K <sub>d</sub>	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)	R <sup>2</sup>
293	629.48	2.735	-6.662			
298	641.03	2.939	-7.282			
303	643.58	2.989	-7.530			
308	646.15	3.042	-7.789	14.177	71.349	0.985
313	651.28	3.155	-8.210			
318	653.85	3.216	-8.503			
323	656.41	3.280	-8.809			

#### 3.6. Comparison with other chitosan derived adsorbents

The adsorption efficiency of CS/CA@AG towards crude oil was compared with other chitosan-derived adsorbents, as presented in Table 6. The results obtained show that the existing adsorbents' adsorption capability is higher than what has been reported in the literature, suggesting that modifications to the biosorbent enhance crude oil removal efficiency. The findings align with those of other researchers, supporting the potential of these adsorbents for effective crude oil removal from oily wastewater.

Table 6: Comparison of crude oil adsorption by CS/CA@AG with other modified chitosan adsorbents.

Adsorbent	Adsorption capacity/ Removal efficiency	Ref.	
chitosan hydrogel-coated aluminium electrodes	95.85%	[6]	
Chitosan/polyethylene glycol hydrogel	0.40 g/g	[33]	
Chitosan flakes	0.38 g/g	[34]	
Chitosan powder	0.28 g/g		
Chitosan-based polyacrylamide hydrogel	2.31 g/g	[35]	
Chitosan -based polyacrylamide	2.4 g/g	[21]	
Chitosan- $g_P(\Delta \Delta m)$ hydrogel	1.6 g/g		
Chitosan-g-i (Ar an) nyaroger	2.0 g/g		
Chitosan microspheres	>90%	[36]	
Chitosan flakes	0.45 g/g	[27]	
Chitosan powder	0.55 g/g	[37]	
CS/CA@AG	7.33 g/g / 99.99%	This study	

### 3.7. Applications on Real Wastewater

The CS/CA@AG composite was utilized to remove oil from three real wastewater samples: diesel engine oil, bilge tank oil collected from a marine vessel (PMS Abu-Qir) at Petroleum Marine Services Company, and crude oil from the Arab Petroleum Pipelines Co. (SUMED) in Alexandria, Egypt. The oil concentrations in the three samples were 2000 mg/L for diesel engine oil, 17916.67 mg/L for bilge tank oil, and 2000.08 mg/L for crude oil.

Oil removal was conducted using a column system packed with 0.37 g of CS/CA@AG adsorbent. The column, made of glass, had a diameter of 1.5 cm and a length of 17.5 cm. Diesel engine oil and crude oil samples were mixed with real saline water from El Mora Lake (Abu Sultan Station), while the bilge tank oil sample was used directly after collection. One liter of wastewater samples containing diesel oil was flowed at a rate of 15.90 mL/min through the column, while crude oil was treated at a flow rate of 11.10 mL/min, and bilge tank oil at 9.10 mL/min.

The effluents were collected, and residual oil was extracted using dichloromethane (DCM) for analysis. The removal efficiencies achieved were 99.44% for diesel oil, 99.92% for crude oil, and 99.84% for bilge tank oil, demonstrating the effectiveness of the CS/CA@AG composite in real-world applications.

### 4. Conclusions

For the first time CS/CA@AG bioadsorbent was synthesized and thoroughly characterized using FT-IR, TGA, SEM, XRD, and BET techniques. The adsorption process was examined using batch adsorption studies revealing that the adsorption is pH-dependent, with pH 8 identified as the optimal value. According to kinetic investigations, the adsorption kinetics were best elucidated by the pseudosecond-order model. Both the Freundlich and Langmuir isotherm models fit the equilibrium data well; the maximum adsorption capacity (Qmax) was 7142.86 mg/g, and the correlation value (R<sup>2</sup>) was 0.9725. The adsorption process appears to be both endothermic and spontaneous based on the positive enthalpy ( $\Delta$ H) and negative Gibbs free energy ( $\Delta$ G) values. Additionally, during oil sorption onto the surface of the adsorbent, the negative entropy ( $\Delta S$ ) value shows a decrease in randomness at the solid-liquid interface. These findings suggest that CS/CA@AG is a promising, ecofriendly, and economical method for the removing of oil from wastewater.

# 5. Conflicts of interest

There are no conflicts to declare

#### 6. References

- M.A. Kaczorowska, D. Bożejewicz, The Application of Chitosan-Based Adsorbents for the Removal of Hazardous Pollutants from Aqueous Solutions—A Review, Sustainability. 16 (2024). https://doi.org/10.3390/su16072615.
- [2] A.K. Bairagi, R.R. Puthiyonnan, S.S. Mohapatra, A. Sahoo, Efficient oil-water emulsion separation using chitosan hydrogel-coated aluminium electrodes, Water Pract. Technol. 19 (2024) 1769–1793. https://doi.org/10.2166/wpt.2024.104.
- [3] A. Mubarak, M., Mohamed, R., Ahmed Rizk, S., Abuzalat, O., Eid M. Ali, M. Competent CuS QDs@Fe MIL101 heterojunction for Sunlight-driven degradation of pharmaceutical contaminants from wastewater. Environmental Nanotechnology, Monitoring and Management, 2024, 22, 101013
- [4] M.E.M Ali, R. Mohammed, S.M. Abdel-Moniem, M.A. El-Liethy, Ibrahim, H.S. Green MoS2 nanosheets as a promising material for decontamination of hexavalent chromium, pharmaceuticals, and microbial pathogen disinfection: spectroscopic study. Journal of Nanoparticle Research, 2022, 24(10),191
- [5] R.Mohammed, M.E.M. Ali, E. Gomaa, M. Mohsen.Copper sulfide and zinc oxide hybrid nanocomposite for wastewater decontamination of pharmaceuticals and pesticides. Scientific Reports, 2022, 12(1), 18153
- [6] Y. Gong, X. Zhao, Z. Cai, S.E. O'Reilly, X. Hao, D. Zhao, A review of oil, dispersed oil and sediment

Egypt. J. Chem. 67, SI: M. R. Mahran (2024)

interactions in the aquatic environment: Influence on the fate, transport and remediation of oil spills, Mar. Pollut. Bull. 79 (2014) 16–33. https://doi.org/10.1016/j.marpolbul.2013.12.024.

- [7] Y. Wu, S. Zhao, Status quo and change characteristics of groundwater resources pollution in the Hami region based on sustainable development strategies, Water Supply. 23 (2023) 1478–1494. https://doi.org/10.2166/ws.2023.063.
- [8] EPA, Oil Spill Response Techniques, EPA's Response Techniques, 2017. https://www.epa.gov/emergencyresponse/epas-response-techniques#Oil Spill Response Techniques.
- [9] Daily News Egypt, Egypt's Environment Ministry reviews plan to combat marine oil pollution, (2021). https://www.dailynewsegypt.com/2021/06/02/egypts-environment-ministry-reviews-plan-to-combat-marine-oil-pollution/.
- [10] K. Seth, M. Busse, G. Jang, S. Joag, K. Kim, T. Pankratz, D. Sahu, R. Sharma, J. Stokes-Draut, C. Tsouris, S. Chellam, Electrocoagulation of high-salinity produced water: lessons learned from its early applications in unconventional reservoir plays, Curr. Opin. Chem. Eng. 42 (2023) 100952. https://doi.org/https://doi.org/10.1016/j.coche.2023.100952
- . [11] G. Crini, P.-M. Badot, Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch
- natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature, Prog. Polym. Sci. 33 (2008) 399–447. https://doi.org/https://doi.org/10.1016/j.progpolymsci.2007. 11.001.
- [12] R.A.A. Muzzarelli, 10.06 Nanochitins and Nanochitosans, Paving the Way to Eco-Friendly and Energy-Saving Exploitation of Marine Resources, in: K. Matyjaszewski, M.B.T.-P.S.A.C.R. Möller (Eds.), Elsevier, Amsterdam, 2012: pp. 153–164. https://doi.org/https://doi.org/10.1016/B978-0-444-53349-4.00257-0.
- [13] Saruchi, V. Kumar, Separation of crude oil from water using chitosan based hydrogel, Cellulose. 26 (2019) 6229– 6239. https://doi.org/10.1007/s10570-019-02539-1.
- [14] W. Pitakpoolsil, M. Hunsom, Treatment of biodiesel wastewater by adsorption with commercial chitosan flakes: Parameter optimization and process kinetics, J. Environ. Manage.133(2014)284–292.
- https://doi.org/https://doi.org/10.1016/j.jenvman.2013.12.0 19.
- [15] A.A. Taha, S. Kandil, L.A. Mohamed, M.G. Sallam, H.F. Heiba, Surface investigations of selective biosorption and reduction of hexavalent chromium ions Cr(VI) over chitosan@MoO3 and chitosan-cellulose@MoO3 biocomposite., J. Mol. Struct. 1288 (2023) 135716. https://doi.org/https://doi.org/10.1016/j.molstruc.2023.1357 16.
- [16] H.F. Heiba, A.A. Taha, A.R. Mostafa, L.A. Mohamed, M.A. Fahmy, Preparation and characterization of novel mesoporous chitin blended MoO3-montmorillonite nanocomposite for Cu(II) and Pb(II) immobilization, Int. J. Biol. Macromol. 152 (2020) 554–566. https://doi.org/https://doi.org/10.1016/j.ijbiomac.2020.02.2 54.
- [17] Y. Gutha, Y. Zhang, W. Zhang, X. Jiao, Magnetic-epichlorohydrin crosslinked chitosan schiff's base (m-ECCSB) as a novel adsorbent for the removal of Cu(II) ions from aqueous environment, Int. J. Biol. Macromol. 97 (2017)

https://doi.org/https://doi.org/10.1016/j.ijbiomac.2017.01.0 04.

- [18] F.A. Razmi, N. Ngadi, S. Wong, I.M. Inuwa, L.A. Opotu, Kinetics, thermodynamics, isotherm and regeneration analysis of chitosan modified pandan adsorbent, J. Clean. Prod. 231 (2019) 98–109. https://doi.org/https://doi.org/10.1016/j.jclepro.2019.05.22.
- [19] S. Ibrahim, S. Wang, H.M. Ang, Removal of emulsified oil from oily wastewater using agricultural waste barley straw, Biochem. Eng. J. 49 (2010) 78–83. https://doi.org/https://doi.org/10.1016/j.bej.2009.11.013
- [20] D. Liu, X. Yang, L. Zhang, Y. Tang, H. He, M. Liang, Z. Tu, H. Zhu, Immobilization of Biomass Materials for Removal of Refractory Organic Pollutants from Wastewater, Int. J. Environ. Res. Public Health. 19 (2022). https://doi.org/10.3390/ijerph192113830.
- [21] M.S. Masoud, S.S. Haggag, H.F. Heiba, O.H. Abd El-Hamed, N.S. Habila, I.A.M. Abdel-hamid, L.A. Mohamed, Comparative Adsorption Affinities of Nano-Metal Oxides Towards Cr(VI): Synthesis, Characterization, Kinetics, Isotherms, Thermodynamic and Techno-Economics Study, Environ. Process. 10 (2023) 33. https://doi.org/10.1007/s40710-023-00651-w.
- [22] M. Ververi, A.M. Goula, Pomegranate peel and orange juice by-product as new biosorbents of phenolic compounds from olive mill wastewaters, Chem. Eng. Process. - Process Intensif. 138 (2019) 86–96. https://doi.org/https://doi.org/10.1016/j.cep.2019.03.010.
- [23] J. Li, M. Luo, C.-J. Zhao, C.-Y. Li, W. Wang, Y.-G. Zu, Y.-J. Fu, Oil removal from water with yellow horn shell residues treated by ionic liquid, Bioresour. Technol. 128 (2013) 673–678. https://doi.org/10.1016/j.biortech.2012.11.00 9.
- [24] A.S. Gulistan, Oil Removal From Produced Water Using Natural Materials, (2014). https://repository.aus.edu/entities/publication/8942c3b8-1821-469f-ad3c-1aee815a8c73.
- [25] H.F. Heiba, A.A. Taha, A.R. Mostafa, L.A. Mohamed, M.A. Fahmy, Synthesis and characterization of CMC/MMT nanocomposite for Cu2+ sequestration in wastewater treatment, Korean J. Chem. Eng. 35 (2018) 1844–1853. https://doi.org/10.1007/s11814-018-0096-7.
- [26] C. Jeon, K. Ha Park, Adsorption and desorption characteristics of mercury(II) ions using aminated chitosan bead, Water Res. 39 (2005) 3938–3944. https://doi.org/https://doi.org/10.1016/j.watres.2005.07.02.
- [27] A. Ummadisingu, S. Gupta, Characteristics and kinetic study of chitosan prepared from seafood industry waste for oil spills cleanup, Desalin. Water Treat. 44 (2012) 44–51. https://doi.org/https://doi.org/10.5004/dwt.2012.2425
- [28] E. Nwankwere, G. Casimir, K. Adagadzu, N. Yusuf, Sorption Studies of Crude Oil on Acetylated Rice Husks, Arch. Appl. Sci. Res. 2 (2010).
- [29] R.E. Khalifa, A.M. Omer, T.M. Tamer, A.A. Ali, Y.A. Ammar, M.S.M. Eldin, Efficient eco-friendly crude oil adsorptive chitosan derivatives: kinetics, equilibrium and thermodynamic studies, Desalin. Water Treat. 159 (2019) 269–281.

https://doi.org/https://doi.org/10.5004/dwt.2019.24166.

[30] A.A. Taha, M.A. Shreadah, A.M. Ahmed, H.F. Heiba, Multi-component adsorption of Pb(II), Cd(II), and Ni(II) onto Egyptian Na-activated bentonite; equilibrium, kinetics, thermodynamics, and application for seawater desalination, J. Environ. Chem. Eng. 4 (2016) 1166–1180.

Egypt. J. Chem. 67, SI: M. R. Mahran (2024)

- https://doi.org/https://doi.org/10.1016/j.jece.2016.01.025. [31] H. Li, X. Zhuang, M. Bao, Kinetics and thermodynamics of dissolved petroleum hydrocarbons in sediment under sophorolipid application and their effects on oil behaviour end-results in marine environment, RSC Adv. 7 (2017) 45843–45851. https://doi.org/10.1039/C7RA07423A.
- [32] H. Mottaghi, Z. Mohammadi, M. Abbasi, N. Tahouni, M.H. Panjeshahi, Experimental investigation of crude oil removal from water using polymer adsorbent, J. Water Process Eng. 40 (2021) 101959. https://doi.org/https://doi.org/10.1016/j.jwpe.2021.101959.
- [33] R.R.L. Vidal, J.S. Moraes, Removal of organic pollutants from wastewater using chitosan: a literature review, Int. J. Environ. Sci. Technol. 16 (2019) 1741–1754. https://doi.org/10.1007/s13762-018-2061-8.
- [34] A.M. Omer, R.E. Khalifa, T.M. Tamer, A.A. Ali, Y.A. Ammar, M.S. Mohy Eldin, Kinetic and thermodynamic studies for the sorptive removal of crude oil spills using a low-cost chitosan-poly (butyl acrylate) grafted copolymer, Desalin. Water Treat. 192 (2020) 213–225. https://doi.org/https://doi.org/10.5004/dwt.2020.25704.
- [35] H.H Sokker, El-Sawy, M.A. Hassan and B. N.M E El-Anadouli, Adsorption of crude oil from aqueous solution by hydrogel of chitosan based polyacrylamide prepared by radiation induced graft polymerization, J. Hazard. Mater. (2011). 190, 359–365.
- [36] I.C.S. Grem, B.N.B. Lima, W.F. Carneiro, Y.G.C. Queirós, C.R.E. Mansur, Chitosan microspheres applied for removal of oil from produced water in the oil industry, Polímeros. Ciência. Tecnol., (2013).23, 705–711
- [37] A.L. Ahmad, S. Sumathi, and B.H Hameed, Adsorption of residue oil from palm oil mill effluent using powder and flake chitosan: equilibrium and kinetic studies, Water Res. (2005). 39 (12), 2483–2494.