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## Development of a novel low-cost adsorbent Chitosan@EDTA@Cellulose composite to effectively remove Methyl Orange dye from wastewater: Experimental and theoretical investigation

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## ABSTRACT

Methyl Orange, a toxic and persistent azo dye, poses significant environmental challenges in aquatic ecosystems. This study investigates the efficiency of a novel Chitosan@EDTA@Cellulose composite, synthesized by linking shrimp-derived chitosan and cactus-derived cellulose using EDTA as a linking agent. Comprehensive characterization techniques, including Fourier-transform infrared spectroscopy, scanning electron microscopy, X-ray diffraction, and Brunauer-Emmett-Teller surface area analysis, were employed.

Under optimal conditions (pH 5, 50 mg/L dye concentration, 55 min, 0.1 g adsorbent), the composite achieved a maximum adsorption capacity of 55.87 mg/g, significantly outperforming chitosan (7.29 mg/g) and cellulose (5.69 mg/g). Adsorption followed the pseudo-second-order kinetic model and the Langmuir isotherm model, with thermodynamic analysis confirming a spontaneous and endothermic process. Competitive adsorption tests demonstrated >90 % removal efficiency despite the presence of interfering ions, attributed to the chelating properties of EDTA and the synergistic effect of the composite structure. Reusability tests showed a slight efficiency decline from 97.8 % to 81.86 % after four cycles.

Box-Behnken Design optimization identified adsorbent mass, pH, and dye concentration as key factors in removal efficiency. Density Functional Theory analysis clarified the functional group interactions driving adsorption. These findings underscore the composite's potential as an effective and eco-friendly adsorbent for Methyl Orange removal.

## 1. Introduction

Water pollution has emerged as one of the most pressing environmental challenges of the 21st century, significantly impacting public health and ecosystems [1]. Aqueous solutions can be contaminated by a wide range of pollutants, posing significant challenges to water quality and public health [2]. Among these pollutants, heavy metals, organic compounds, synthetic dyes, pharmaceuticals, and microplastics are particularly concerning due to their persistence and harmful effects on ecosystems and human health [3]. Heavy metals such as lead, cadmium, mercury, and chromium are highly toxic and non-biodegradable, meaning they accumulate in water systems over time [4]. Even at low concentrations, these metals can cause severe health issues, including neurological damage, kidney dysfunction, and cancer. For example, lead exposure can impair cognitive development in children, while cadmium is linked to kidney and bone disorders [5].

Organic contaminants, on the other hand, include a diverse array of chemicals such as pesticides, industrial solvents, and hydrocarbons [6].

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Received 22 December 2024; Received in revised form 6 February 2025; Accepted 12 February 2025 Available online 13 February 2025 0141-8130/© 2025 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies. These compounds often originate from agricultural runoff, industrial discharges, and accidental spills. Once released into water bodies, they can persist for long periods, leading to bioaccumulation in aquatic organisms and entering the food chain [7]. Pesticides, for instance, are known to disrupt endocrine systems in both humans and wildlife, while industrial solvents like benzene and toluene are carcinogenic and can cause liver and kidney damage [8].

Among the various contaminants, dyes represent a major concern due to their persistence and toxicity in aquatic environments [9]. These dyes are commonly used in industries such as textiles, food, cosmetics, and pharmaceuticals. Due to their complex chemical structures, they are highly resistant to degradation, making them difficult to remove from wastewater. When released into water bodies, dyes can cause severe environmental damage, disrupting aquatic ecosystems by reducing oxygen levels, inhibiting photosynthesis in aquatic plants, and harming aquatic organisms [10].

Furthermore, the presence of dyes in water can lead to bioaccumulation, where these toxic substances build up in the food chain, ultimately posing risks to human health [11]. This contamination is particularly concerning as dyes often contain toxic chemicals that can cause long-term harm to both aquatic life and humans. For instance, the release of dyes into water sources can lead to discoloration of water, making it unfit for consumption or recreational activities. As the contamination persists, the impact on biodiversity and water quality becomes increasingly detrimental [12].

Studies have highlighted the importance of effective dye removal techniques, with research showing the significant adsorption capacities of various adsorbents in removing these pollutants. For example, Langmuir adsorption capacities for dyes using raw and calcined alluvium have been calculated, with values of 49.36 mg/g for one dye and 57.84 mg/g for another [13].

In addition to dyes, other pollutants such as phosphate ions have also been the focus of adsorption studies. For example, an investigation using a magnesium oxide@ferric molybdate nanocomposite revealed that the adsorption of phosphate ions exhibited a maximum sorption capacity of 30.21 mg/g [14]. Similarly, the chromium biosorption capacity of modified *S. oligocystum* biomass was found to be 34.46 mg/g [15]. Moreover, cadmium elimination from wastewater has been studied using potato peel biochar modified by ZIF-8 and magnetic nanoparticles. The removal of  $Cd^{2+}$  using BPP/MnFe<sub>2</sub>O<sub>4</sub>@ZIF-8 was maximized at pH 6, a temperature of 45 °C, and a time of 100 min. The adsorption capacity for cadmium was calculated as 33.76 mg/g for BPP, 45.02 mg/g for BPP/MnFe<sub>2</sub>O<sub>4</sub>, and 80.52 mg/g for BPP/MnFe<sub>2</sub>O<sub>4</sub>@ZIF-8 [16]. Additionally, pulsed sonication applied to powdered zeolite-zirconium for the removal of fluoride from water resulted in a maximum adsorption capacity of 32.98 mg/g [17].

Among the various pollutants, synthetic dyes, particularly azo dyes like methyl orange, pose severe threats due to their persistence in water bodies and their toxic effects on aquatic life and humans [18]. Methyl orange, a widely used pH indicator and dye in textiles, is characterized by its bright orange color and its ability to impart toxicity to the aquatic environment [19]. Its chemical structure consists of azo bonds, which can resist degradation in natural water systems, leading to long-term contamination [20]. The presence of such dyes in wastewater is concerning, as they can disrupt the photosynthetic activity of aquatic organisms and may even lead to bioaccumulation in the food chain, ultimately posing risks to human health [21]. Several methods have been developed for the removal of dyes from aqueous solutions, broadly categorized into physical, chemical, and biological approaches [22]. Physical methods include adsorption, membrane filtration, and ion exchange [23,24]. Membrane filtration processes, such as reverse osmosis and ultrafiltration, effectively remove dye molecules based on size and charge but are costly and susceptible to fouling [25]. Ion exchange replaces dye ions with harmless ions using resins but is limited to specific dyes [26]. Chemical methods, including coagulation, oxidation, and electrochemical processes, are widely used. Coagulation and

flocculation use coagulants like alum or ferric chloride to destabilize dye particles for sedimentation [27]. Oxidation processes, such as photocatalysis and ozone treatment, degrade dyes into non-toxic compounds but require high energy and complex equipment [28]. Electrocoagulation employs electric currents to remove dyes, offering an ecofriendly solution despite high costs and slow operation under specific conditions [29]. Among all these techniques, adsorption has gained considerable attention due to its remarkable advantages [30]. It is a highly effective method for removing a wide range of dyes, even at low concentrations, and is relatively simple, cost-effective, and easy to operate [31]. Adsorption offers a high dye removal capacity, rapid kinetics, and the potential for adsorbent regeneration [32]. Furthermore, adsorption produces minimal secondary pollution, making it a highly sustainable option for water treatment [33]. These advantages, coupled with its adaptability to various dye types, position adsorption as one of the most promising methods for addressing dye pollution in water systems [34]. The choice of adsorbents is crucial in the adsorption process for dye removal, as the effectiveness of dye adsorption depends largely on the adsorbent's structural and chemical properties. Dyes, commonly classified into cationic, anionic, and nonionic types, differ in their chemical structures, requiring adsorbents tailored to specific dve interactions. Recently, adsorbents derived from renewable and natural resources have gained significant attention due to their sustainability and environmental friendliness. These bio-based adsorbents, such as chitosan, cellulose, and biochar from agricultural waste [35], offer unique advantages for dye adsorption [36]. Chitosan and cellulose are increasingly recognized as effective and sustainable adsorbents for the removal of synthetic dyes from aqueous solutions, owing to their unique chemical structures and advantageous properties [37].

Chitosan, a biopolymer derived from chitin, which is abundant in the exoskeletons of crustaceans, contains an abundance of functional groups, including amino (-NH<sub>2</sub>) and hydroxyl (-OH) groups [38]. These functional groups play a crucial role in the adsorption process, as they allow for effective interactions with a wide range of dye molecules, particularly those with anionic or cationic properties [39]. The amino groups of chitosan facilitate electrostatic interactions with negatively charged dye molecules, while the hydroxyl groups promote hydrogen bonding, improving the overall dye binding capacity [40]. The combination of these interactions allows chitosan to effectively adsorb a variety of dyes, even at low concentrations, making it an efficient material for wastewater treatment. Additionally, chitosan's biodegradability, non-toxicity, and renewability make it an environmentally friendly choice for dye removal [41] [42].

To enhance the adsorption capacity of chitosan, various modifications have been proposed, including the incorporation of chelating agents such as ethylenediaminetetraacetic acid (EDTA) and blending with other biopolymers like cellulose [43]. EDTA is a well-known chelating agent that forms stable complexes with metal ions, and its incorporation into the chitosan matrix can significantly increase the number of available functional groups for dye adsorption [44]. This modification is particularly beneficial in enhancing the binding capacity of the adsorbent toward methyl orange, as the additional functional groups provide more sites for interaction with the dye molecules [45]. In parallel, Cellulose, another natural polymer, offers complementary benefits in the removal of synthetic dyes from aqueous solutions. Cellulose is composed of  $\beta$ -D-glucose units, forming long chains with numerous hydroxyl (-OH) groups that enable interaction with various dye molecules. While cellulose itself may not have the same degree of charge as chitosan, its hydroxyl groups allow it to interact with a wide range of dye types, including both cationic and anionic dyes, through hydrogen bonding and dipole interactions [46]. This versatility makes cellulose a valuable adsorbent for a broad spectrum of dye molecules. Furthermore, cellulose is abundant, cost-effective, biodegradable, and renewable, all of which contribute to its environmental sustainability and suitability for large-scale applications [47]. Although its intrinsic adsorption capacity may be lower compared to other adsorbents like

chitosan, cellulose can be chemically modified to enhance its dye removal efficiency. By introducing functional groups or combining it with other materials, the adsorption capacity of cellulose can be increased, making it more effective for dye removal. The flexibility in modification and its eco-friendly nature make cellulose a promising adsorbent for industrial dye removal applications. Cactus, particularly species like Opuntia (commonly known as prickly pear), is emerging as a promising source of cellulose, a biopolymer with a wide range of industrial and environmental applications [48]. Cellulose is the primary structural component of the plant cell wall, and cacti, like many other plants, contain a substantial amount of cellulose in their cladodes (stems) and pads [49]. Cactus, in contrast, thrives in arid and semi-arid environments with minimal water, making it a renewable resource that can be harvested with less environmental impact [50].

The cellulose content in cactus varies depending on the species and the part of the plant used, but studies have shown that it can be extracted from the stems (cladodes) and pads of the cactus [51]. Cactus cellulose is extracted through physical and chemical treatments to remove hemicellulose and lignin. Alkali treatment breaks down non-cellulosic substances, and bleaching enhances cellulose purity. The extracted cellulose is used for paper, textiles, and as adsorbents for water treatment [52]. Chitosan@EDTA@Cellulose composite stands out as a highly effective and environmentally sustainable material for the removal of pollutants from aqueous solutions. By combining the unique properties of chitosan, EDTA, and cellulose, this composite benefits from the synergistic effects of each component. Chitosan provides biopolymeric adsorption sites for organic contaminants and metals, while EDTA serves as a linker between chitosan and cellulose increasing the composite's versatility. The inclusion of cellulose, particularly from renewable sources like cactus, strengthens the composite's structural integrity and provides a larger surface area for adsorption, significantly improving its efficiency.

The Chitosan@EDTA@Cellulose composite is particularly advantageous due to its sustainability, cost-effectiveness, and biodegradability, making it a viable alternative to conventional synthetic adsorbents. Furthermore, its ability to adsorb a wide range of pollutants, from heavy metals to synthetic dyes, positions it as a promising material for diverse environmental applications, such as wastewater treatment and industrial effluent purification. The composite's ease of preparation, low-cost nature, and reusability make it an attractive solution for large-scale water treatment processes, providing a green alternative for mitigating the harmful effects of water contamination.

The primary objective of this study was to evaluate and compare the adsorption capacities of chitosan, cellulose, and the novel Chitosan@EDTA@Cellulose composite for the removal of Methyl Orange (MO) dye from aqueous solutions. First, the novel composite was synthesized by linking shrimp-derived chitosan and cactus-derived cellulose using EDTA as a linking agent. The incorporation of EDTA was expected to enhance the adsorption properties due to the synergistic effects of its components. Comprehensive characterization techniques, including Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area analysis, Scanning Electron Microscopy (SEM), and Point of Zero Charge (pHzpc) analysis, were employed to understand the structural, chemical, and surface characteristics of the materials. The adsorption study investigated the performance of individual components and the composite under various conditions, including the influence of pH, adsorbent mass, dye concentration, and contact time. To assess the adsorption kinetics and mechanisms, various models were applied, including the pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models, as well as Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherms. These models provided insight into the adsorption behavior and helped determine the most appropriate model for each material. The reusability of the adsorbents was also examined, along with competitive adsorption tests to assess the impact of interfering ions on the dve removal efficiency. To optimize the adsorption process, Box-Behnken Design (BBD) was utilized to identify key factors influencing dye

removal efficiency and their interactions. Furthermore, Density Functional Theory (DFT) was applied to explore the molecular interactions involved in the adsorption process, providing a theoretical perspective on the adsorption mechanism. Overall, this study aimed to compare the adsorption performance of chitosan, cellulose, and the Chitosan@EDTA@Cellulose composite and to demonstrate the composite's potential as an efficient and eco-friendly adsorbent for Methyl Orange dye removal in environmental remediation.

## 2. Material and methods

## 2.1. Chemical and reagents

The materials used in this study include hydrochloric acid (HCl, 37 % purity, molecular weight = 36.46 g/mol), sodium hydroxide (NaOH, molecular weight = 40.00 g/mol, 98 %), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, molecular weight = 34.01 g/mol, 30 %), and acetic acid (CH<sub>3</sub>COOH, molecular weight = 60.05 g/mol, 99 %), all sourced from Sigma-Aldrich. Methyl orange (C<sub>11</sub>H<sub>11</sub>N<sub>3</sub>NaO<sub>3</sub>S, molecular weight = 327.33 g/mol, 99 %) was used as the target dye in the adsorption experiments. Methyl orange exhibits a maximum absorption wavelength ( $\lambda$  max) of approximately 464 nm [18], which facilitates its detection and quantification in aqueous solutions.

## 2.2. Preparation of Chitosan@EDTA@Cellulose

## 2.2.1. Extraction of cellulose from cactus

Cellulose was extracted from fresh cactus cladodes. The cladodes were air-dried for 2 days, cut into 1–2 cm pieces, and ground into a fine powder. The powder was then treated with hot water at 70 °C for 2 h to remove impurities, followed by centrifugation at 4000 rpm to isolate the cellulose-rich material [53]. The cellulose-rich material underwent alkaline treatment with a 15 % NaOH (sodium hydroxide) solution at 98 °C for 90 min, with a solid powder to alkaline liquid ratio of 1:10, to remove residual hemicellulose, lignin, fats, and waxes [54]. The alkaline-treated fibers were filtered, washed with distilled water to neutralize the pH, treated with H<sub>2</sub>O<sub>2</sub> (hydrogen peroxide) for decolorization, and air-dried under ambient conditions, yielding purified cellulose for composite production [55]. Fig. 1 illustrates the various steps involved in the extraction of cellulose form cactus.

## 2.2.2. Extraction of chitosan from shrimps

Chitosan was extracted from shrimp shells through a multi-step process involving demineralization, deproteinization, and deacetylation. First, the fresh shrimp shells were thoroughly cleaned to remove any organic residues [56]. The shells were then demineralized by soaking in a 2 M (HCl) solution, which dissolved calcium carbonate and other minerals [57]. After several hours of acid treatment, the demineralized shells were washed with distilled water and filtered. Next, deproteinization was carried out using a 2 N (NaOH) solution to remove any remaining proteins. The resulting chitin was then subjected to deacetylation, where it was treated with concentrated NaOH at elevated temperatures. This step removed acetyl groups from the chitin, converting it into chitosan [58]. Finally, the product was thoroughly washed to remove residual alkali, neutralized, dried, and stored for future use. The degree of deacetylation (DDA) of the chitosan was determined by titration. Specifically, 150 mg of chitosan was dissolved in 10 mL of 0.1 N HCl, and the solution was titrated with 0.1 N NaOH, measuring conductivity after each addition of NaOH. The percentage of deacetylation was determined using Eq. (1):

$$DDA\% = \frac{203 \times (V_2 - V_1) \times N}{m + 42(V_2 - V_1) \times N} \times 100$$
(1)

where:  $V_1$  and  $V_2$  are the equivalent volumes of NaOH, N is the normality of NaOH, and m is the mass of chitosan. The calculated degree of



Fig. 1. Representation of the extraction process of cellulose from cactus.

deacetylation (DDA) of the chitosan was 92.2 %.

## 2.2.3. Preparation of Chitosan@EDTA@Cellulose composite

The Chitosan@EDTA@Cellulose composite was prepared by first dissolving 1 g of chitosan in acetic acid and stirring for 24 h to obtain a homogeneous structure. Separately, 0.5 g of cellulose was dispersed in water for proper dispersion. EDTA was then added to the chitosan solution, allowing the formation of the chitosan@EDTA complex after 8 h of agitation. Finally, the cellulose suspension was gradually introduced into the chitosan@EDTA solution under continuous stirring, leading to the formation of the Chitosan@EDTA@Cellulose composite with uniform interaction [59]. The mixture was shaped into beads by dripping the solution into a 1 N NaOH solution, allowing the beads to solidify

[60]. The beads were left in the NaOH solution for several hours to ensure complete crosslinking and structural integrity. Finally, they were washed repeatedly with distilled water to remove excess alkali. Fig. 2 illustrates the beads formation process of Chitosan@EDTA@Cellulose [61].

## 2.3. Instruments for characterization

The characterization of the synthesized materials, including cellulose, chitosan, and the Chitosan@EDTA@Cellulose composite, was carried out using various analytical techniques to assess their structural, morphological, and surface properties. Fourier-transform infrared spectroscopy (FTIR) was employed to verify the presence of key



Fig. 2. Representation of beads formation process of Chitosan@EDTA@Cellulose.

functional groups and ensure the proper synthesis of the Chitosan@EDTA@Cellulose composite before adsorption. After the adsorption process, FTIR was used to observe any shifts or changes in the functional groups, indicating interactions between the composite materials and the Methyl Orange dye. [62]. X-ray diffraction (XRD) was used to investigate the crystalline structure of the materials, offering insights into crystallinity changes upon composite formation [63]. The surface area and porosity of the Chitosan@EDTA@Cellulose beads were analyzed using Brunauer-Emmett-Teller (BET) measurements to assess the material's adsorption capacity [64]. Scanning electron microscopy (SEM) was used to examine the surface morphology of cellulose, chitosan, and the composite beads before and after the adsorption process. Before adsorption, SEM provided insights into surface texture, and structural homogeneity of the materials, allowing a detailed view of their initial characteristics. After the adsorption process, SEM was employed again to analyze any changes in the surface morphology.

## 2.4. Surface charge and zero point of charge (pHzpc)

The surface charge of cellulose, chitosan, and the Chitosan n@EDTA@Cellulose composite was evaluated by determining their point of zero charge (pHpzc). The pHpzc is the pH at which the material's surface has no net electrical charge, making it crucial for predicting the adsorption behavior of methyl orange (MO) [65]. The point of zero charge (pHzpc) was measured using the pH drift method [66]. For each material, 0.1 g was dispersed in sodium chloride (NaCl) solutions with an initial pH range of 2 to 12, adjusted using acide chlorhydrique (HCl), and sodium hydroxide (NaOH). After allowing the system to reach equilibrium, the final pH of each solution was recorded. The pHpzc was determined as the point where the initial and final pH values showed no significant change [67].

## 2.5. Chemical stability

Chemical stability is a critical factor in determining the durability and performance of materials, especially in applications where they are exposed to varying environmental conditions [68]. In In this study, the chemical stability of chitosan, cellulose, and the Chitosan@EDTA@-Cellulose composite was evaluated by examining the deformation behavior of chitosan and Chitosan@EDTA@Cellulose beads, as well as cellulose powder, under different pH conditions ranging from pH 2 to pH 10). The materials were subjected to these pH conditions for a specific duration, and the degree of deformation was monitored. The extent of deformation at each pH level served as an indicator of the materials' chemical stability.

## 3. Adsorption

#### 3.1. Adsorbate preparation

The preparation of the adsorbate, methyl orange, began with the preparation of a stock solution at a concentration of 1 g/L. To achieve this, 1 g of methyl orange (MO) dye was accurately weighed using an analytical balance and then dissolved in 1 L of distilled water [69]. To achieve this, 1 g of methyl orange (MO) dye was accurately weighed using an analytical balance and dissolved in 1 L of distilled water. The solution was prepared by vigorous stirring to ensure complete dissolution of the dye, resulting in a uniform adsorbate. This 1 g/L concentration was selected to evaluate the adsorption capacity of chitosan, cellulose, and Chitosan@EDTA@Cellulose beads. The prepared solution was stored in a clean, labeled container for subsequent experiments.

The optimum conditions for Methyl Orange removal using these adsorbents were determined by evaluating the effects of various factors, including adsorbent mass (0.02–2 g), solution pH (2–12), dye concentration (25–300 mg/L), and temperature (25–55 °C). These parameters were systematically tested to identify the conditions that maximize the

adsorption efficiency of Methyl Orange (MO) using chitosan, cellulose, and Chitosan@EDTA@Cellulose beads.

## 3.2. Study of MO adsorption kinetics

## 3.2.1. Effect of contact time on adsorption efficiency

The adsorption kinetics of Methyl Orange (MO) onto chitosan, cellulose, and Chitosan@EDTA@Cellulose beads were studied by evaluating the effect of contact time on dye removal efficiency. For each experiment, 0.1 g of adsorbent was mixed with 50 mg/L of methyl orange (MO) solution, and samples were collected at intervals ranging from 10 to 150 min to assess the adsorption rate. The adsorption efficiency (R%) and adsorption capacity (qe, mg/g) were calculated based on Eqs. (2) and (3), respectively [70]. The concentration of methyl orange (MO) in the solution was measured using spectrophotometry at its maximum absorption wavelength ( $\lambda_{max}$ ), which is approximately 464 nm [71].

$$Q_e = (C_i - C_e) \times \frac{V}{m} \tag{2}$$

$$R\% = \left(\frac{C_i - C_e}{C_i}\right) \times 100\tag{3}$$

where:  $C_i$  represents the initial dye concentration in the solution (mg/L), while  $C_e$  denotes the equilibrium dye concentration (mg/L). V stands for the volume of the solution (L), and m represents the mass of the adsorbent (g).

## 3.3. Study of MO adsorption kinetics

#### 3.3.1. Modeling the adsorption kinetics

The adsorption kinetics of Methyl Orange (MO) dye onto chitosan, cellulose, and the Chitosan@EDTA@Cellulose composite were modeled using various kinetic models to understand the adsorption rate and mechanism. The kinetic parameters derived from these models helped in evaluating the effectiveness and potential of each adsorbent for Methyl Orange removal.

*3.3.1.1. Pseudo-first-order kinetics.* To gain a deeper understanding of the adsorption kinetics of methyl orange (MO) onto chitosan, cellulose, and Chitosan@EDTA@Cellulose beads, the pseudo-first-order kinetic model was applied to analyze the experimental data. This model operates on the principle that the rate of adsorption is directly proportional to the difference between the maximum adsorption capacity and the quantity of dye adsorbed at any given time [72]. Eq. (4) expresses the linear form of the pseudo-first-order model [30]:

$$ln(Q_e - Q_t) = lnQ_e - k_1 t \tag{4}$$

In this equation,  $Q_e$  represents the equilibrium adsorption capacity (mg/g), while  $Q_t$  denotes the adsorption capacity at time t (mg/g).  $k_1$  is the pseudo-first-order rate constant for adsorption, and t represents time.

*3.3.1.2. Pseudo-second-order kinetics.* The pseudo-second-order kinetic model suggests that the adsorption process is influenced by more complex interactions, such as chemical bonding or the involvement of multiple adsorption sites. This model indicates that the system approaches equilibrium more gradually, particularly at higher dye concentrations [36]. Eq. (5) present the linear form of the pseudo-second-order model [73].

$$\frac{t}{Q_t} = \frac{1}{k_2(Q_e)^2} + \frac{t}{Q_e}$$
(5)

In this equation,  $k_2$  represents the rate constant for the pseudo-second-order adsorption.

*3.3.1.3. Elovich model.* The Elovich model is commonly used to describe adsorption processes on heterogeneous surfaces, where the adsorption rate decreases exponentially with increasing surface coverage [74]. It is particularly applicable to systems involving chemisorption. The Elovich model is represented by Eq. (6):

$$Q_{t} = \frac{1}{\beta} ln \left(\alpha\beta\right) + \frac{1}{\beta} ln \left(t\right)$$
(6)

where:  $Q_t$  is the amount of adsorbate adsorbed at time t (mg/g),  $\alpha$  is the initial adsorption rate (mg/g·min),  $\beta$  is a constant related to the extent of surface coverage and the activation energy for chemisorption (g/mg), and t represents time (min). This model assumes that the adsorption sites are heterogeneous and that no desorption occurs during the process.

*3.3.1.4. Intraparticle diffusion model.* The intraparticle diffusion model is used to evaluate the role of diffusion in the adsorption process, particularly within porous adsorbents. This model is expressed by Eq. (7):

$$Q_t = k_{id} t^{0.5} + C_{id} \tag{7}$$

where:  $Q_t$  is the amount of adsorbate adsorbed at time t (mg/g),  $k_{id}$  represents the intraparticle diffusion rate constant (mg/g·min<sup>0.5</sup>), t is the time (min), and  $C_{id}$  is a constant that reflects the thickness of the boundary layer (mg/g).

## 3.4. Adsorption isotherm

#### 3.4.1. The Langmuir model

In our study, the adsorption of methyl orange (MO) onto chitosan, cellulose, and Chitosan@EDTA@Cellulose beads was evaluated using the Langmuir adsorption isotherm model. This model is relevant for exploring the adsorption characteristics and capacities of materials, assuming that adsorption occurs at distinct, uniform sites on the adsorbent surface [75]. The Langmuir model is represented by the Eq. (8):

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \tag{8}$$

where:  $C_e$  is the equilibrium concentration of the adsorbate in the solution (mg/L),  $Q_e$  is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g),  $Q_m$  is the maximum adsorption capacity of the adsorbent (mg/g), and  $K_L$  is the Langmuir constant related to the affinity of the adsorbate for the adsorbent (L/mg).

#### 3.4.2. The Freundlich model

This model is particularly useful as it accounts for heterogeneous adsorption sites on the adsorbent surface and is expressed [76]. This model is expressed by the following Eq. (9):

$$ln(Q_e) = ln(K_F) + \frac{1}{n_F} ln(C_e)$$
(9)

where:  $Q_e$  represents the amount of dye adsorbed at equilibrium (mg/g),  $C_e$  is the equilibrium concentration of the dye in the solution (mg/L),  $K_F$  is the Freundlich constant indicative of the adsorption capacity, and n is a dimensionless constant that reflects the adsorption intensity. A value of  $n_F < 1$  suggests favorable adsorption conditions, while  $n_F > 1$  indicates that adsorption becomes less favorable as the concentration increases [61].

## 3.4.3. The Temkin model

The Temkin adsorption model considers the effects of indirect adsorbate-adsorbent interactions and assumes that the heat of adsorption of all molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate interactions [77]. This model is expressed by Eq. (10):

$$ln(Q_e) = \frac{RT}{b} lnK_T + \frac{RT}{b} C_e$$
(10)

where: Qe is the amount of dye adsorbed at equilibrium (mg/g), Ce is the equilibrium concentration of the dye in the solution (mg/L),  $K_T$  is the Temkin constant related to the equilibrium binding constant (L/g), R is the universal gas constant (8.314 J/mol·K), T is the absolute temperature (K), and b is the Temkin constant related to the heat of adsorption (J/mol).

## 3.4.4. The Dubinin-Radushkevich (D-R) model

The Dubinin-Radushkevich (D-R) model is used to describe adsorption on microporous adsorbents and to differentiate between physical and chemical adsorption. It provides insights into the adsorption mechanism based on the potential energy of the adsorbate molecules and the adsorption sites. The Dubinin-Radushkevich (D-R) model assumes that the adsorption process involves a heterogeneous surface with a distribution of adsorption energies. The D-R model described by Eq. (11):

$$\ln Q_e = \ln Q_{DR} - \beta_{DR} \varepsilon^2 \tag{11}$$

where:  $\beta_{DR} (mol^2/J^2)$  and  $Q_{DR} (mg/g)$  represent the constants of the Dubinin-Radushkevich (D-R) isotherm model;  $\epsilon$  is the Polanyi potential, determined using Eq. (12):

$$\varepsilon = RTln\left(1 + \frac{1}{Ce}\right) \tag{12}$$

where: R is the universal gas constant (8.314 J/mol·K) and T is the absolute temperature (K).

## 3.5. Adsorption thermodynamic

The study of adsorption thermodynamics is crucial for understanding the energetics of methyl orange (MO) removal using chitosan, cellulose, and Chitosan@EDTA@Cellulose beads. Analyzing the thermodynamic parameters provides insights into the nature of the adsorption interactions and the stability of the formed complexes [78]. Key thermodynamic parameters, such as Gibbs free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ), and entropy change ( $\Delta S^\circ$ ), can be calculated to offer a comprehensive understanding of the adsorption process [79]. Eqs. (13), (14), and (15) present the relationships for these thermodynamic parameters.

$$K_e = \frac{Qe}{Ce} \times W \tag{13}$$

$$lnK_e = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$
(14)

$$\Delta G^{\circ} = -RT ln K_e \tag{15}$$

where: Qe is the amount of adsorbate at equilibrium (mg/g), Ce is the concentration of adsorbate at equilibrium (mg/L), W is the weight of the adsorbent per solution volume (g/L), T is the absolute temperature in Kelvin, and Ke represents the adsorption equilibrium constant.

## 3.6. Effect of interfering ions on adsorption performance

This study evaluates the extent to which these ions influence the adsorption process, providing insights into the practical application of these materials in complex aqueous environments. To investigate the impact of interfering ions on the adsorption of Methyl Orange, solutions of sodium (Na<sup>+</sup>), calcium (Ca<sup>2+</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>), and nitrate (NO<sub>3</sub><sup>-</sup>) ions were prepared at a concentration of 50 mg/L. These ions, commonly found in natural and wastewater systems, were chosen to

assess their potential to compete with Methyl Orange for adsorption sites. Separate stock solutions of sodium, calcium, sulfate, and nitrate ions were prepared using analytical-grade NaCl, CaCl<sub>2</sub>·2H<sub>2</sub>O, Na<sub>2</sub>SO<sub>4</sub>, and KNO<sub>3</sub>, respectively. A 50 mg/L stock solution of Methyl Orange was prepared and mixed with the ion solutions. Adsorption experiments were performed using chitosan, cellulose, and Chitosan@EDTA@-Cellulose as adsorbents under controlled conditions.

## 3.7. Reusability and regeneration of adsorbents

The reusability of the adsorbents, including chitosan, cellulose, and Chitosan@EDTA@Cellulose, was assessed over four consecutive cycles. After each adsorption cycle, the adsorbents were regenerated using a 0.1 M NaOH solution under constant stirring to facilitate dye desorption. Subsequently, they were washed with distilled water to remove residual alkali and any desorbed dye before reuse. This process was repeated for four cycles to evaluate the regeneration efficiency and adsorption stability of the materials [77].

## 4. Box-Behnken Design

The Box-Behnken Design (BBD) is a statistical method used in Response Surface Methodology (RSM) to optimize processes and products. Developed by George E. P. Box and D. Behnken in 1960, BBD is effective for studying the relationships between multiple independent variables and their effects on a dependent response, especially with a limited number of trials. Unlike other designs, such as the central composite design, BBD does not require experiments at extreme factor levels, reducing the risk of experimental failure or costly errors [80].

BBD is highly efficient in exploring quadratic response surfaces, making it ideal for optimizing complex systems where variable interactions significantly impact outcomes. It is well-suited for evaluating non-linear relationships and enables comprehensive modeling of both main effects and interactions [81]. The response (Yi) can be described by a second-order polynomial Eq. (16):

$$Y_{i} = \beta_{0} + \sum_{i=1}^{n} (\beta_{i}X_{i}) + \sum_{i=1}^{n} (\beta_{ii}X_{i}^{2}) + \sum_{i=1}^{n-1} \sum_{j=1}^{n} (\beta_{ij}X_{i}X_{j})$$
(16)

where: Y is the predicted response,  $\beta_0$  is the intercept,  $\beta_i$  represents the linear coefficients,  $\beta_{ii}$  represents the quadratic coefficients, and  $\beta_{ii}$  represents the interaction coefficients between factors X<sub>i</sub> and X<sub>i</sub> [82]. In this study, Design Expert software was used to implement the Box-Behnken Design (BBD) model, optimizing the removal of methyl orange (MO) dye from aqueous solutions [83]. Three factors were selected for optimization: the mass of adsorbent (chitosan, cellulose, and Chitosan@EDTA@Cellulose), pH, and the initial MO concentration. Table 1 presents the experimental factors and levels used in the BBD to optimize MO removal. Design Expert was used to generate experimental runs, systematically varying these parameters and creating a response surface model to predict MO removal efficiency. Three responses were evaluated: MO removal using chitosan, cellulose, and Chitosan@EDTA@-Cellulose. The software enabled precise statistical analysis, revealing key interactions between variables and highlighting the significant effect of adsorbent type on removal efficiency [18]. The Chitosan@EDTA@Cellulose composite exhibited the highest MO adsorption capacity, attributed to the synergistic effects of chitosan and EDTA functional groups. The Chitosan@EDTA@Cellulose composite exhibited

Table 1

Experimental factors and levels for Box-Behnken Design.

Factor	Name	Units	Minimum	Maximum	Mean
A B C	Mass of adsorbent pH [MO]	g mg/l	0.0200 4.00 50.00	0.2000 8.00 200.00	0.1100 6.00 125.00

the highest MO adsorption capacity, attributed to the synergistic effects of chitosan and EDTA functional groups. Table 2 summarizes the experimental data, detailing the MO removal efficiency for chitosan, cellulose, and Chitosan@EDTA@Cellulose beads under varying conditions of adsorbent mass, pH, and initial concentration.

# 5. Mechanism and calculations of Density Functional Theory (DFT)

In our study, we conducted quantum analyses using Density Functional Theory (DFT) with the Gaussian09W program and Gauss View 5.0.8 software to investigate the electronic structure and properties of chitosan, cellulose, and Chitosan@EDTA@Cellulose beads, focusing on their interactions with methyl orange (MO) [84]. We employed the B3LYP hybrid functional method and the 6-31G(d,p) basis set for accurate geometry optimization and energy calculations [85]. The primary objective was to understand the adsorption mechanisms of methyl orange (MO) on these adsorbents by examining the energetic and structural characteristics of their interactions [86]. We calculated the energies of the Highest Occupied Molecular Orbital (HOMO), the Lowest Unoccupied Molecular Orbital (LUMO), and the energy gap ( $\Delta$ Egap) between them [19]. The optimized molecular geometry revealed the binding sites and stability of complexes, which helped predict the adsorption capacity. For cellulose, its hydroxyl groups enhance adsorption through hydrogen bonding with the dye. Density Functional Theory (DFT) calculations demonstrated how variations in molecular arrangement influence the adsorption process [19]. For Chitosan@EDTA@Cellulose beads, the Density Functional Theory (DFT) analvsis highlighted how the inclusion of EDTA alters the electronic properties and binding characteristics of the composite material [54]. By examining the electron density distribution and molecular orbitals, we could assess the enhanced affinity of the modified adsorbent for methyl orange. The parameters were calculated using the following formulas: Eqs. (17), (18), and (19) are employed to determine the electronic chemical potential ( $\mu$ ), absolute hardness ( $\eta$ ), and softness ( $\sigma$ ), based on the Highest Occupied Molecular Orbital (EHOMO) and Lowest Unoccupied Molecular Orbital (ELUMO) values [87], electrophilicity (a) [88]. The presence of EDTA is expected to introduce additional coordination sites, further promoting interaction with the dye and potentially leading to improved adsorption performance.

$$\Delta E_{Gap} = E_{Lumo} - E_{Homo} \tag{17}$$

$$\eta = \frac{E_{Lumo} - E_{Homo}}{2} \tag{18}$$

$$x = \frac{-(E_{Homo} - E_{Lumo})}{2} \tag{19}$$

The overall softness (S) is the inverse of the overall hardness according to Eq. (20):

$$S = \frac{1}{\eta} \tag{20}$$

The electrophilicity index  $\omega$  is determined by applying Parr's concept according to the Eq. (21):

$$\omega = \frac{x^2}{2\eta} \tag{21}$$

#### 6. Results and discussion

### 6.1. Characterization

## 6.1.1. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra in Fig. 3 confirm the extraction of cellulose from cactus and chitosan from shrimp, highlighting interactions within the

#### Table 2

Experimental data for Methyl Orange (MO) removal using chitosan, cellulose, and Chitosan@EDTA@Cellulose beads.

	Mass of adsorbent	pH	[MO]	[MO] removal with chitosan	[MO] removal with cellulose	[MO] removal with Chitosan@EDTA@Cellulose
1	0.2	6	50	80.23	53.63	73.78
2	0.11	4	50	69.3	58.57	78.32
3	0.2	8	125	37.22	29	49.87
4	0.02	8	125	5.88	4.48	24.48
5	0.11	8	50	48.68	30.66	50.53
6	0.11	6	125	40.23	35.6	55.33
7	0.11	6	125	40.23	35.67	55.34
8	0.02	6	50	26.12	9.25	29.02
9	0.11	6	125	40.23	35.88	55.83
10	0.02	4	125	12.28	27.09	47.12
11	0.02	6	200	15.49	4.20	24.21
12	0.11	8	200	29.38	10.23	30.23
13	0.11	6	125	40.23	35.6	55.21
14	0.11	4	200	23.9	40.6	60.35
15	0.2	4	125	45.55	64.55	84.78
16	0.11	6	125	40.23	35.67	55
17	0.2	6	200	25.56	20.3	40.89

composite. The broad band at 3265  $\text{cm}^{-1}$  (Fig. 3a) corresponds to O–H stretching, indicating the presence of hydroxyl groups typically found in water and polysaccharides like cellulose [89]. The band at 2924 cm<sup>-1</sup>, characteristic of C-H stretching vibrations from aliphatic chains, confirms the organic nature of the material [90]. Additionally, the absorption band at 1621 cm<sup>-1</sup> is attributed to C=O stretching, likely from carboxyl groups, suggesting the presence of pectin or hemicellulose [91]. Another important band at 1412 cm<sup>-1</sup> corresponds to O-H deformation or C—H bending, further indicating the presence of plantbased polysaccharides [92]. The strong band at 1034 cm<sup>-1</sup>, associated with C-O-C stretching, indicates the presence of cellulose or related polysaccharides [93], supporting the successful extraction of cellulose from cactus [27]. For the cellulose extracted from cactus (Fig. 3B), the broad absorption at 3361 cm<sup>-1</sup>, characteristic of O-H stretching, indicates the presence of cellulose's extensive hydrogen bond network [94]. The C—H stretching vibration at 2906 cm<sup>-1</sup> is also consistent with the aliphatic structure of cellulose [95]. A notable band at 1648  $\rm cm^{-1}$ corresponds to O-H bending from adsorbed water, highlighting cellulose's hydrophilic nature [96]. The band at 1510 cm<sup>-1</sup> may indicate some residual lignin or hemicellulose, while the sharp band at 1034 cm<sup>-1</sup> (also observed in the cactus sample) confirms C–O–C stretching, characteristic of the  $\beta$ -glucosidic linkages in cellulose [91]. These features collectively verify the presence of high-purity cellulose [97]. The chitosan spectrum (Fig. 3c) reveals a broad band at 3322 cm<sup>-1</sup>, characteristic of both O-H and N-H stretching, expected due to the presence of hydroxyl and amine groups in chitosan's structure [98]. The smaller bands at 2865 and 2355 cm<sup>-1</sup> correspond to C-H stretching, associated with the aliphatic backbone of chitosan [99]. The strong band at 1659 cm<sup>-1</sup> is assigned to amide I vibrations (C=O stretching), confirming the partial deacetylation of chitin to form chitosan [100]. The absorption at 1557 cm<sup>-1</sup>, corresponding to N-H bending (amide II), further supports the presence of amide groups [101]. Additionally, the band at 1386 cm<sup>-1</sup> likely arises from C—N stretching vibrations, while the C-O stretching band at 1034 cm<sup>-1</sup> is consistent with the polysaccharide structure of chitosan [102]. The FTIR spectra of chitosan@EDTA (Fig. 3d) and Chitosan@EDTA@Cellulose (Fig. 3e) reveal significant interactions within the respective systems. For chitosan@EDTA (Fig. 3d), the broad band at 3377  $\text{cm}^{-1}$ , representing O—H and N-H stretching vibrations, becomes more pronounced, reflecting enhanced hydrogen bonding due to the introduction of carboxyl groups from EDTA. The increased intensity of peaks at 1661  $\rm cm^{-1}$  (C=O stretching), 1482 cm<sup>-1</sup> (C—N stretching), 1373 cm<sup>-1</sup> (C—H bending), and 1064 cm<sup>-1</sup> (C—O stretching) confirms the successful chemical grafting of EDTA onto chitosan [103]. These spectral changes highlight the formation of strong interactions between the amine groups of chitosan and the carboxyl groups of EDTA [104]. For

Chitosan@EDTA@Cellulose (Fig. 3e), additional changes indicate strong interactions between chitosan, EDTA, and cellulose. The broad O—H and N—H stretching band shifts to 3291 cm<sup>-1</sup>, reflecting extensive hydrogen bonding between cellulose and chitosan. The band at 1556 cm<sup>-1</sup>, attributed to N-H bending, confirms interactions between the amine groups of chitosan and the carboxyl groups of EDTA. The presence of the band at 1447 cm<sup>-1</sup>, characteristic of C-H deformation, suggests contributions from both cellulose and chitosan. Furthermore, the appearance of a new band at 863  $\text{cm}^{-1}$  highlights the interactions between EDTA and the composite matrix. These observations validate the successful integration of cellulose into the chitosan@EDTA structure, forming a robust composite material. The FTIR spectra of chitosan, cellulose, and Chitosan@EDTA@Cellulose after Methyl Orange adsorption (Fig. 3f) exhibit significant spectral shifts, confirming successful dye adsorption onto the materials. For chitosan (Fig. 3f(A)), the broad O-H and N-H stretching band shifts from 3329 cm<sup>-1</sup> to 3309 cm<sup>-1</sup>, indicating hydrogen bonding interactions, while the C–O stretching band at 1034 cm<sup>-1</sup> shifts to 1022 cm<sup>-1</sup>, suggesting electrostatic attraction between protonated amine groups and the anionic dye molecules. In cellulose (Fig. 3f(B)), the O-H stretching band moves from 3319 cm<sup>-1</sup> to 3313 cm<sup>-1</sup>. Furthermore, the C–O stretching vibrations at 1034 cm<sup>-1</sup> shift to 1039 cm<sup>-1</sup>, indicating structural modifications due to dye binding. Chitosan@EDTA@Cellulose composite (Fig. 6f(C)), the O—H and N—H stretching band shifts from 3291 cm<sup>-1</sup> to 3251 cm<sup>-1</sup>, and the C=O stretching band at 1556 cm<sup>-1</sup>, attributed to N-H bending, moves to 1560 cm<sup>-1</sup>, reinforcing the presence of electrostatic interactions and hydrogen bonding. Additionally, the C-O stretching band at 1025 cm<sup>-1</sup> shifts to 1039 cm<sup>-1</sup>, indicating changes in the polysaccharide structure due to dye adsorption. The peak at 1447 cm<sup>-1</sup>, associated with C—H deformation, shifts to 1433 cm<sup>-1</sup>, further supporting structural modifications upon adsorption.

## 6.1.2. Scanning electron microscopy (SEM)

6.1.2.1. SEM images before adsorption. The SEM images provide a detailed view of the structural morphology of cactus, cellulose, chitosan, and Chitosan@EDTA@Cellulose beads, highlighting key differences in their surface characteristics. For the cactus (Fig. 4a), the images show a rough, fibrous surface with irregularly shaped particles. The cactus material exhibits a web-like structure with loose fibers and a porous, uneven texture [52]. These natural fibers contribute to the material's structural integrity, featuring visible cavities and voids throughout the surface. This fibrous network is typical of plant-based materials, which are often utilized in various applications due to their mechanical strength and versatility [93]. In the case of cellulose (Fig. 4b), extracted from cactus, the SEM images reveal a more refined and organized



Fig. 3. Infrared spectra of: (a) cactus, (b) cellulose, (c) chitosan, (d) chitosan@EDTA, (e) Chitosan@EDTA@Cellulose, and (f) FTIR of (A) chitosan, (B) cellulose, and (C) Chitosan@EDTA@Cellulose after Methyl Orange adsorption.

fibrous structure compared to the raw cactus. The cellulose fibers appear tighter and more compact, forming a dense network [27]. The uniformity of the fibers enhances the material's mechanical properties, providing stability and durability. Cellulose exhibits a layered, interconnected structure that helps maintain its shape [91]. The refining of cactus into cellulose highlights the increase in structural regularity and compactness of the fibers. For chitosan (Fig. 4c), the SEM images reveal a much smoother and less fibrous surface compared to cactus or cellulose. Chitosan appears as layered flakes with some fibrous formations; however, the overall surface is more compact and organized [105]. Chitosan's morphology reflects its biopolymer nature, resulting in sheetlike structures. Finally, the Chitosan@EDTA@Cellulose composite beads (Fig. 4d) exhibit a highly porous structure with a rough, uneven surface, which is critical for efficient adsorption of pollutants like methyl orange



Fig. 4. SEM images of: (a) cactus, (b) cellulose, (c) chitosan, and (d) Chitosan@EDTA@Cellulose before adsorption.

(MO). The SEM images of the bead show enhanced porosity, allowing for a larger surface area and more binding sites. The roughness and interconnected pores suggest that the beads are well-suited for trapping MO [106], making them an effective adsorbent material.

6.1.2.2. SEM images after adsorption. The SEM analysis of the materials after the adsorption of Methyl Orange (MO) reveals notable differences in surface morphology among chitosan, cellulose, and the Chitosan@EDTA@Cellulose composite. The surface of chitosan, as shown in (Fig. 5a), exhibits a smoother appearance with a noticeable reduction in porosity following the adsorption process. This suggests that the surface of chitosan became less distinct as they were partially covered by the adsorbed dye molecules. In contrast, the surface of cellulose, presented in (Fig. 5b), shows minimal changes after adsorption, maintaining a relatively smooth and unaltered texture, indicating that it was not significantly impacted by the presence of MO. This suggests that cellulose interacted only weakly with the dye, resulting in limited morphological transformation. However, the Chitosan@EDTA@Cellulose composite, displayed in (Fig. 5c), demonstrates the most striking change in surface morphology. After adsorption, its surface appears compact and densely packed, with the pores effectively masked or entirely covered by the deposited MO molecules.

#### 6.1.3. X-ray diffraction (XRD)

The Segal method, commonly referred to as the peak height method, is a widely recognized analytical approach for assessing the crystallinity of cellulose samples [97]. This technique involves determining the crystallinity index (CrI) by comparing the intensity of the diffraction peak corresponding to crystalline cellulose (I<sub>a</sub>c) at approximately  $2\theta = 22.2605^{\circ}$  with the intensity of the amorphous phase (I<sub>a</sub>m) at  $2\theta = 20.53^{\circ}$ , which represents the minimum intensity in the diffraction pattern. The crystallinity index is calculated using the following Eq. (22):

$$\operatorname{CrI}(\%) = \frac{I_C - I_{am}}{I_c} \times 100 \tag{22}$$

The average size of the crystal units was determined using the Scherrer equation Eq. (23) as described in [107]. This method relies on the half-value width of the diffraction peaks observed in the X-ray diffraction pattern of the crystalline region. The crystallite size ( $L_{hkl}$ ) was calculated based on the diffraction pattern data.

$$L_{hkl} = \frac{K\lambda}{\beta \cos\theta}$$
(23)

where k is the Scherrer constant whose value is 0.94,  $\lambda$  is the wavelength of the X-ray (0.154 nm),  $\beta$  in radians is the total width of the diffraction peak and  $\theta$  is the corresponding Bragg angle. In Fig. 6a, the diffractogram of cactus reveals several characteristic peaks: 14.42° corresponds to weddellite, 14.93° to whewellite, another at 24.40° to whewellite, with the main peak at 29.45° indicating calcite. Peaks at 36.05°, 39.48°, and 42.90° are attributed to both whewellite and calcite, while 48.57° represents whewellite. Finally, 60.80° and 62.29° are assigned to calcite. Studies by Contreras-Padilla et al. [108], and Rojas-Molina et al. [109],



Fig. 5. SEM images of: (a) chitosan, (b) cellulose, and (c) Chitosan@EDTA@Cellulose after adsorption.



Fig. 6. X-ray diffraction (XRD) patterns of: (a) cactus, (b) cellulose, (c) chitosan, and (d) Chitosan@EDTA@Cellulose.

identified two distinct peaks for oxalate monohydrate at  $14-15^{\circ}$  and 24–25° (2 $\theta$ ) in various Cactaceae species, particularly within the Opuntioideae subfamily, such as Opuntia ficus-indica, consistent with the PDF #20-0231 from the ICDD-JCPDS database. These authors also observed prominent peaks for calcium carbonate at 29-30°, 39-40°, and 45–50° (2 $\theta$ ), aligning with the PDF #47-1743 reference, confirming calcium carbonate (CaCO<sub>3</sub>) presence in the cactus samples. In (Fig. 6b), the X-ray diffraction (XRD) pattern of cellulose extracted from cactus reveals peaks at 20 values of 15.93°, 22.2605°, and 34.42°, which correspond to the cellulose I $\alpha$  and I $\beta$  allomorphs [32]. These distinct peaks reflect the crystalline phases commonly found in native cellulose, where cellulose I $\alpha$  has a triclinic unit cell structure, and cellulose I $\beta$  has a monoclinic unit cell structure. The ratio between these allomorphs varies based on the cellulose's source, influencing its crystallinity and structural properties [110]. The peak detected at approximately 22.2605° in the X-ray diffraction (XRD) pattern corresponds to the (200) crystallographic plane of cellulose IB, typically observed near 22.5° [91]. In proximity to the (200) peak at 22,2605°, an amorphous phase is detected around  $2\theta = 20.53^{\circ}$ , primarily attributed to lignin. Lignin is a component closely associated with the cell wall structure and contributes significantly to the mechanical strength of wood by providing rigidity and resistance to compression [111]. The (110) plane of cellulose Iα produces prominent peaks at 15.8834°, confirming the presence of cellulose I $\alpha$  and emphasizing the structural distinctions between the I $\alpha$ and I $\beta$  allomorphs. In (Fig. 6c), the diffractogram of chitosan shows a combination of both the  $\alpha$  and  $\beta$  forms. The two prominent diffraction peaks, with the highest intensities between 20 ranges of 7.77°-13.45° and 17.23°-25.53°, are primarily associated with the hydrated crystalline planes (020) and (110). Secondary peaks characteristic of the  $\alpha$  form are also present, with typical peaks around 12.8° and 22.8°, corresponding to the anhydrous planes (110) a and (120) a reflections, respectively Crystallinity index and the crystal size were determined as described earlier. The (Fig. 6d) illustrates the X-ray diffraction (XRD) pattern of the composite synthesized from chitosan and cellulose, with EDTA serving as a chelating agent. Distinct peaks are observed at  $2\theta$ angles of 14.94°, 22.60°, and 34.54°, which are characteristic of the cellulose I $\alpha$  and I $\beta$  allomorphs. Native cellulose typically presents a mixture of these crystalline phases, where cellulose Ia has a triclinic unit cell and cellulose I $\beta$  has a monoclinic unit cell, with the ratio of these forms varying based on the cellulose's source [112].

Additional peaks at  $10.32^{\circ}$ ,  $19.97^{\circ}$ , and  $20.41^{\circ}$  are characteristic of chitosan, primarily corresponding to the hydrated planes (020) and (110), which reflect the crystalline structure of chitosan within the composite. Table 3 present the crystal peaks of cactus, cellulose,

#### Table 3

Lict	of	crystal	neal
LIST	OI.	crystat	bea

chitosan, Chitosan@EDTA@Cellulose.

## 6.1.4. Adsorption/desorption analysis with $N_2$ (BET)

The provided Fig. 7 illustrates the adsorption and desorption behavior of nitrogen (N2) for the three distinct materials: Chitosan, Cellulose, and Chitosan@EDTA@Cellulose, as depicted by their respective isotherm curves. Table 4 presents the quantitative findings from the BET (Brunauer-Emmett-Teller) analysis, detailing the surface area, pore volume, and pore size for each material [113]. The BET analysis results provide critical insights into the surface properties and porosity of chitosan, cellulose, and Chitosan@EDTA@Cellulose. Chitosan exhibited a BET surface area of 11.5180 m<sup>2</sup>/g, a pore volume of  $0.009779 \text{ cm}^3/\text{g}$ , and an average pore size of 3.3960 nm, reflecting its mesoporous structure. Cellulose showed a slightly lower surface area of 7.7890  $m^2/g$  and a comparable pore size of 3.4109 nm, indicating similar mesoporous characteristics. In contrast, Chitosan@EDTA@-Cellulose demonstrated a significant enhancement in surface area, reaching 32.2453  $m^2/g$ , which is nearly three times that of chitosan. This increase is attributed to the incorporation of EDTA and the synergistic effects of the composite formation, which create more active adsorption sites. The slight reduction in pore size (3.3102 nm) and pore volume (0.008012  $\text{cm}^3/\text{g}$ ) for the composite suggests structural modifications, likely due to EDTA functionalization partially occupying the pore spaces. The isotherms confirm the mesoporous nature of all materials, corresponding to Type IV isotherms, which are characteristic of mesoporous structures. Among them, Chitosan@EDTA@Cellulose exhibited the highest nitrogen adsorption. These observations highlight the significance of BET analysis in understanding surface area enhancements and structural modifications critical for adsorption performance [114,115]. BET analysis is crucial in understanding the structural properties of adsorbents, as demonstrated in previous studies. Waste sludge from shipping docks, treated at 400 °C, showed a decrease in BET surface area from 4.4  $m^2/g$  to 3.6  $m^2/g$  after amoxicillin (AMX) adsorption, indicating surface modifications during the process [116]. Similarly, brine-treated clay catalysts optimized for azithromycin degradation exhibited a mesoporous structure with a surface area of 11.52  $m^2/g$ , demonstrating the impact of brine-to-water ratios and calcination conditions on catalytic properties [117]. These findings highlight the importance of BET analysis in tailoring materials for effective pollutant removal.

## 6.1.5. Energy dispersive X-ray spectroscopy

Fig. 8 presents the EDS spectra and elemental composition of four materials: cactus (Fig. 8a), cellulose extracted from cactus (Fig. 8b),

Sample	Pos. (°2Th)	Height	β (radians)	(%) CrI	Lhkl (nm)
Cactus	29.45436	791.81205	0.19822	80.55 %	0.7528
	39.48436	126.76758	0.18887	46.66 %	0.8143
	42.90136	294.35875	0.17842	68.55 %	0.8717
	43.25836	114.97747	0.27496		0.5663
	48.57936	108.19931	0.2497		
Cellulose	15.8834	28.75	0.0900		
	22.2605	97.52	0.9792	35.23 %	0.1506
	24.7146	17.04	0.0900		1.6465
	34.42	1.32	0.0900		
Chitosan	10.3918	150.08	0.0900	32.05 %	
	19.0417	117.39	0.8029	26.10 %	0.1828
	21.3500	265.23	0.8029	25.13 %	0.1834
	78.9582	186.00	0.4015		0.6358
Chitosan@EDTA@Cellulose	10.3283	12.1741	0.6298		
	14.9440	415.2159	0.3936	34.49 %	0.3709
	19.9718	742.7214	0.3936		0.3734
	20.4115	666.7032	0.3936		0.3736
	22.6018	698.0891	0.0900	43.50 %	1.6402
	28.1128	44.0225	0.4723		
	34.5454	440.66	0.3149		



Fig. 7. Adsorption-desorption isotherms of cellulose, chitosan, and Chitosan@EDTA@Cellulose.

#### Table 4

Specific surface area and pore size distribution of cellulose, chitosan, and Chitosan@EDTA@Cellulose.

Materials	BET surface area (m²/g)	Pore volume (cm <sup>3</sup> /g)	Pore size (nm)
Chitosan	11.5180	0.009779	3.3960
Cellulose	7.7890	0.009923	3.4109
Chitosan@EDTA@Cellulose	32.2453	0.008012	3.3102

chitosan (Fig. 8c), and Chitosan@EDTA@Cellulose (Fig. 8d). The cactus sample shows a high carbon content (44.39 wt%) and oxygen content (20.74 wt%), along with trace amounts of magnesium, chlorine, and potassium, indicating a primarily organic composition with some mineral elements. This reflects the natural composition of plant-based materials like cactus. The cellulose extracted from cactus reveals a much higher carbon content (76.01 wt%) and oxygen content (18.45 wt%), as expected for pure cellulose, which consists mainly of polysaccharides. A small amount of cerium (5.54 wt%) is detected, which might result from residual chemicals or surface treatments used during the extraction process. Chitosan displays a high carbon content (78.66 wt%) and oxygen content (21.34 wt%), consistent with its polysaccharide structure, which includes amino and hydroxyl groups known for their binding potential. The absence of other significant elements in the chitosan sample suggests it is a relatively pure organic material. The composite Chitosan@EDTA@Cellulose shows a more varied elemental composition, with carbon (32.12 wt%) and oxygen (37.82 wt%) being dominant. This indicates that the incorporation of EDTA into the chitosan-cellulose matrix significantly alters its composition.

## 6.1.6. Chemical stability under different pH conditions

The chemical stability of chitosan, cellulose, and the Chitosan n@EDTA@Cellulose composite was evaluated across a pH range of 2 to 10, as shown in Table 5. Chitosan beads exhibited significant deformation at pH 2, with weaker structural integrity due to protonation, but showed gradual improvement in stability at pH 4–7. However, further swelling and softening occurred at pH 8–10. In contrast, cellulose maintained its structure without any deformation across the entire pH range, indicating high chemical stability. The Chitosan@EDTA@Cellulose composite beads displayed improved stability compared to pure chitosan, with minimal deformation and a stronger structure across all pH conditions, suggesting enhanced chemical stability, especially at higher pH.

## 6.2. Adsorption

## 6.2.1. Effect of contact time

Fig. 9a shows the effect of time on Methyl Orange (MO) removal by chitosan beads, cellulose, and Chitosan@EDTA@Cellulose beads. Initially, all adsorbents exhibit a rapid increase in MO removal due to the abundant active sites on their surfaces, with a fast mass transfer of MO molecules. Chitosan beads achieve 70.89 % removal in 70 min. cellulose reaches 52.87 % removal after 80 min, and Chitosan@EDTA@Cellulose beads show the highest efficiency, achieving 95.78 % removal in 55 min [118]. The rapid initial phase of Methyl Orange (MO) removal is due to the high concentration gradient between the Methyl Orange (MO) dye in the solution and the available active sites on the adsorbent surfaces. This creates a driving force for the fast mass transfer of Methyl Orange (MO) molecules toward the adsorbent. As a result, the Methyl Orange (MO) molecules quickly occupy the vacant adsorption sites, leading to a swift increase in removal efficiency. As the concentration gradient between the solution and the adsorbent decreases, the rate of adsorption slows down. [65].

## 6.2.2. Effect of mass

Fig. 9b shows the effect of adsorbent mass on Methyl Orange (MO) removal efficiency for three adsorbents: chitosan beads, cellulose, and Chitosan@EDTA@Cellulose beads. All adsorbents exhibit a rapid increase in MO removal efficiency as their mass increases, attributed to the higher availability of active sites. With only 0.1 g of Chitosan@EDTA@Cellulose, 95.78 % Methyl Orange (MO) removal was achieved, compared to 74.55 % with chitosan beads at 0.14 g and 60.77 % with cellulose at 0.16 g. Initially, the rapid adsorption phase is due to the high concentration gradient between Methyl Orange (MO) molecules and active sites. However, as adsorption progresses, the rate slows due to the depletion of active sites and the reduced concentration gradient.

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Fig. 8. EDS spectra and elemental composition of a) cactus, b) cellulose, c) chitosan, and d) Chitosan@EDTA@Cellulose.

Increased adsorbent mass may also lead to particle aggregation, reducing surface area and hindering Methyl Orange (MO) molecule access to adsorption sites [119]. However, as adsorption progresses, the rate slows due to the depletion of active sites and the reduced concentration gradient. An increase in adsorbent mass may also lead to particle aggregation, which reduces surface area and hinders Methyl Orange (MO) molecule access to adsorption sites [120].

#### 6.2.3. Effect of pH and pHzpc

Fig. 9d illustrates the effect of pH on the removal efficiency of Methyl Orange (MO) using three different adsorbents: chitosan, cellulose, and Chitosan@EDTA@Cellulose beads, along with their respective point of zero charge (pHzpc) values [121]. The results demonstrate distinct removal patterns across varying pH levels, highlighting the significant role of pH in the adsorption process [122]. Fig. 9d shows that chitosan exhibits optimal Methyl Orange removal of 80.88 % at a pH of 6, while cellulose reaches a maximum removal efficiency of 64.78 % at a pH of 4. The Chitosan@EDTA@Cellulose composite demonstrates the highest efficiency, achieving 97.7 % MO removal at a pH of 5. These results are closely linked to the point of zero charge (pHzpc) values of the adsorbents: chitosan (pHzpc 6.37) shown in Fig. 9c(A), cellulose (pHzpc 4) shown in Fig. 9-c(B), and Chitosan@EDTA@Cellulose (pHzpc 5.17) shown in Fig. 9-c(C). Understanding the pHzpc is crucial as it determines the surface charge of the adsorbent at various pH levels. When the pH is below the pHzpc, the surface of the adsorbent carries a positive charge.

In this state, the positively charged adsorbent surfaces can attract negatively charged Methyl Orange molecules through electrostatic interactions, enhancing dye removal efficiency [65]. For instance, at a pH of 4, cellulose has a favorable positive charge, contributing to its ability to remove Methyl Orange effectively. Conversely, when the pH exceeds the pHzpc, the surface of the adsorbent becomes negatively charged [74]. This change can lead to repulsive forces between the negatively charged dye and the adsorbent surface, resulting in decreased adsorption efficiency [123]. As the pH rises, the adsorption capacity tends to decline, as seen in the decreasing MO removal percentages for chitosan and cellulose when the pH surpasses their respective pHzpc values. For chitosan, the pH of 6 is close to its pHzpc of 6.37, which allows for effective electrostatic interactions and optimal dye removal [124]. Similarly, the Chitosan@EDTA@Cellulose composite, with a pHzpc of 5.17, achieves maximum dye removal at a pH of 5. At this pH, the surface charge of the composite is still conducive to electrostatic attraction, leading to the highest removal efficiency [125].

## 6.2.4. Effect of concentration initial

Fig. 9e presents the adsorption performance of chitosan, cellulose, and the Chitosan@EDTA@Cellulose composite for the removal of Methyl Orange (MO) from aqueous solutions. The Chitosan@EDTA@-Cellulose composite demonstrated the highest removal efficiency, maintaining over 90 % removal at lower MO concentrations (25–50 mg/ L) and over 70 % efficiency at higher concentrations (150–200 mg/L).

#### Table 5

Chemical stability of chitosan, cellulose, and Chitosan@EDTA@Cellulose at different pH levels.

Adsorbent	Observations at pH 2	Observations at pH 4–7	Observations at pH 8–10
Chitosan Beads	Deformation of beads, weak and softened texture. Chemical stability is lower due to protonation of amino groups, leading to weakened structure.	Beads swell gradually, remain firm but softer with slight surface changes. Chemical stability improves, with less deformation compared to pH 2.	Significant swelling, becoming very soft and highly hydrated. Chemical stability remains moderate, but further deformation occurs as the beads soften.
Cellulose	No visible change, the cellulose structure remains chemically stable, with no deformation observed at low pH.	No visible change, retains structure, remains dry and intact. No deformation observed, with the structure maintaining its integrity.	No visible change. The structure remains stable across the pH range with no deformation.
Chitosan@EDTA @Cellulose Beads	More stable than chitosan beads alone, with very slow deformation and a stronger structure.	Chemically stable with minimal structural changes. The beads remain firm with slight deformation but retain their overall structure.	Structure remains stable without significant deformation. Chemical stability is maintained, and the beads show only minor deformation.

Pure chitosan exhibited moderate performance, with removal efficiency declining from 70 % at lower concentrations to below 30 % at higher concentrations. Cellulose showed the least efficiency, dropping below 20 % as MO concentrations increased. The decrease in removal efficiency with increasing MO concentration is due to the saturation of available adsorption sites [126]. At lower concentrations, ample active sites allow for effective adsorption. However, as the concentration increases, the limited number of sites becomes insufficient to accommodate the rising number of Methyl Orange (MO) molecules, leading to decreased efficiency [127]. Additionally, competition for adsorption sites at higher concentrations further reduces performance. This saturation and competition effect is typical in adsorption processes [128].

## 6.2.5. Temperature effect

The effect of temperature on Methyl Orange (MO) removal was evaluated using Chitosan, Cellulose, and Chitosan@EDTA@Cellulose as adsorbents, as shown in Fig. 9f. The results reveal distinct trends for each material. For Chitosan, Methyl Orange removal efficiency increases with temperature, from 54.67 % at 25 °C to 69.12 % at 55 °C, suggesting that higher temperatures enhance adsorption by increasing molecular movement and interaction between the dye and active sites. In contrast, Cellulose shows a decrease in efficiency as temperature rises, with removal dropping from 52.67 % at 25 °C to 50.12 % at 55 °C, indicating that the adsorption process may be exothermic, with higher temperatures weakening interactions due to reduced Van der Waals forces or increased desorption. The Chitosan@EDTA@Cellulose composite exhibits the highest and most consistent performance, with MO removal increasing from 93.88 % at 25  $^\circ \text{C}$  to 97.89 % at 55  $^\circ \text{C}.$  This increase in efficiency suggests an endothermic adsorption process, where the composite's enhanced active sites and affinity for MO benefit from the thermal energy, improving adsorption [30].

#### 6.2.6. Modeling of adsorption kinetic

The adsorption kinetics of Methyl Orange (MO) dye onto chitosan,

cellulose, and Chitosan@EDTA@Cellulose were analyzed using various kinetic models, including the pseudo-first-order (PFO), pseudo-secondorder (PSO), Elovich, and intraparticle diffusion (IPD) models, as illustrated in Fig. 10a, b, c, and d and detailed in Table 6, provided significant insights into the adsorption mechanisms. [129]. The results indicated that the adsorption behavior is best described by the pseudosecond-order model across all three materials [79]. Chitosan@EDTA@Cellulose exhibited the highest calculated adsorption capacity (qe) of 212.77 mg/g, alongside a pseudo-second-order rate constant (k<sub>2</sub>) of 1.71  $\times$  10<sup>-5</sup> g·mg<sup>-1</sup>·min<sup>-1</sup>. In contrast, Chitosan and Cellulose displayed lower capacities, with qe values of 71.75 mg/g and 46.22 mg/g, respectively. However, the goodness-of-fit metrics ( $R^2$ ) for the pseudo-second-order model (Fig. 10b) were markedly higher for all adsorbents compared to the pseudo-first-order model (Fig. 10a), the pseudo-second-order model implies that adsorption occurs through chemical interactions between the dye molecules and the active sites, meaning that the adsorption rate depends on the concentration of both the dye and the available functional groups on the adsorbent. A good fit to the pseudo-second-order model indicates that chemisorption, involving electron sharing or exchange, plays a significant role in the adsorption process [130]. This reinforces the notion that the adsorption process is more complex than initially indicated by the pseudo-firstorder model, highlighting the role of chemical interactions and the availability of adsorption sites [131]. The Elovich model and Intraparticle Diffusion (IPD) model provide important insights into the adsorption kinetics of chitosan, cellulose, and Chitosan@EDTA@Cellulose. The Elovich model (Fig. 10c), which is typically used for chemisorption processes, reveals the rate of adsorption and surface coverage. For chitosan, the  $\alpha$  value of 2.2951 mg/g·min indicates a moderate initial adsorption rate, while the  $\beta$  value of 0.0771 g/mg suggests a relatively slow desorption process and moderate surface coverage at equilibrium. The R<sup>2</sup> value of 0.924 shows a good fit, although the adsorption process is less rapid and efficient than the composite. In the case of cellulose, the  $\alpha$  value is lower at 1.5620 mg/g·min, indicating a slower initial adsorption rate compared to chitosan and Chitosa*n*@EDTA@*Cellulose*. The higher  $\beta$  value of 0.1074 g/mg reflects a greater surface coverage and slower adsorption process, with an R<sup>2</sup> value of 0.932 indicating a reasonable but less efficient adsorption than chitosan and the composite. Chitosan@EDTA@Cellulose, on the other hand, demonstrates the highest  $\alpha$  value of 3.0680 mg/g·min, suggesting the fastest initial adsorption rate, with the lowest  $\beta$  value of 0.0536 g/ mg, pointing to lower surface coverage at equilibrium and more efficient adsorption in the early stages. While the R<sup>2</sup> value of 0.878 is slightly lower than the other two materials, it still indicates good agreement with the data. The IPD model (Fig. 10d) further elucidates the role of intraparticle diffusion, showing that Chitosan@EDTA@Cellulose has the highest  $K_{id}$  value (9.0315 mg/m·min<sup>1/2</sup>), indicating that diffusion plays a crucial role in its rapid adsorption process, with dye molecules moving quickly into the material. The Cid value for Chitosan@EDTA@Cellulose (20.851 mg/g) is the highest, suggesting a larger boundary layer effect and greater resistance to diffusion, which reflects that the adsorption process is influenced by both surface interactions and diffusion into the adsorbent's interior. In comparison, chitosan has a Kid value of 5.6404  $mg/m{\cdot}min^{1/2}$  and  $C_{id}$  of 10.959 mg/g, suggesting a slower diffusion process with moderate resistance. Cellulose has the lowest K<sub>id</sub> (3.8261  ${\rm mg/m\cdot min^{1/2}})$  and  $C_{id}$  (7.398 mg/g), indicating even slower diffusion and less resistance to dye movement.

## 6.2.7. Modeling of adsorption isotherms

The equilibrium adsorption behavior of Methyl Orange (MO) dye onto chitosan, cellulose, and Chitosan@EDTA@Cellulose was evaluated using four isotherm models: Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R), as illustrated in Fig. 10e, f, g, h, i, and j, and detailed in Table 7, providing valuable insights into their respective adsorption capacities and mechanisms [132]. The Langmuir model (Fig. 10e), which assumes monolayer adsorption on a homogeneous



Fig. 9. a) Effect of contact time on the adsorption of Methyl Orange onto chitosan, cellulose, and Chitosan@EDTA@Cellulose composite; b) effect of adsorbent mass on the adsorption capacity of Methyl Orange; c) determination of the point of zero charge (pHzpc) for chitosan, cellulose, and the composite; d) effect of solution pH on the adsorption of Methyl Orange; e) effect of initial dye concentration on the adsorption capacity of the materials; f) effect of temperature on the adsorption of Methyl Orange onto chitosan, cellulose, and Chitosan@EDTA@Cellulose.



**Fig. 10.** (a) Adsorption kinetics: pseudo-first-order model, (b) adsorption kinetics: pseudo second-order model, (c) adsorption isotherm: Elovich model, (d) adsorption kinetics: Intraparticle diffusion model. (e) Adsorption isotherm: Langmuir model. (f) Adsorption isotherm: Freundlich model. (g) Adsorption isotherm: Temkin model. (h) Adsorption isotherm: Dubinin-Radushkevich (D-R) model for chitosan. (i) Adsorption isotherm: Dubinin-Radushkevich (D-R) model for Chitosan@EDTA@Cellulose. (k) Adsorption thermodynamics analysis.

surface, showed excellent correlation with the experimental data for all three adsorbents. This strong agreement suggests that the adsorption process is predominantly governed by the formation of a single uniform layer of dye molecules on the surface of the adsorbent, rather than multilayer adsorption or interactions within heterogeneous surface structures [133], as reflected by high  $R^2$  values (ranging from 0.994 to 0.999), indicating a strong fit to this model. Chitosan exhibited a moderate maximum adsorption capacity (qm = 7.29 mg/g) with a high

#### Table 6

Kinetic parameters for MO adsorption on chitosan, cellulose, Chitosan@EDTA@Cellulose.

Model	Parameter	Chitosan	Cellulose	Chitosan@EDTA@Cellulose
Pseudo-first-order (PFO)	q <sub>e,cal</sub> (mg/g)	71.75	46.22	101.68
	$k_1 (min^{-1})$	0.0586	0.0464	0.0667
	R <sup>2</sup>	0.842	0.863	0.770
Pseudo-second-order (PSO)	q <sub>e,cal</sub> (mg/g)	128.21	79.37	212.77
	$k_2(g \cdot mg^{-1} \cdot min^{-1})$	$4.57 imes10^{-5}$	$8.26 imes10^{-5}$	$1.71 imes10^{-5}$
	R <sup>2</sup>	0.958	0.977	0.972
Elovich model	α (mg/g·min)	2.2951	1.5620	3.0680
	β (g/mg)	0.0771	0.1074	0.0536
	R <sup>2</sup>	0.924	0.932	0.878
Intraparticle diffusion (IPD)	$K_{id}$ (mg/m·min <sup>1/2</sup> )	5.6404	3.8261	9.0315
	C <sub>id</sub> (mg/g)	10.959	7.398	20.851
	R <sup>2</sup>	0.989	0.993	0.9634

#### Table 7

Parameters for Langmuir and Freundlich isotherm models for MO adsorption onto chitosan, cellulose, Chitosan@EDTA@Cellulose.

Model	Parameter	Chitosan	Cellulose	Chitosan@EDTA@Cellulose
Langmuir	qm(mg/g)	7.29	5.69	55.87
	K <sub>l</sub> (L/mg)	6.29	5.48	2.27
	R <sup>2</sup>	0.999	0.994	0.997
Freundlich	K <sub>F</sub> (mg/g)	14.33	9.18	59.10
	1/nF	0.2482	0.2629	0.1788
	R <sup>2</sup>	0.934	0.816	0.963
Temkin	B <sub>T</sub> (J/mol)	0.1393	0.1842	0.0867
	K <sub>T</sub> (L/mg)	46,770.13	215.66	$4.20 \times 10^{30}$
	R <sup>2</sup>	0.976	0.823	0.867
Dubinin-Radushkevich	$Q_{DR}$ (mg/g)	38.87	28.76	93.69
	$\beta_{DR}(mol^2/kJ^2)$	$1 imes 10^{-6}$	$5  imes 10^{-6}$	$8  imes 10^{-9}$
	Es (kJ/mol)	707.11	316.23	7905.69
	R <sup>2</sup>	0.863	0.885	0.684

affinity for MO ( $K_L = 6.29$  L/mg). Cellulose, though similar, demonstrated a slightly lower capacity (qm = 5.69 mg/g) and affinity ( $K_L =$ 5.48 L/mg), but still maintained an excellent fit to the Langmuir model. In contrast, the Chitosan@EDTA@Cellulose composite outperformed both Chitosan and Cellulose with a significantly higher qm = 55.87 mg/g, despite having a lower  $K_L = 2.27$  L/mg, suggesting that the composite's enhanced structure allowed for greater adsorption capacity [35]. The Freundlich model (Fig. 10f), which accounts for adsorption on heterogeneous surfaces and multilayer adsorption, also provided valuable information [78]. The adsorption process for all three adsorbents was favorable, as indicated by 1/nF values well below 1, with the composite showing the most favorable adsorption intensity (1/nF =0.17881) and the highest Freundlich constant ( $K_F = 59.10 \text{ mg/g}$ ). Chitosan and Cellulose followed similar trends, with  $K_F = 14.33 \text{ mg/g}$  and  $K_F = 9.18$  mg/g, respectively, and adsorption intensities of  $1/n_F =$ 0.2482 for Chitosan and  $1/n_F=$  0.26291 for Cellulose [134]. The  $R^2$ values for the Freundlich model were slightly lower compared to the Langmuir model, particularly for Cellulose ( $R^2 = 0.816$ ), suggesting that monolayer adsorption is the dominant mechanism in this system. The Temkin model (Fig. 10g) accounts for the adsorbate-adsorbent interactions, assuming a linear decrease in adsorption heat with increasing surface coverage. The B<sub>T</sub> parameter, related to the adsorption heat, was lowest for Chitosan@EDTA@Cellulose (0.0867 J/mol) compared to chitosan (0.1393 J/mol) and cellulose (0.1842 J/mol). This lower value for B<sub>T</sub> indicates that the adsorption process for Chitosan@EDTA@-Cellulose involves less energy dissipation, suggesting a stronger affinity and more stable adsorption sites for the MO dye. The K<sub>T</sub> values, representing the equilibrium binding constant, were also significantly higher for Chitosan@EDTA@Cellulose ( $4.20 \times 10^{34}$ ) than for cellulose (215.66 L/mg). These results confirm that Chitosan@EDTA@Cellulose has a more favorable interaction with MO molecules, contributing to its superior adsorption performance. However, the R<sup>2</sup> value for Chitosan@EDTA@Cellulose (0.867) was lower than that of chitosan (0.976), suggesting a moderate fit to the Temkin model. The D-R model (Fig. 10h,

i, and j) provides insight into the porosity and adsorption energy, differentiating between physical and chemical adsorption mechanisms. The highest adsorption capacity  $(Q_{DR})$  was observed for Chitosan@EDTA@Cellulose (93.69 mg/g) (Fig. 10j), which significantly outperformed chitosan (38.87 mg/g) (Fig. 10h) and cellulose (28.76 mg/g) (Fig. 10i). This result highlights the enhanced adsorption efficiency of the composite material, likely due to the increased number of active adsorption sites provided by the integration of EDTA. The mean adsorption energy (Es), derived from  $\beta_{DR}$ , provides information about the adsorption mechanism. For Chitosan@EDTA@Cellulose, Es was exceptionally high (7905.69 kJ/mol), indicating a chemisorption process. In contrast, the Es values for chitosan (707.11 kJ/mol) and cellulose (316.23 kJ/mol) were significantly lower, suggesting weaker adsorption interactions dominated by physisorption. The R<sup>2</sup> values for the D-R model were lower for all materials, particularly for Chitosan@EDTA@Cellulose (0.684), indicating a less precise fit to the experimental data compared to the Langmuir and Freundlich models. Nevertheless, the high Es and QDR values for Chitosan@EDTA@Cellulose emphasize its suitability for chemisorption-driven dye removal.

## 6.2.8. Thermodynamic study

The thermodynamic parameters provide critical insights into the nature and mechanisms of Methyl Orange (MO) adsorption onto

## Table 8

Thermodynamic parameters for the adsorption of Methyl Orange (MO) onto Chitosan, Cellulose, and Chitosan@EDTA@Cellulose.

Adsorbents	ΔH° (kJ/ mol)	ΔS° (J/ mol·K)	ΔG° at 298 K (kJ/ mol)	ΔG° at 308 K (kJ/ mol)	∆G° at 318 K (kJ∕ mol)
Chitosan Cellulose Chitosan@EDTA@Cellulose	5.28 -5.54 64.76	27.12 -16.15 245.1	$-2.80 \\ -0.73 \\ -8.26$	$-3.07 \\ -0.57 \\ -10.78$	$-3.35 \\ -0.40 \\ -13.30$

chitosan, cellulose, and the Chitosan@EDTA@Cellulose composite, as detailed in Table 8 and illustrated in Fig. 10k. The thermodynamic parameters of Chitosan, Cellulose, and the Chitosan@EDTA@Cellulose composite provide a comprehensive understanding of their adsorption behaviors toward Methyl Orange. Starting with Chitosan, the positive value of the enthalpy change ( $\Delta H^{\circ} = 5.28 \text{ kJ/mol}$ ) indicates that the adsorption process is endothermic, meaning it requires heat to proceed. This suggests that the process is facilitated at higher temperatures, leading to a higher adsorption capacity. The positive entropy change  $(\Delta S^{\circ} = 27.12 \text{ J/mol} \cdot \text{K})$  indicates an increase in randomness at the solidliquid interface during the adsorption, which is often associated with the breaking of bonds or changes in the structure of the adsorbent or adsorbate. The negative values of Gibbs free energy ( $\Delta G^{\circ} = -2.80 \text{ kJ/}$ mol at 298 K, decreasing to -3.35 kJ/mol at 318 K) confirm that the adsorption process is spontaneous, with increasing spontaneity as the temperature rises [122]. This suggests that Chitosan's dye adsorption is thermodynamically favorable and becomes more efficient as the temperature increases. For Cellulose, the negative enthalpy change ( $\Delta H^{\circ} =$ -5.54 kJ/mol) indicates that the adsorption process is exothermic, meaning it releases heat. This implies that the process is more favorable at lower temperatures, and the interaction between dye molecules and cellulose is strengthened as the temperature decreases. The negative value of the entropy change ( $\Delta S^{\circ} = -16.15 \text{ J/mol} \cdot \text{K}$ ) suggests that the adsorption leads to a decrease in the system's randomness, possibly due to the formation of a more structured interaction between the dye and the cellulose surface. The negative Gibbs free energy values ( $\Delta G^{\circ} =$ -0.73 kJ/mol at 298 K, to -0.40 kJ/mol at 318 K) also show that the process is spontaneous, but the spontaneity decreases with rising temperature, implying that the adsorption efficiency may be reduced at higher temperatures. The Chitosan@EDTA@Cellulose composite, on the other hand, displays distinctly different thermodynamic behavior. The high positive enthalpy change ( $\Delta H^{\circ} = 64.76 \text{ kJ/mol}$ ) signifies a strongly endothermic process, indicating that the composite adsorbs more efficiently at higher temperatures. The significant increase in entropy ( $\Delta S^{\circ}$ = 245.1 J/mol·K) suggests a substantial increase in randomness, possibly due to the structural changes caused by the incorporation of EDTA, which enhances the adsorption sites and the overall flexibility of the composite. The extremely negative Gibbs free energy values ( $\Delta G^{\circ} =$ -8.26 kJ/mol at 308 K, and -13.30 kJ/mol at 318 K) further confirm that the adsorption process is highly spontaneous and becomes more favorable as the temperature rises [135].

## 6.2.9. Ion competition in MO dye removal efficiency

Fig. 11a provide a comprehensive analysis of the removal efficiency of Methyl Orange (MO) dye in the presence of various competing ions, including Na<sup>+</sup>, Ca<sup>2+</sup>, SO4<sup>2-</sup>, and NO<sub>3</sub><sup>-</sup>, using three different adsorbents: Chitosan, Cellulose, and Chitosan@EDTA@Cellulose. Among the adsorbents, Chitosan@EDTA@Cellulose consistently exhibited the highest MO removal percentages, with efficiencies of 92.91 %, 88.02 %, 90.95 %, and 94.87 % for Na<sup>+</sup>, Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup>, respectively. This remarkable performance can be attributed to the synergistic integration of Chitosan, EDTA, and Cellulose, which significantly enhances the number and accessibility of active adsorption sites. The inclusion of EDTA in the composite structure contributes additional chelation and complexation capabilities, which not only improve the interaction with MO molecules but also provide greater resistance to interference from competing ions. The robust functional groups, such as amino (-NH<sub>2</sub>) and hydroxyl (-OH) groups, further strengthen the dye-adsorbent interactions, resulting in consistently high removal efficiencies even in the presence of divalent ions like Ca<sup>2+</sup>. In comparison, Chitosan alone exhibited moderate adsorption performance, achieving MO removal efficiencies of 69.8 %, 62.2 %, 66.1 %, and 73.9 % for Na<sup>+</sup>, Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup>, respectively. The adsorption efficiency of Chitosan is primarily driven by its functional groups, which facilitate electrostatic interactions and hydrogen bonding with MO dye. However, the limited surface area and fewer active sites compared to the composite material result in lower overall removal percentages. Additionally, the presence of divalent ions such as Ca<sup>2+</sup> negatively affects its adsorption capacity, likely due to their stronger competition for the active sites. Cellulose demonstrated the lowest MO removal efficiencies, with values of 60.25 %, 55.06 %, 58.3 %, and 61.54 % for Na<sup>+</sup>, Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup>, respectively. This poor performance can be attributed to its relatively inert nature and the absence of sufficient functional groups capable of forming strong interactions with the MO dye molecules. The adsorption efficiency of Cellulose is further hindered by the presence of competing ions, particularly divalent ions like Ca<sup>2+</sup>, which exhibit a larger hydration radius and stronger electrostatic forces, thereby occupying the limited adsorption sites available on the Cellulose surface.

## 6.2.10. Reusability of adsorbents for Methyl Orange removal

The Fig. 11b illustrates the comparative performance of Chitosan, Cellulose, and Chitosan@EDTA@Cellulose adsorbents in the removal of Methyl Orange (MO) dye across four cycles. Chitosan@EDTA@Cellulose demonstrated the highest efficiency, achieving a remarkable 97.8 % MO



Fig. 11. (a): Recyclability of adsorbents for Methyl Orange (MO) removal. (b): Effect of coexisting ions on Methyl Orange (MO) removal efficiency.

removal in the first cycle, which decreased slightly to 87.78 % in the second cycle and further to 81.86 % by the fourth cycle. In contrast, Chitosan exhibited a moderate initial removal efficiency of 77.88 %, which gradually declined to 49.86 % in the fourth cycle. Cellulose, however, showed the lowest performance, starting at 64.78 % in the first cycle and dropping to 39.01 % by the fourth cycle. The observed decline in efficiency across cycles for all adsorbents may be due to the partial saturation of adsorption sites and incomplete desorption of MO dye. Nevertheless, Chitosan@EDTA@Cellulose exhibited significantly better reusability, maintaining high removal percentages even after multiple cycles, making it a promising adsorbent for sustainable dye removal applications.

#### 6.3. Optimization results

## 6.3.1. Analysis of variance (ANOVA)

The ANOVA analysis for the Methyl Orange (MO) removal experiments using chitosan, cellulose, and Chitosan@EDTA@Cellulose presents in Table 9 provides a detailed understanding of the impact of various factors adsorbent mass, pH, and concentration on the dye removal efficiency. The overall model for each system (chitosan, cellulose, and Chitosan@EDTA@Cellulose) is highly significant, as evidenced by the extremely large F-values (49,212.32 for chitosan, 11,890.39 for cellulose, and 5183.59 for Chitosan@EDTA@Cellulose) and p-values <0.0001 [136]. The high F-values (161,300 for chitosan, 39,650 for cellulose, and 17,926.78 for Chitosan@EDTA@Cellulose) and extremely low p-values (<0.0001) indicate that the models effectively capture the variability in Methyl Orange (MO) removal. These results highlight the significant impact of adsorbent mass (factor A) on adsorption efficiency across all three systems. Similarly, pH (factor B) is also a highly significant factor, with F-values such as 8675.11 for chitosan, 35,857.52 for cellulose, and 15,420.43 for Chitosan@EDTA@Cellulose, all showing pvalues below 0.05 [137]. For dye concentration (factor C), high F-values (164,400 for chitosan, 15,593.56 for cellulose, and 6676.02 for Chitosan@EDTA@Cellulose) again emphasize the significance of concentration. The study reveals that interaction effects (AB, AC, and BC) and quadratic terms (A<sup>2</sup>, B<sup>2</sup>, and C<sup>2</sup>) are statistically significant, demonstrating non-linear relationships in Methyl Orange (MO) removal. High F-values, such as 35,996.58 for chitosan A<sup>2</sup> and 6875.00 for cellulose A<sup>2</sup>, highlight their strong influence. Minimal residual sums of squares (0.0899 for chitosan, 0.3309 for cellulose, and 0.7564 for Chitosan@EDTA@Cellulose) indicate excellent model alignment with experimental data [137]. Additionally, additionally, the non-significant lack of fit for chitosan and Chitosan@EDTA@Cellulose (with p-values 0.2341 and 0.3767, respectively) confirm the models' reliability, whereas the lack of fit for cellulose is significant (p-value = 0.0453), suggesting that the model does not fit the experimental data perfectly for this system. The low pure error values further confirm the precision of the experimental procedures, ensuring accurate predictions of MO removal [138].

The statistical evaluation of Methyl Orange (MO) removal using chitosan, cellulose, and the Chitosan@EDTA@Cellulose composite confirms the robustness and accuracy of the models, as summarized in Table 10. The low standard deviation values (0.1133 for chitosan, 0.2174 for cellulose, and 0.3287 for Chitosan@EDTA@Cellulose) indicate minimal variation between observed and predicted results, demonstrating high reproducibility and precision. The exceptionally high R<sup>2</sup> values 1.0000 for chitosan, 0.9999 for cellulose, and 0.9998 for Chitosan@EDTA@Cellulose show that the models explain nearly all variability in MO removal, reflecting an almost perfect fit between observed and predicted outcomes [139]. While the high predicted R<sup>2</sup> values (0.9997, 0.9991, and 0.9987, respectively) confirm the models' reliability for predicting new data. The mean MO removal values (36.52 for chitosan, 31.24 for cellulose, and 51.19 for Chitosan@EDTA@-Cellulose) highlight the superior efficiency of the composite, attributed to its enhanced surface area and active binding sites. The low coefficients of variation (C.V. %) 0.3104 % for chitosan, 0.6969 % for

Mean	R-value	auleV.n	Cellulose Sum of	df 1	Mean	enlex-	enleV-c	Chitosan(	<b>JEDTA</b>	@Cellulose			
-		p-vaue	squares	n s	square		2010						
	49,212.32	<0.0001 Significant	5058.42	6	562.05	11,890.39	<0.0001 Signific	ant 5041.39	6	560.15	5183.59	<0.0001 Si	gnificant
	1.613E+05	<0.0001	1874.22	-	1874.22	39,650.11	<0.0001	1937.22	1	1937.22	17,926.78	<0.0001	
	8675.11	<0.0001	1694.95	-	1694.95	35,857.52	<0.0001	1666.38	1	1666.38	15,420.43	< 0.0001	
	$1.644E \pm 05$	<0.0001	737.09	1	737.09	15,593.56	<0.0001	721.43	1	721.43	6676.02	< 0.0001	
	72.34	<0.0001	41.88	1	41.88	885.95	<0.0001	37.64	1	37.64	348.30	< 0.0001	
	37,731.28	<0.0001	200.07	1	200.07	4232.53	<0.0001	197.12	1	197.12	1824.14	< 0.0001	
	13,259.36	< 0.0001	1.50	1	1.50	31.79	0.0008	1.36	1	1.36	12.56	0,0094	
•••	35,996.58	< 0.0001	324.97	1	324.97	6875.00	<0.001	292.25	1	292.25	2704.49	< 0.0001	
	6682.39	< 0.0001	80.94	1	80.94	1712.39	<0.001	87.21	1	87.21	807.07	< 0.0001	
	16,536.79	< 0.0001	107.44	1	107.44	2272.96	<0.001	106.80	1	106.80	988.29	< 0.0001	
			0.3309	7	0.0473			0.756	4	0.1081			
	1.21	0.2341 Not	0.2780	ŝ	0.0927	7.00	0.0453 Signific	ant 0.380	33	0.1269	1.35	0.3767 No	ot
		significant										sig	gnificant
			0.0529	4	0.0132			0.375	4	0.0939			
			5058.75	16				5042.14	16				

Table

#### Table 10

statistical parameters and model performance for the removal of Methyl Orange (MO) using different adsorbents: chitosan, cellulose, and Chitosan@EDTA@Cellulose.

Statistic	MO removal with chitosan	MO removal with cellulose	MO removal with composite
Std. Dev.	0.1133	0.21741	0.3287
Mean	36.52	31.24	51.19
C.V. %	0.3104	0.6969	0.6421
R <sup>2</sup>	1.0000	0.9999	0.9998
Adjusted R <sup>2</sup>	1.0000	0.9999	0.9997
Predicted R <sup>2</sup>	0.9997	0.9991	0.9987
Adeq precision	854.9280	362.0174	240.7002

cellulose, and 0.6421 % for Chitosan@EDTA@Cellulose demonstrate high precision with minimal variability. The exceptionally high adequate precision values (854.9280 for chitosan, 362.0174 for cellulose, and 240.7002 for Chitosan@EDTA@Cellulose) far exceed the threshold of 4, indicating strong model reliability and robustness [140]. These metrics, combined with low standard deviations and near-perfect  $R^2$  values, establish that the models for MO removal are highly accurate, predictive, and reproducible, offering robust tools for optimizing adsorption processes.

## 6.3.2. Normal probability plot of residuals

The normal probability plots of residuals for Methyl Orange (MO) removal using chitosan, cellulose, and Chitosan@EDTA@Cellulose (Fig. 10) show how well the residuals follow a normal distribution [141]. In Fig. 12(a), for chitosan, the residuals generally align with the normal distribution, though slight deviations at the extremes indicate minor prediction issues for very low or high MO removal values. Fig. 12 (b), for cellulose, shows near-perfect alignment, suggesting a strong model fit and high reliability of predictions. Similarly, Fig. 12(c), for Chitosan@EDTA@Cellulose, demonstrates a strong fit with only a slight deviation at the lower end [142].

## 6.3.3. Response surface analysis

*6.3.3.1. MO removal with chitosan.* In the 3D surface plot in Fig. 13(a) for Methyl Orange (MO) removal using chitosan, the interaction between the adsorbent mass and pH is particularly notable. As the mass of chitosan increases, the removal efficiency shows a marked increase at higher pH levels. This interaction suggests that a higher mass of chitosan

provides more available active sites for adsorption, while the higher pH enhances the ionization of chitosan's amino groups, making it more conducive for binding negatively charged MO. When examining the interaction between adsorbent mass and MO concentration, the plot indicates that an increase in the mass of chitosan positively correlates with MO removal efficiency, yet this relationship diminishes at higher concentrations of MO. This suggests that while more adsorbent improves removal, saturation effects may limit efficacy at excessive dye concentrations. Furthermore, the interaction between pH and MO concentration reveals that as pH increases, the removal efficiency also rises; however, this improvement plateaus at higher dye concentrations.

6.3.3.2. MO removal with cellulose. The 3D surface plot in Fig. 13(b) for Methyl Orange (MO) removal using cellulose presents interesting insights into the interactions between adsorbent mass, pH, and MO concentration, The interaction between mass and pH shows that, although higher pH levels generally improve removal efficiency, the degree of enhancement is not as pronounced as with chitosan. This indicates that cellulose may have a lower capacity for ionization and, consequently, a weaker binding affinity for MO, even when the mass is increased. When examining the relationship between adsorbent mass and MO concentration, the plot suggests a positive correlation between mass and removal efficiency. However, this effect appears to be limited at higher dye concentrations, indicating that cellulose may also experience saturation and thus lose its efficiency at elevated MO levels. The interaction between pH and MO concentration indicates that while an increase in pH boosts removal efficiency, the benefits diminish as the concentration of MO increases.

6.3.3.3. MO removal with Chitosan@EDTA@Cellulose. In the 3D surface plot in Fig. 13(c) for Methyl Orange (MO) removal using the Chitosan@EDTA@Cellulose composite, the interactions between adsorbent mass, pH, and MO concentration reveal a more robust performance compared to the previous adsorbents. This suggests that the composite material offers enhanced adsorption efficiency under varying conditions. The interaction between mass and pH indicates a synergistic effect; increasing the mass of the composite while also raising the pH significantly enhances removal efficiency. This suggests that the combined properties of chitosan and EDTA facilitate better ionization and chelation, creating a more effective adsorbent environment for MO. The relationship between adsorbent mass and MO concentration shows that, similar to chitosan, higher masses improve removal efficiency. However, the composite appears more resilient, maintaining higher adsorption levels even at elevated dye concentrations, likely due to the enhanced



Fig. 12. Plot (a): normal probability plot of residuals for chitosan in MO removal, Plot (b): normal probability plot of residuals for cellulose in MO removal, Plot (c): normal probability plot of residuals for Chitosan@EDTA@Cellulose composite in MO removal.

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Fig. 13. 3D surface plots of Methyl Orange (MO) removal efficiency using: (a) chitosan, (b) cellulose, (c) Chitosan@EDTA@Cellulose.

binding capabilities afforded by the EDTA. Additionally, the interaction between pH and MO concentration indicates that increased pH consistently improves dye removal, with the composite effectively handling higher MO concentrations without a significant drop in efficiency.

## 6.4. DFT analysis

## 6.4.1. Interaction between chitosan, EDTA and cellulose

The molecular structure illustrated in Fig. 14 presents a sophisticated composite material where EDTA serves as a crucial cross-linking agent that binds chitosan and cellulose together, creating a strong,



Fig. 14. Chemical structure of Chitosan@EDTA@Cellulose.

interconnected network. Chitosan is rich in reactive amine (-NH<sub>2</sub>) and hydroxyl (-OH) groups, which enable it to form covalent or ionic bonds with EDTA's carboxyl (-COOH) groups [143]. These interactions between chitosan and EDTA contribute to the formation of a stable and flexible matrix [103]. On the other hand, cellulose has numerous hydroxyl (-OH) groups that interact with EDTA through hydrogen bonding or covalent esterification [144]. EDTA, with its multiple carboxyl groups, effectively bridges these two biopolymers by linking the hydroxyl groups of cellulose with the amine and hydroxyl groups of chitosan [145]. Without EDTA, chitosan and cellulose would have limited direct bonding capabilities, making EDTA essential for establishing strong chemical connections between these two natural polymers.

## 6.4.2. Global reactivity descriptions

Fig. 15 and Table 11 presents a comparative analysis of the frontier molecular orbitals (FMOs), specifically the HOMO and LUMO, for three materials: chitosan, cellulose, and Chitosan@EDTA@Cellulose. Chitosan (Fig. 15(a)) exhibits a HOMO energy of -5.08 eV and a LUMO energy of -0.76 eV, resulting in an energy gap of 5.84 eV. Although chitosan contains reactive amine (-NH<sub>2</sub>) and hydroxyl (-OH) groups that facilitate interactions with MO through hydrogen bonding or ionic interactions, its relatively large energy gap suggests moderate reactivity [146]. In comparison, cellulose (Fig. 15(b)) exhibits a HOMO energy of -6.58 eV and a LUMO energy of -0.48 eV, resulting in a significant energy gap of 6.10 eV. This large energy gap indicates that cellulose is inherently more stable but less reactive than chitosan. While cellulose contains numerous hydroxyl groups that could interact with MO, its

## Table 11

HOMO, LUMO, and energy gap (Eg) values for cellulose, chitosan, Methyl Orange, and their complexes.

Name of the molecules	HOMO (eV)	LUMO (eV)	Eg (eV)
Cellulose	-6.86	-0.48	6.38
Chitosan	-5.98	-0.70	5.28
Methyl Orange	-5.12	-1.83	3.29
Chitosan@EDTA@Cellulose	-6.07	-0.70	5.35
Cellulose@MO	-5.50	-2.32	3.18
Chitosan@MO	-5.53	-2.34	3.19
Chitosan@EDTA@Cellulose@MO	-5.13	-1.87	3.26



Fig. 15. Molecular orbital diagrams (HOMO-LUMO): a) cellulose, b) of chitosan, c) Methyl Orange, d) Chitosan@EDTA@Cellulose, e) Cellulose@Methyl Orange complex, f) Chitosan@Methyl Orange complex, g) Chitosan@EDTA@Cellulose@Methyl Orange complex.

lower reactivity may limit its effectiveness in adsorbing MO [147]. (Fig. 15(c)) show that MO has large energy gap (3.29 eV) between the HOMO and LUMO suggests moderate reactivity. The composite of Chitosan@EDTA@Cellulose (Fig. 15(d)), however, represents a significant advancement in enhancing the adsorption of methyl orange. In this composite, the HOMO energy is -5.13 eV and the LUMO energy is -1.87 eV, resulting in a notably reduced energy gap of 3.26 eV. This decrease in the energy gap indicates higher reactivity compared to cellulose and chitosan alone, making the composite material more favorable for interactions with MO. The incorporation of EDTA acts as a crosslinking agent, effectively binding chitosan and cellulose together and facilitating stronger intermolecular interactions with methyl orange. Fig. 15(e) shows the FMO analysis for Cellulose@Methyl Orange. The energy levels for the HOMO and LUMO are -5.50 eV and -2.32 eV, respectively, with an energy gap of 3.18 eV. The lower energy gap suggests that cellulose, after the adsorption of MO, maintains its stability. Despite the lower energy gap compared to chitosan, its reactivity remains limited. Fig. 15(f) illustrates the FMO for Chitosan@Methyl Orange. The HOMO energy is -5.53 eV, and the LUMO energy is -2.34eV, yielding an energy gap of 3.19 eV. This result suggests that chitosan, after the adsorption of MO, exhibits slightly better interaction than cellulose, but still has a substantial energy gap. Fig. 15(g) shows the Chitosan@EDTA@Cellulose@Methyl Orange composite. The HOMO is at -5.13 eV, and the LUMO is at -1.87 eV, resulting in a significantly smaller energy gap of 3.26 eV. This reduced energy gap indicates enhanced reactivity compared to the other two adsorbents alone. The EDTA acts as a cross-linker, improving the binding between chitosan and cellulose, which significantly enhances the composite's adsorption capacity for MO. The interaction between chitosan's reactive groups and MO, along with the structural integrity and enhanced hydrogen bonding from cellulose, makes this composite the most favorable for the adsorption of MO.

## 6.4.3. Characteristics of global reactivity

Table 12 summarizes the physicochemical properties of various adsorbents before and after Methyl Orange (MO) adsorption. Cellulose, with its high hardness (3.19) and low softness (0.31), shows stability but limited adsorption efficiency [148], while chitosan, with lower hardness (2.64) and higher softness (0.39), has greater reactivity and a higher charge transfer ( $\Delta Nmax = 1.26$ ), improving its potential for MO adsorption. Methyl Orange, with a hardness of 1.645 and softness of 0.61, exhibits high reactivity and substantial charge transfer ( $\Delta Nmax =$ 2.11), making it suitable for adsorption [149]. The Chitosan@EDTA@-Cellulose composite demonstrates effective MO adsorption, with moderate hardness (2.685) and flexibility (softness = 0.37), a chemical potential of 3.385, and high electrophilicity (15.38). After MO adsorption, cellulose shows reduced hardness (1.59) and increased softness (0.63), enhancing its reactivity and charge transfer ( $\Delta$ Nmax = 2.46) [150]. Chitosan after MO adsorption displays potential instability with negative hardness (-1.595) and softness (-0.63), but its strong electron-donating capacity (chemical potential = 3.935) suggests it could still participate in electron transfer [151]. Finally, Chitosan@EDTA@Cellulose after MO adsorption shows significant flexibility and electron transfer ( $\Delta Nmax = 2.15$ ), despite low electrophilicity, confirming its strong adsorption capacity for MO. Overall, the composites and modified adsorbents show improved properties for effective MO adsorption through enhanced electron transfer and reactivity [152].

#### 6.4.4. MEP geometries

Fig. 16 presents the molecular electrostatic potential (MEP) maps [153], offering a comprehensive understanding of the adsorption behavior of chitosan, cellulose, methyl orange (MO), and the Chitosan@EDTA@Cellulose composite, before and after MO adsorption. Chitosan exhibits strongly negative regions around its hydroxyl (-OH) and amine (-NH<sub>2</sub>) groups, which serve as active sites for adsorption through electrostatic interactions and hydrogen bonding with the highly negative sulfonic acid groups (-SO<sub>3</sub><sup>-</sup>) of MO [154]. These regions, combined with the overall polarity of chitosan, make it a highly effective adsorbent [155]. In contrast, cellulose shows negative regions concentrated around its hydroxyl groups, but the lower charge density and fewer active sites result in a reduced adsorption potential compared to chitosan. The composite Chitosan@EDTA@Cellulose presents a more uniform and intensified negative charge distribution due to the integration of EDTA, which introduces carboxylate (-COO<sup>-</sup>) groups. This enhanced charge distribution allows the composite to interact more efficiently with MO, offering a greater number of active sites and stronger electrostatic interactions. After adsorption, the MEP maps of all materials reveal a significant reduction in negative potential around their active sites, indicating successful binding of MO molecules. Chitosan shows a marked decrease in active site availability, confirming its strong interaction with MO, while cellulose exhibits a similar but less pronounced reduction. The composite shows the most significant changes, reflecting its superior adsorption capacity, which arises from the synergistic effects of chitosan, cellulose, and EDTA. This analysis highlights that the composite outperforms both chitosan and cellulose individually, making it the most efficient adsorbent for MO due to its enhanced charge distribution, improved active site availability, and the cooperative effect of its components.

#### 6.5. Mechanism of adsorption for MO

The adsorption mechanism of Methyl Orange (MO) onto chitosan, cellulose, and the Chitosan@EDTA@Cellulose composite is governed by a complex interplay of various interactions that collectively contribute to the overall adsorption efficiency, as shown in Fig. 17. Chitosan, as a biopolymer with a high density of amino (-NH2) and hydroxyl (-OH) functional groups, serves as a robust adsorbent, particularly in acidic conditions. In such environments, the amino groups are protonated to form -NH<sub>3</sub><sup>+</sup> ions, which establish strong electrostatic attractions with the negatively charged sulfonate groups (-SO3<sup>-</sup>) present in MO. This electrostatic attraction is pivotal, as it ensures a strong binding affinity between chitosan and the dye molecules. Furthermore, the hydroxyl groups in chitosan engage in hydrogen bonding with the functional groups of MO, such as the azo (-N=N-) and sulfonate groups. This dual interaction mechanism electrostatic attraction and hydrogen bonding enhances the adsorption capacity of chitosan significantly [156]. Additionally,  $\pi$ - $\pi$  stacking interactions between the aromatic rings of MO and the polysaccharide backbone of chitosan further stabilize the adsorbed molecules, creating a multi-dimensional binding framework

## Table 12

Calculated global reactivity descriptors for cellulose, chitosan, Methyl Orange, and their complexes.

Name of the molecules	η (hardness)	S (softness)	μ (chemical potential)	$\chi$ (electronegativity)	$\omega$ (electrophilicity)	$\Delta$ Nmax (total charge transfer)
Cellulose	3.19	0.31	-3.67	3.67	21.48	1.15
Chitosan	2.64	0.39	-3.34	3.34	14.73	1.26
Methyl Orange	1.645	0.61	-3.475	3.475	9.93	2.11
Chitosan@EDTA@Cellulose	2.685	0.37	-3.385	3.385	15.38	1.26
Cellulose@MO	1.59	0.63	-3.91	3.91	12.15	2.46
Chitosan@MO	-1.595	-0.63	3.935	-3.935	-12.35	2.47
Chitosan@EDTA@Cellulose@MO	-1.63	-0.61	3.5	-3.5	-9.98	2.15



Fig. 16. Optimized structures and MEP maps for cellulose, chitosan, Methyl Orange, and their complexes.

that boosts adsorption performance. On the other hand, cellulose, although lacking the amino groups necessary for electrostatic interactions, plays a vital role in the adsorption process through its hydroxyl groups. These groups act as active sites for hydrogen bonding with the azo and sulfonate groups of MO, enabling cellulose to adsorb the dye molecules despite its lower efficiency compared to chitosan. The linear and crystalline structure of cellulose also contributes to its adsorption capacity by providing a high surface area for interaction, facilitating the alignment of dye molecules for better contact and bonding. However, the absence of protonated amino groups in cellulose limits its ability to engage in electrostatic interactions, making hydrogen bonding the primary mechanism driving its adsorption process. The Chitosan@EDTA@Cellulose composite represents a significant advancement in adsorption performance due to the synergistic contributions of its components. In this composite, chitosan provides a matrix rich in amino and hydroxyl groups, facilitating electrostatic attractions and hydrogen bonding. The cellulose component enhances the structural integrity and increases the surface area of the composite, offering additional active sites for interaction. The inclusion of EDTA introduces carboxyl (-COOH) and amine (-NH) groups into the system, which not only expand the range of available adsorption sites but also enable complexation interactions with MO molecules. These complexation interactions occur when the carboxyl groups of EDTA form chelation bonds with the Methyl Orange, creating stable complexes that enhance the adsorption process. Furthermore, the aromatic nature of MO allows it to participate in  $\pi$ - $\pi$  stacking interactions with the composite surface, particularly with regions enriched by the chitosan and EDTA components. This stacking interaction stabilizes the adsorbed dye molecules, reducing the likelihood of desorption and increasing the overall adsorption efficiency. The combination of these mechanisms results in the Chitosan@EDTA@Cellulose composite exhibiting superior adsorption performance compared to either chitosan or cellulose alone. The composite benefits from the cooperative action of electrostatic attractions, hydrogen bonding,  $\pi$ - $\pi$  stacking, and complexation interactions, which collectively optimize the adsorption process. The high density of functional groups, increased surface area, and structural stability of the composite make it an effective adsorbent for MO. This mechanism not only underscores the role of individual functional groups but also demonstrates how their synergistic interplay can enhance adsorption efficiency, making the composite a promising adsorbent for environmental remediation applications [157] [158] [159].



Fig. 17. Proposed adsorption mechanism of Methyl Orange onto chitosan, cellulose, and Chitosan@EDTA@Cellulose composite.

## 7. Comparison of adsorption capacities of chitosan, cellulose, and Chitosan@EDTA@Cellulose with other adsorbents for the adsorption of Methyl Orange (MO)

The adsorption capacities of Chitosan, Cellulose, and Chitosan n@EDTA@Cellulose are noteworthy when compared to other adsorbents reported in the literature, as shown in Table 13. Chitosan's adsorption capacity of 7.29 mg/g and Cellulose's 5.69 mg/g are relatively modest compared to other adsorbents, such as orange and lemon peels (33.00 mg/g) and Chitosan-diatomite (35.12 mg/g). However, these capacities remain competitive within the range of natural and biopolymer-based adsorbents. The Chitosan@EDTA@Cellulose composite, with a remarkable adsorption capacity of 55.87 mg/g,

Tabl	e 13
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Comparison of maximum	adsorption	capacities	(qmax)	for	various	adsorbents.
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	rtererenees
0.1800	[160]
7.45	[161]
13.56	[162]
16.83	[163]
19.70	[164]
20.53	[165]
20.62	[166]
33.00	[167]
35.12	[168]
7.29	
5.69	This work
55.87	
	0.1800 7.45 13.56 16.83 19.70 20.53 20.62 33.00 35.12 7.29 5.69 55.87

demonstrates superior performance compared to several other materials, including activated *Acacia mangium* wood-based carbon (7.45 mg/ g), graphene oxide (16.83 mg/g), and zeolite Y (20.62 mg/g).

#### 8. Conclusion

This research explores the use of chitosan, cellulose, and a novel chitosan-based composite, Chitosan@EDTA@Cellulose, for the adsorption of Methyl Orange dye from aqueous solutions. The composite is synthesized by linking shrimp-derived chitosan and cactus-derived cellulose using EDTA as a linking agent, creating a hybrid material designed to enhance dye removal efficiency. A range of characterization techniques, including Fourier-Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area analysis, and Scanning Electron Microscopy (SEM), were used to evaluate the structural and surface properties of the composite both before and after dye adsorption. These analyses indicated significant changes in the surface area and chemical structure, confirming the material's suitability for adsorption applications.

The composite's performance was optimized under conditions that included a dye concentration of 50 mg/L, a pH of 5, and an adsorbent mass of 0.1 g, with a contact time of 55 min, resulting in a maximum adsorption capacity of 55.87 mg/g. Kinetic studies revealed that the adsorption followed a pseudo-second-order model, suggesting that the process is controlled by chemical interactions. Adsorption isotherms, including the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich models, demonstrated that the adsorption was most closely aligned with the Langmuir model, indicative of a monolayer adsorption on a surface with uniform adsorption sites.

Thermodynamic analyses showed that the adsorption process was both spontaneous and endothermic, which indicates that the process favors higher temperatures and occurs naturally without the need for external energy input. In tests for ion interference, the composite demonstrated a high removal efficiency of over 90 %, even in the presence of common competing ions such as sodium, calcium, sulfate, and nitrate, highlighting the effectiveness of EDTA in enhancing the composite's chelation and adsorption capabilities. Furthermore, the material retained a substantial portion of its adsorption efficiency (from 97.8 % to 81.86 %) after four cycles, confirming its reusability and stability.

Optimization using Box-Behnken Design (BBD) revealed that adsorbent mass, pH, and dye concentration are key parameters that significantly affect the adsorption process, with interaction effects between these factors showing statistical significance. The analysis also emphasized the importance of these parameters in maximizing Methyl Orange removal efficiency. Additionally, Density Functional Theory (DFT) simulations provided insight into the adsorption mechanism, demonstrating that EDTA effectively cross-links the composite components, reducing the energy gap and improving the material's reactivity for Methyl Orange adsorption.

The findings from this study underscore the potential of the Chitosan@EDTA@Cellulose composite as an efficient, eco-friendly adsorbent for the removal of Methyl Orange dye from aqueous environments, offering promising applications for water treatment and environmental cleanup.

## CRediT authorship contribution statement

Soukaina El Bourachdi: Writing – original draft, Formal analysis, Data curation. Abdelhay El Amri: Methodology, Formal analysis, Data curation. Ali Raza Ayub: Visualization, Methodology, Data curation, Conceptualization. Fatima Moussaoui: Methodology, Formal analysis, Data curation. Yassine Rakcho: Visualization, Methodology, Formal analysis, Conceptualization. Faiçal El Ouadrhiri: Software, Methodology, Investigation, Formal analysis. Abderrazzak Adachi: Software, Methodology, Formal analysis, Data curation. Mahdi Lechheb: Visualization, Methodology, Formal analysis, Data curation. José Alberto Herrera-Melián: Validation, Supervision, Formal analysis, Data curation, Conceptualization. Amal Lahkimi: Writing – review & editing, Validation, Supervision, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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