CELLULOSE CHEMISTRY AND TECHNOLOGY

EFFICIENT REMOVAL OF METHYL ORANGE ON CHITOSAN-DIALDEHYDE PECTIN FILM ELABORATED VIA SCHIFF BASE REACTION

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The aim of this study was the elaboration of a chitosan/oxidized pectin film for use in the adsorption of methyl orange. To valorize the food waste from juice manufacturing, pectin was extracted from orange peel waste. The highest extraction yield of 21.1% was achieved at a temperature of 80 °C, a time of 50 min, pH of 1.5, and a liquid-to-solid ratio of 25:1 (v/w). Chitin was extracted from shrimp shells through acid and alkaline treatment. The deacetylation of chitin to chitosan was carried out using a 40% NaOH treatment with a liquid-to-solid ratio of 4:1. The conversion of pectin to its dialdehyde derivatives by periodate oxidization in acid solutions with pH 4 at 35 °C has been investigated. The prepared chitosan-dialdehyde pectin films, elaborated via Schiff base reaction, were characterized using FTIR and XRD analyses. The results of methyl orange adsorption showed an efficiency that can reach 100%. The adsorption data were best described by the Freundlich isotherm and the pseudo-second-order kinetic model, indicating a heterogeneous surface and a chemisorption-dominated process.

Keywords: pectin, chitosan, extraction, oxidation, Schiff-base reaction, adsorption, methyl orange

INTRODUCTION

The removal of synthetic dyes from polluted water has become a challenge for environmental preservation, as most dyes are toxic, non-biodegradable and carcinogenic to humans.[1] To address this, several techniques have been developed for wastewater treatment, such as selective separation membranes,[2] coagulation/flocculation,[3] photodegradation[4] and adsorption using various adsorbents.[5,6,7] Among these methods, adsorption is considered the most effective due to its high efficiency, simple operation and low cost. Various types of adsorbents have been employed for removing dyes from wastewater.

Natural polysaccharides can be considered an excellent adsorbent for pollutants present in aqueous effluents. Chitosan is a unique, naturally cationic polysaccharide that has demonstrated high removal efficiency of both inorganic (heavy metal ion) and organic (dyes and pesticide formulations) pollutants through adsorption, attributed to the presence of amino groups in its chemical structure.[8,9] The protonation of these amino groups enables chitosan to effectively adsorb negatively charged compounds via electrostatic attraction.[10] However, its high solubility in acidic media and poor mechanical properties restrict its applications. Consequently, modifying chitosan is necessary to make it more suitable for such applications.

Two main methods can be used to improve the adsorbent properties of chitosan: (1) blending with other polymers, and (2) chemical crosslinking with crosslinking agents. Conventional crosslinking agents, such as glutaraldehyde and other small molecular aldehydes, often exhibit biological toxicity, which limits their applications.[11] However, blending polymers appears to be the best solution.

Various natural polymers have been applied to obtain composite films. Pectin, cellulose and gelatin are examples of such polymers.[12,13] Pectin is basically composed of poly α-1,4-galacturonic acid.[13] The chemical structure of pectin possesses reactive functional groups, including carboxylic groups, methyl ester groups and methyl amide groups.

In this work, chitosan-dialdehyde pectin (CS-DP) was prepared through a Schiff-base reaction, using water-soluble chitosan (CS) and pectin modified by sodium periodate as an oxidant, which produced dialdehyde pectin (DP) with active aldehyde groups. DP can be used as a new type of biological crosslinking agent. The CS-DP films were used to remove orange methyl via adsorption.

EXPERIMENTAL

Sample preparation

Orange peels were obtained from a local seller in Blida, Algeria. The peels were finely cut, washed and dried (50 °C, 24 hours) in a convection oven. The dried peels were then ground and passed through a 45-mesh sieve. The powdered samples were packed in dark bags and stored in a dry environment before experimental analyses. Shrimp shells (*Parapenaeus longirostris)* were obtained from a local fish market. All the chemical reagents were used without any purification.

Extraction of pectin from orange peels

Orange peels have undergone the following procedures:

- *Bleaching*: a process used to inactivate enzymes that may still be present after juice extraction. The aim of bleaching is to guarantee the stability of the raw materials during the transport and storage until the use. The operation consists in immersing the sample in hot water at 90 °C for 10 to 15 minutes.
- *Washing*: after bleaching, the samples were immediately cooled by successive washes with water. Note that these washes prevent the degradation of pectin, remove sugars, bitter products, coloring agents and water-soluble compounds.
- *Drying*: after washing, the raw materials were dried on absorbent paper, and then further dried in a vacuum oven at 40 °C for 48 h.

The extraction of pectin was carried out in a hot acid medium using a conventional protocol, at a temperature ranging from 70 to 90 °C, a pH varying from 1.5 to 6, for 40 to 90 minutes.

After filtration of the dry residues, the pectin was precipitated by adding ethanol, while maintaining vigorous agitation for 20 minutes. The pectin gel was then centrifuged for 20 minutes at 4000 rpm. The obtained pectin was dried in an oven at 40 °C for 24 hours and conserved in a bottle before use.

The yield of pectin (YP) was calculated using the following equation (1):

$$\text{YP \%} = \frac{w0}{w} \qquad (1)$$

where w_0 is the dry weight of extracted pectin; w is the dry weight of raw material.

The equivalent weight of pectin was determined using the method described by Khamsucharit.[14] Briefly, 0.5 g of pectin was mixed with 2 mL of ethanol and placed in a 250 mL flask. It was then dissolved in 100 mL of water and 1 g of sodium chloride was added. To determine the endpoint of the titration, 6 drops of phenolphthalein indicator were added. The equivalent weight was calculated using the following equation (2):

$$\text{EW (g. moL}^{-1}) = \frac{W}{V*N} * 1000 \qquad (2)$$

where W is the weight of sample (g); V is the volume of alkali (mL), and N is normality of alkali.

The number of methoxylated groups of pectin is the most important parameter that determines the properties of its aqueous solutions and gels.[15] The degree of esterification (DE) of extracted pectin was determined using both a titration method and conductimetric titration. For this, 0.2 g of dried pectin was suspended in 5 mL of ethanol and 100 mL of distilled water, and stirred for 2 hours at 40 °C. The resulting solution was titrated with 0.1 N NaOH in the presence of a few drops of phenolphthalein until a pale rose color persisted. The volume of NaOH consumed to reach this endpoint, representing the titration of free carboxylic acid groups, was recorded as the initial volume V_1. Subsequently, 20 mL of 0.5 M NaOH was added to the neutralized solution, and the mixture was stirred at ambient temperature for 2 hours to further hydrolyze the side ester groups.

After that, 20 mL of HCl (0.5M) was added to neutralize the remaining NaOH, and the excess HCl was titrated against 0.1 M NaOH. The total titration volume was recorded, and the degree of esterification (DE) was calculated using the following equation (3):

$$\text{DE\%} = \frac{V2}{V1+V2} * 100 \qquad (3)$$

where V_1 is the volume of NaOH used to titrate the free carboxylic acid groups (mL), V_2 is the volume of NaOH used to titrate the saponified methyl ester groups (mL).

The methoxy content was calculated using the following equation (4):

$$\text{MeO\%} = mL\ titrated\ NaOH * 31 * \frac{100}{pectin\ weight} \qquad (4)$$

where 31 represents the molecular weight of the methoxy group (CH_3O).

Extraction of chitin and chitosan from shrimp shell

The shrimp shells were washed and dried in an oven for 4 days at 60 °C before being ground into powder form,[16] and stored in a closed container prior to use. The extraction of chitin involved two steps: deproteinization, which removes proteins and glucans, and demineralization.

Deproteinization

30 g of shrimp shell powder was treated with 1M sodium hydroxide at a solid-to-solvent ratio of 1:5 (w/v) for 20 hours at ambient temperature. The residue was washed and soaked in distilled water until it neutralized.[17] After that, the powder was filtered and

dried at temperature 60 °C in an oven before proceeding with demineralization.

Demineralization

The demineralization process was carried out using 1M and 1.5M of hydrochloride acid respectively with a solid to solvent ratio of 1:9 (w/v) at the temperature of 35 °C for 2 hours.[18] Following this process, chitin was obtained.

Deacetylation of chitin

Deacetylation was performed by treating the chitin with a 40% NaOH solution. The ratio of chitin/NaOH (w/v) was 1:4. The reaction mixture was initially heated at 60 °C for one hour, and subsequently at 100 °C for 2 h. At the completion of the reaction, the biopolymer chitosan was obtained.[18]

Preparation of dialdehyde pectin

In order to oxidize pectin into a dialdehyde structure, 2% solution of pectin in distilled water was stirred in the dark with 30 mL of periodate solution under varying conditions of time, temperature (20-60 °C) and pH (2-8).[19] Upon completion of the reaction, 80 mL of ethanol was added to the flask contents. Besides inhibiting further oxidation, the ethanol also promoted pectin gelation. The resulting mixture was then poured into polystyrene Petri dishes and left to dry at 40 °C for 24 hours.

Determination of aldehyde content

The aldehyde group content was calculated using the rapid quantitative alkali consumption method.[20] From 0.15 to 0.20 g of oxidized pectin DP was suspended in 10 mL of standardized 0.25N sodium hydroxide, and the flask was swirled in a water bath at 70 °C for 2 minutes, and then cooled immediately under running tap water with rapid swirling for 1 minute. After that, 15 mL of 0.125N sulfuric acid was added, 30 mL of distilled water and 1 mL of 0.2% phenolphthalein was added in turn.

Titration of the acid solution was carried out using 0.25M sodium hydroxide. The percentage of dialdehyde units was calculated using the following equation (5):

$$\text{DA (\%)} = 100 \times \frac{C1 \times V1 - 2C2 \times V2}{w/173 \times 1000} \tag{5}$$

where C_1, C_2 (mol/L) represent the normality of NaOH and H_2SO_4, respectively; V_1, V_2 (mL) represent the total volume of NaOH and H_2SO_4, respectively; W is the dry weight of the galacturonic acid sample, 173 is the average molecular weight of the repeat unit in DP. The experiments were performed in triplicate.

Elaboration of chitosan-DP films

CS-DP films were prepared via the Schiff-base reaction by mixing different amounts of CS with DP (w/w) (4/1 and 3/2) in distilled water at a temperature of 60 °C and pH 4 for 30 minutes. The resulting gel was then separated by centrifugation for 20 minutes at 6000 rpm. The gel was spread onto a glass plate. After drying, the CS-DP film was obtained.

Adsorption study

The adsorption of methyl orange (MO) (purity 85%, Sigma-Aldrich) onto the CS-DP films was investigated using batch adsorption experiments.

Films with a surface area of 5*3 cm^2 were brought into contact with MO solutions at different concentrations (20, 40 and 60 $mg.L^{-1}$). To optimize adsorption, the effect of pH, initial pollutant concentration and contact time were studied. The pH of the solution was adjusted using 0.1 M HCl or NaOH solutions.

A portion of the methyl orange MO solution was withdrawn at specific times to analyze the residual dye concentration using a UV spectrophotometer at 464 nm. The removal percentage of adsorbed MO was calculated based on the following equation (6):

$$Y = \frac{(C0 - Ct)}{C0} * 100 \tag{6}$$

where C_0 is the initial MO concentration (mg/L); C_t is the MO concentration at time t.

Adsorption kinetics

To evaluate the kinetic parameters, the pseudo-first-order model and the pseudo-second-order model were applied.

The pseudo-first-order model (Lagergren model)[21] is presented by Equation (7):

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{7}$$

The linear form of the above equation is given by:

$$\text{Ln}\,(q_e - q_t) = \ln q_e - k_1 t \tag{8}$$

where k_1: the first-order adsorption reaction rate constant (min^{-1}), q_e: the quantity adsorbed at equilibrium (mg/g), q_t: the quantity adsorbed at time t (mg/g), t: contact time (min).

The pseudo-second-order model[21] is presented by the equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 . \tag{9}$$

$$\frac{dq_t}{q_t} = \frac{1}{k_2\, q_e{}^2} + \frac{1}{q_e} \tag{10}$$

where K_2: the pseudo-second order adsorption rate constant (g/mg.min), q_e: the quantity adsorbed at equilibrium (mg/g), q_t: the quantity adsorbed at time t (mg/g), t: time (hours).

The pseudo-second order rate constants are used to calculate the initial adsorption rate according to the following equation (11):

$$v_i = k_2 \times q_e{}^2 \tag{11}$$

Adsorption isotherms

The most frequently encountered adsorption models are the Langmuir and Freundlich isotherms.

The Langmuir model[21] is simple and widely applied. It is based on the following assumptions: the adsorbed species are located on a well-defined site on the adsorbent (localized adsorption); each site can bind only a single adsorbed species; all adsorption sites have identical adsorption energies, which are independent of the presence of other adsorbed species; there are no interactions between adsorbed species on neighboring sites (homogeneous surface). This model describes the formation of a monolayer of adsorbate molecules on the solid adsorbent surface, and the quantity adsorbed is given by the following equation (12):

$$C_e/Q_t = 1/Q_{max}.k + C_e/Q_{max} \quad (12)$$

The Freundlich model[21] is based on the following two assumptions: the number of adsorption sites available for adsorbing the compound is unlimited; and the strength of binding between the adsorbate and the adsorption sites decreases as the number of occupied sites increases. The Freundlich isotherm equation is frequently used to describe experimental adsorption data. The concentrations adsorbed in solution are linked by the relationship (Eq. 13):

$$Q_{ads} = k_f.C_e^{1/n} \quad (13)$$

Characterization

ATR-FTIR spectra of different films were acquired using a Thermo Scientific (FTIR Nicolet IS10), equipped with a DTGS KBR detector an ATR Platinium mono-reflexion accessory. The OMNIC software was employed for spectra acquisition. The powder sample were deposited in the ATR, and the ATR-FTIR spectra were obtained in the range between 4000 and 400 cm^{-1}, with a resolution of 4 cm^{-1} and scan number 32.

X-ray diffraction analysis was carried out using a **D8 Advance instrument (Bruker AXS)**. This equipment employs **CuK-α radiation** (λ = 1.5406 Å).

RESULTS AND DISCUSSION

The aim of this work was to enhance the adsorption properties of chitosan (CS) and to modify its solubility. For this purpose, we have chosen to modify it with oxidized pectin by the Schiff-base reaction.

Extraction of pectin

Optimal conditions for conventional pectin extraction were determined. The pH was adjusted to 1.5 using 0.1N HCl, the liquid-to-solid ratio was set to 25 (v/w), and the mixture was heated in a 90 °C water bath for 50 minutes. Under these conditions, a pectin yield of 22% was obtained. The degree of esterification (DE) of the extracted pectin reached 92%, indicating that it was highly methylated.

The equivalent weight is another criterion used to assess the quality characteristics of the isolated pectin. It represents the total content of free (not esterified) galacturonic acid present within the pectin's molecular chains. The presence of free galacturonic acid contributes to the viscosity and water-binding properties of pectin. The highest equivalent weight (EW) value of 746 g.moL^{-1} was obtained when hydrochloric acid was used for pectin extraction.

Fourier-transform infrared spectroscopy (FT-IR) analysis of the extracted pectin was carried out and the spectrum is shown in Figure 1. Characteristic peaks of the OH bond are observed in the region from 3300 to 3600 cm^{-1}. The band around 2900 cm^{-1} is attributed to the CH, CH_2 and CH_3 stretching vibrations present in the galacturonic acid methyl esters chains. The peak at 1740 cm^{-1} corresponds to the C=O stretching vibrations of ester groups and the derivative of the acetyl group ($COCH_3$). The peak at 1630 cm^{-1} is related to the OH stretching vibration band, while the band at 1020 cm^{-1} is assigned to the bending or stretching vibrations of the C-O bonds.[22-24]

The XRD pattern of pectin shown in Figure 2 confirms the semi-crystalline nature of the biopolymer.

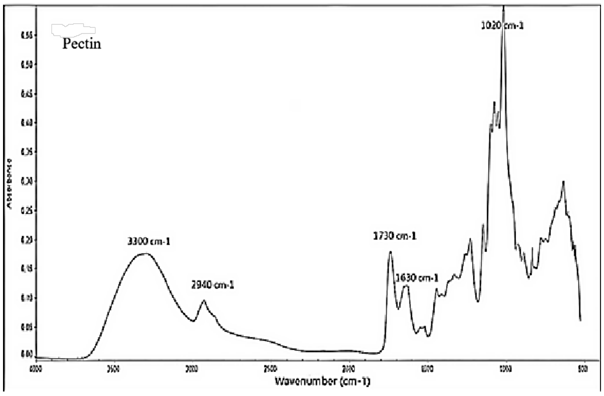

Figure 1: Infrared spectrum of extracted pectin

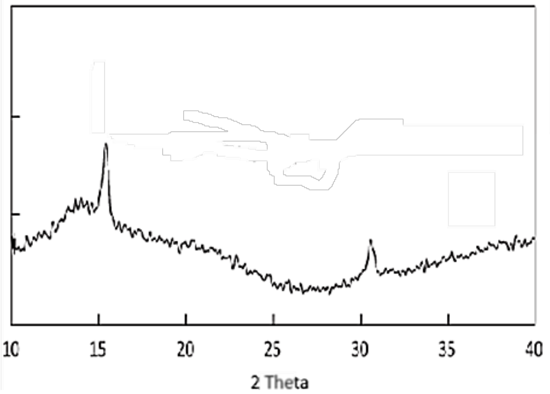

Figure 2: X-ray diffraction pattern of pectin

Extraction of chitin and chitosan

The extraction of chitin by a chemical method was carried out in two steps: demineralisation and deproteinisation. The yield of chitin obtained was 71.41%.

Chitosan was then synthesized through the deacetylation of chitin in a 40% alkaline solution. The resulting yield of chitosan was 37%.

The FTIR spectrum of chitosan is shown in Figure 3. A strong broad band in the region 2200-3500 cm^{-1} corresponds to both N-H and O-H stretching vibrations. The absorption bands around 2930 and 2870 cm^{-1} can be attributed to symmetric and asymmetric C-H stretching, respectively. The presence of residual N-acetyl groups was confirmed by the bands at around 1645 cm^{-1} (C=O stretching of amide I) and 1325 cm^{-1} (C-N stretching of amide III), respectively. We did not find the group corresponding to the N-H bending of amide II at 1550 cm^{-1}. This is the third band characteristic of a typical N-acetyl group and it may overlap with other bands. The band observed at 1589 cm^{-1} corresponds to the N-H bending vibration of the primary amine group.[25]

XRD analysis was carried out to study the crystallinity of the extracted chitosan (Fig. 4). The XRD spectrum of chitosan exhibits very broad peaks at $2\theta \approx 10°$ and $2\theta \approx 20°$.[26] The technique used to determine the crystallinity index is to calculate the ratio between the area of the peaks associated with the crystalline zones and the total area. The crystallinity index for chitosan is therefore 33.33%, which means that chitosan is semi-crystalline.

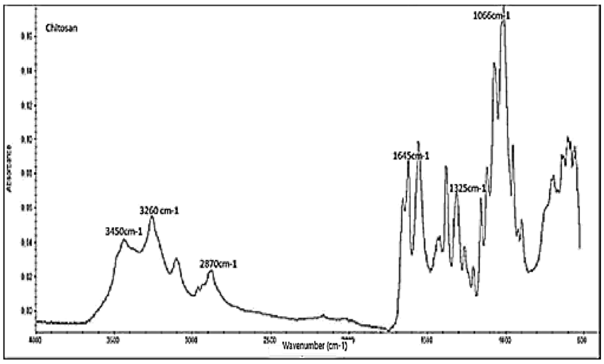

Figure 3: Infrared spectrum of chitosan

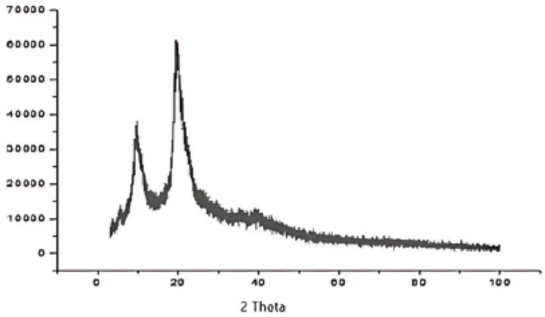

Figure 4: X-ray diffraction pattern of chitosan

Synthesis for dialdehyde pectin (DP)

Pectin undergoes oxidation by sodium periodate according to the Malaprade reaction. It is known to be a highly specific reaction to convert a vicinal diol present on the C_2 and C_3 carbons of the anhydro-D-glucopyranose ring to carbonyl functional groups.[27] Oxidation is not complete in water or other solvents, due to the formation of hemiacetals between the aldehyde and neighboring hydroxyl groups.[28,29] The probability of hemiacetal formation is reduced when the concentration of periodate increases, because a larger number of periodate ions can attack a multiple number of vicinal diols simultaneously.

The aldehyde content generated during the oxidation reaction was estimated using the alkali consumption method, which is based on the Cannizzaro reaction. The calculated aldehyde content was 83.33%, and the esterification degree (DE) was found to be 53%. This indicates that the pectin became weakly methylated after oxidation, in contrast to its highly methylated state before the reaction. The scheme reaction is shown in Figure 5.

The effect of reaction time and temperature on the aldehyde content is presented in Figures 6 and 7. As shown in the graphs, the percent of aldehyde content increases with increasing reaction time. However, it reduced when the pH was raised. The negative charges of the polysaccharides repel the negative charges of the periodate, this can be countered by reducing the pH of the reaction medium. This result coincides well with those reported in the literature.[30-32]

The FTIR spectrum of dialdehyde pectin is presented in Figure 8. The presence of dialdehyde groups in the pectin is confirmed by a characteristic band around 1734 cm^{-1}. According to the work of Fan *et al.*,[33] the peak for the dialdehyde in periodate oxidized polysaccharides is seen in a very narrow range of 1732–1734 cm^{-1}. Our result coincides very well with this report. The band at 1615 cm^{-1} is assigned to free carboxylate COO$^-$ groups.

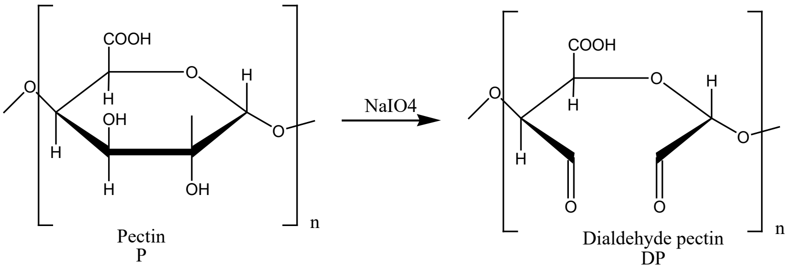

Figure 5: Reaction scheme for the synthesis of dialdehyde pectin

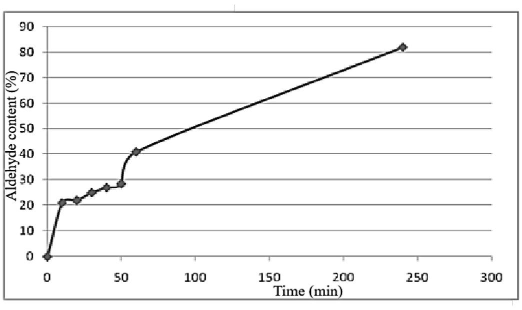

Figure 6: Effect of times on aldehyde content

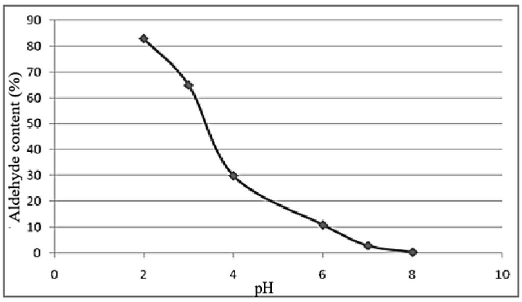

Figure 7: Effect of pH on aldehyde content

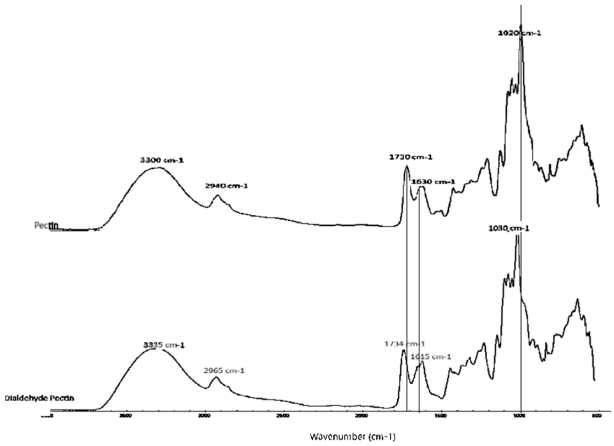

Figure 8: FTIR spectra of pectin and dialdehyde pectin

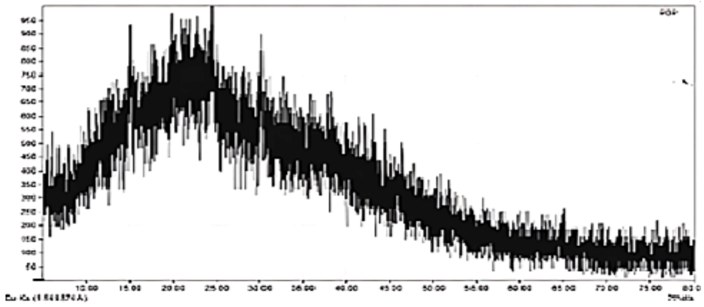

Figure 9: X-ray diffraction pattern of dialdehyde pectin

The oxidation of pectin by periodates leads to a significant change in its crystalline structure, primarily evidenced by the disappearance and shifting of its characteristic diffraction peaks.

Pectin exhibits two characteristic crystalline peaks at 2θ~13° and 31°.[34] Oxidized pectin loses some of its crystallinity and becomes more amorphous (Fig. 9).

Elaboration of chitosan/dialdehyde pectin (CS-DP)

This study investigated the fabrication of chitosan/dialdehyde pectin films through a Schiff-base reaction between the amino groups of chitosan and the aldehyde group of dialdehyde pectin (DP). The reaction scheme is presented in Figure 10.

Infrared spectroscopy of the CS-DP (Fig. 11) confirms the presence of a characteristic band around 1600 cm^{-1}, which is indicative of the imine functional group (C=N) formed via the Schiff-base reaction.

The structural properties of chitosan-dialdehyde pectin were investigated by XRD. The XRD pattern (Fig. 12) provides information on the degree of crystallinity of the materials. The addition of oxidized pectin to chitosan led to changes in the XRD pattern, with the disappearance of some peaks and the appearance of new ones around 13.08° and 14.28° in the case of the CS/DP (4/1 w/w) film, suggesting interactions between the polymers.

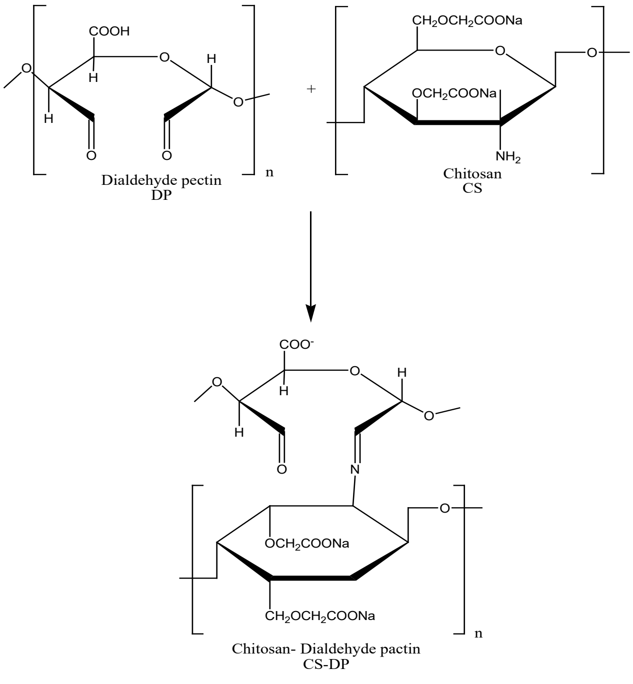

Figure 10: Reaction scheme for the synthesis of chitosan-dialdehyde pectin film

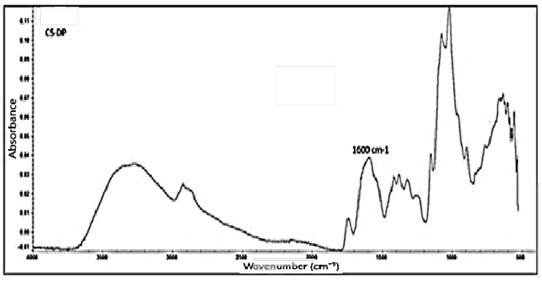

Figure 11: FTIR spectrum of CS-DP (3/2)

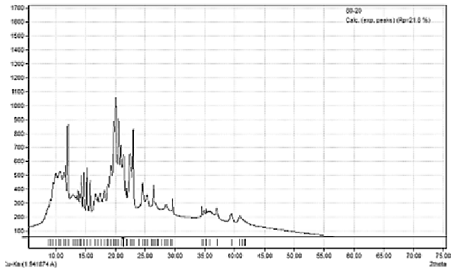

Figure 12: X-ray diffraction pattern of CS-DP film

Adsorption of methyl orange (MO) on CS-DP films

The kinetic adsorption of methyl orange, an anionic dye, on the CS-DP films was investigated in this part. We selected the CS-DP film with the w/w ratio of 4/1 to study the effect of initial methyl orange (MO) concentration and contact time on the adsorption process.

Effect of initial concentration of MO

The effect of the initial MO concentration on the adsorption capacity of CS-DP films is illustrated in Figure 13. Three dye concentrations were investigated (20, 40 and 60 mg.L^{-1}) using CS-DP films with a surfaces area of 15 cm^2 (5 cm × 3 cm) at pH 4 and ambient temperature. The maximum adsorption yield reached 100% with 20 mg.L^{-1} of MO to achieve equilibrium adsorption within 20 min. On the other hand, we have found that the quantity of MO adsorbed decreases when the concentration of MO increases. The adsorption sites on the adsorbent can quickly become saturated. Once all the sites are occupied, the additional quantity of pollutant cannot be adsorbed. These findings are consistent with observations reported in other studies.[34,35]

Effect of pH

The effect of pH on the adsorption process was investigated across a range of pH values from 4 to 10 (Fig. 14). The pH of the MO solution was adjusted using 0.1M of HCl and 0.1 M of NaCl. The pH is an important parameter in adsorption, as it affects the dissociation of functional groups on the active sites, the charge on the adsorbent surface and the behavior of the MO solution. The results demonstrated that the adsorption capacity increased with decreasing pH, the highest removal capacity was obtained at pH 4. On the other hand, adsorption is very low with basic pH ~9. At acid pH, the surface charge of the films is positive. As a result, H$^+$ ions compete with the dissociated sulphonate groups of the MO dye, leading to a reduction in adsorption.

Adsorption isotherm

In order to understand the adsorption mechanism of MO on the CS-DP film, we have used two isotherm models – the Freundlich and the Langmuir models (Fig. 15, Table 1). The simulation of the experimental data by the isotherms studied showed the applicability of both models, with very satisfactory correlation coefficients. The Langmuir model showed good correlation ($R^2 = 0.965$), and provided a maximum adsorption capacity (Q_m) of 21.276 mg/g. However, the results show a slightly better agreement of the experimental points with the Freundlich model ($R^2 = 0.841$), which probably indicates the heterogeneity of the adsorption sites on the surface of the CS-DP film.

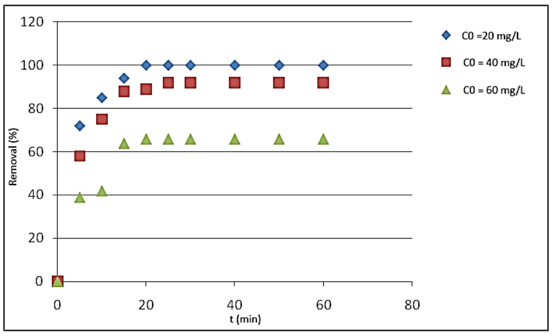

Figure 13: Effect of initial MO concentration on adsorption capacity of CS-DP films (surface of 15 cm^2 at pH = 4 and ambient temperature)

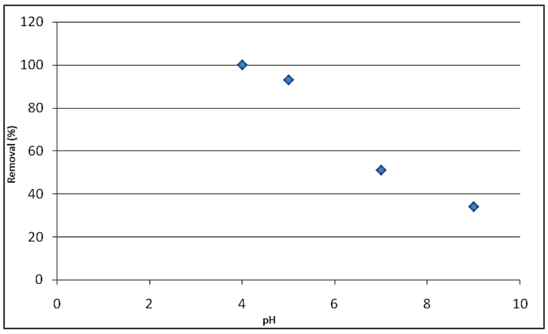

Figure 14: Adsorption kinetics of MO (20 mg.L^{-1}) on CS-DP films at different pH

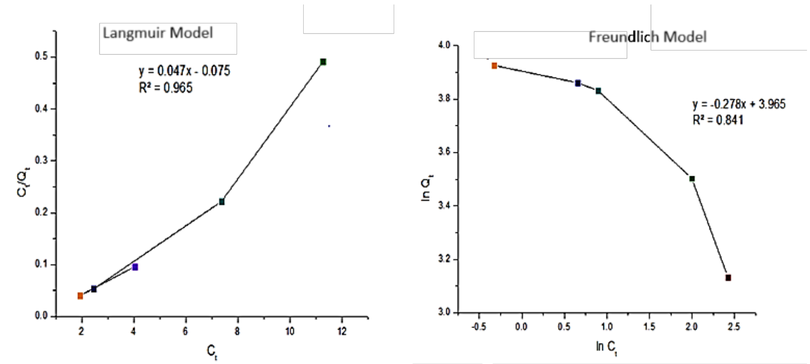

Figure 15: Plots of isotherm models of the adsorption of MO on CS-DP films

Table 1
Data of isotherm adsorption model

Adsorbent	Freundlich			Langmuir		
	n	K_1	R^2	Q_m (mg/g)	K_2	R^2
CS-DP film	3.597	57.72	0.841	21.276	0.62668	0.965

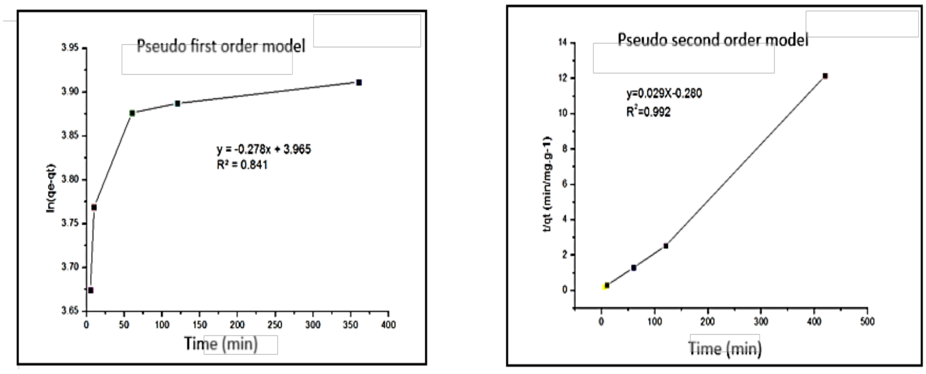

Figure 16: Plots of first-order-model and second-order-model of adsorption of MO on CS-DP films

The study of the modeling of adsorption kinetics shows a discrepancy between the theoretical and experimental adsorption capacity values when using the pseudo-first-order model (Fig. 16), and the correlation coefficient was relatively low ($R^2 = 0.841$).

From these results, we can conclude that the pseudo-second-order model ($R^2 = 0.992$) describes the kinetic data perfectly, suggesting a chemisorption mechanism.

CONCLUSION

In conclusion, this study demonstrated the efficient removal of methyl orange (MO) from aqueous solutions using chitosan-dialdehyde pectin (CS-DP) films elaborated via Schiff base reaction. Pectin was extracted from orange peel waste with a high yield (22%) and degree of esterification (92%). Chitin was extracted from shrimp shells with a yield of 71.41% and subsequently deacetylated to produce chitosan with a yield of 37%. The oxidation of pectin by sodium periodate resulted in dialdehyde pectin with an aldehyde content of 83.33%, leading to a decrease in its crystallinity.

The prepared CS-DP films exhibited a remarkable MO adsorption capacity, reaching 100% removal efficiency at an initial MO concentration of 20 mg/L within 20 minutes at pH 4 and ambient temperature. The adsorption capacity was found to be inversely proportional to the initial MO concentration, indicating site saturation at higher concentrations. The adsorption process was highly pH-dependent, with optimal removal observed at acidic pH (pH 4), attributed to electrostatic interactions between the positively charged CS-DP film surface and the anionic MO dye.

The kinetic study revealed that the adsorption process was best described by the pseudo-second-order model ($R^2 = 0.992$), suggesting a chemisorption mechanism. Furthermore, the equilibrium adsorption data were well-fitted by the Freundlich isotherm model ($R^2 = 0.841$), indicating a heterogeneous adsorption surface and multilayer adsorption.

These findings highlight the potential of utilizing renewable resources like orange peel and shrimp shells to produce an effective bio-adsorbent for the removal of anionic dyes from wastewater. The high adsorption capacity and the use of a Schiff base reaction for film elaboration offer a sustainable and environmentally friendly approach to water treatment.

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