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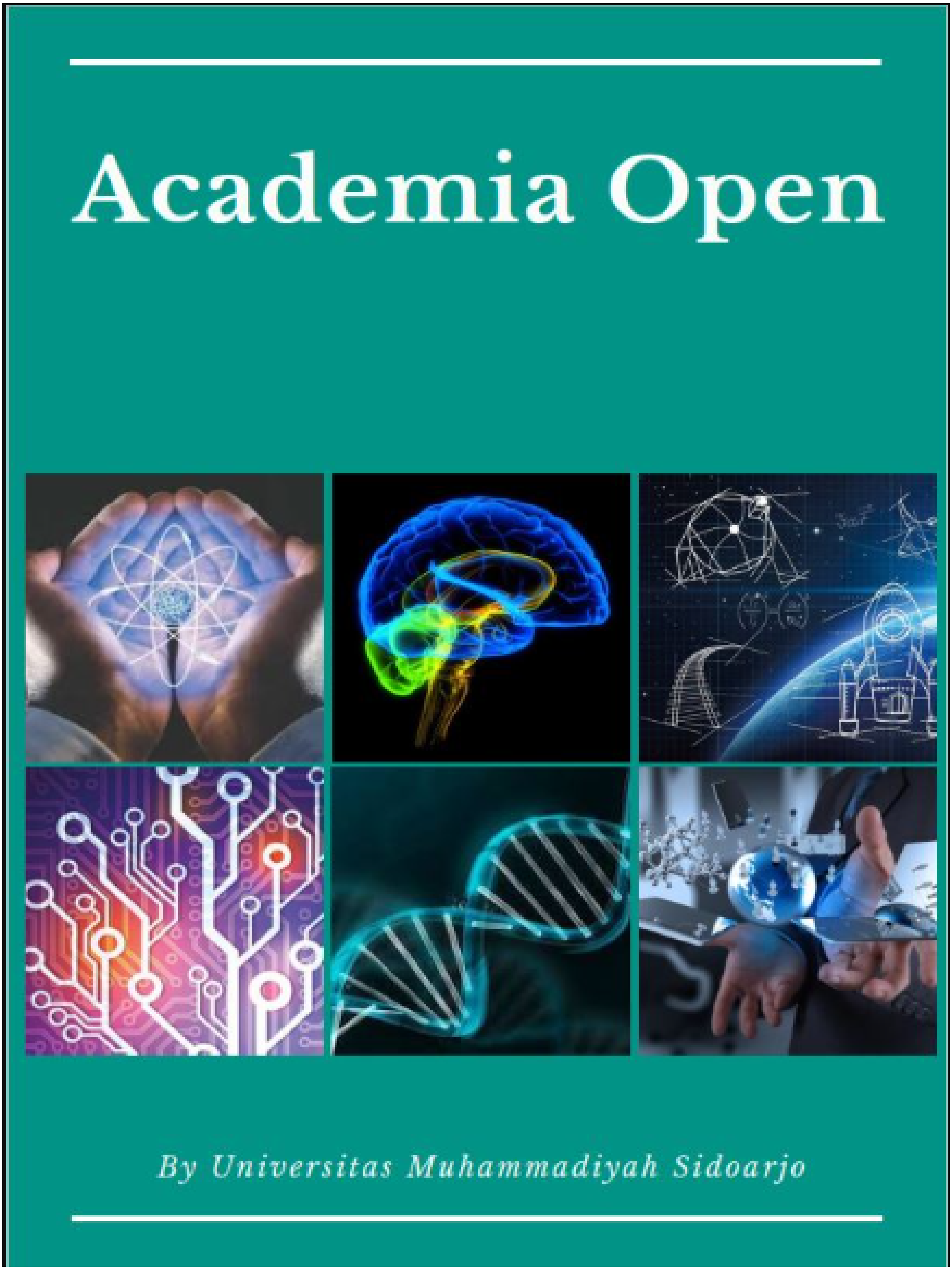

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Applications of Chitosan Polymer Membrane to Removal Methyl Orange Dye from Aqueous Solutions: Aplikasi Membran Polimer Kitosan untuk Menghilangkan Pewarna Metil Oranye dari Larutan Berair

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Abstract

In this study, membranes made from chitosan, a natural polymer derived from shrimp shells, were investigated for their ability to remove toxic methyl orange (MO) dye from water. The membranes were characterized using infrared spectroscopy, and the maximum absorption wavelength of MO dye was determined via UV-Visible spectrophotometry. Solutions of varying MO concentrations were passed through the chitosan membranes, and their absorbance was measured before and after filtration. Results showed high removal rates ranging from 85% to 95%, with the highest efficiency observed at 20 ppm MO concentration. This research highlights the potential of chitosan membranes as effective and sustainable solutions for water purification, addressing a crucial environmental and health concern posed by toxic dye pollution.

Highlights:

1. High removal rates: Chitosan membranes remove dye efficiently (85%-95%).
2. Eco-friendly: Derived from shrimp shells, chitosan offers sustainable water purification.
3. Advanced analysis: Infrared spectroscopy and UV-Visible spectrophotometry characterize membrane properties.

Keywords: Chitosan membranes, Water pollution, Methyl orange dye, Removal efficiency, Environmental sustainability

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Introduction

When several tiny molecules, known as monomers, are joined together, a big molecule known as a polymer is created [1].Polymerization is the process by which monomers associate to produce polymers [2]. In daily life, polymers—both natural and synthetic—play a significant and pervasive role [3]. The supplies for polymers are diverse and include manufactured plastics like polyethylene as well as naturally occurring polymers like DNA (poly nucleotide) and proteins (poly amino acid), which are vital to biological structure and function.

The word "biopolymers" is frequently used to refer to polymers that are spontaneously formed by living organisms. Their repeating units of amino acids, saccharides, or nucleic acids make up their molecular backbones. Occasionally, other chemical side chains are added, which further enhances their capabilities. Although the majority of biopolymers are derived from biomass, such as polysaccharides from cellulose and proteins from collagen or milk, biopolymers can also be made from bio-monomers directly in microorganisms or genetically modified organisms, or via conventional chemical processes like polylactic acid[4].

The second most abundant natural polymer after cellulose is chitin, which is also naturally biodegradable[5]. Animals include large amounts of this structural material; examples include the internal flexible backbone of cephalopods, the shells of arthropods (crabs, shrimp, and beetles), webs of spiders and worms, and the cell walls of fungi and yeasts[6,7].

Chitin's bulk structure and insolubility in common organic solvents and water make it a restricted user resource even with its simple accessibility[8]. With over 1000 tons produced year in nature, chitin derivatives are thought to constitute the primary biomass resource[9]. Shells, which contain around 30% chitin, are a major source of trash for the shellfish processing industry (shrimp or crab shells)[7].

chitosan (CS) a (1-4) connected 2-amino-2-deoxy-β-D glucosan called chitosan (CS) is created by the N-deacetylation of chitin, the primary structural component of shrimp and crab shells. This natural and biodegradable polymer has garnered significant attention because to its several suggested novel uses, which include heavy metal chelation, textile finishes, paper manufacturing, pharmaceutical and biomedical engineering, and cements[10]. Uses of chitin are restricted contrasted with those of chitosan because of its enormous insolubility and challenges in handling. In this way, chitin is all the time joined with chitosan which gives truth be told comparative applications. Chitin increments twisted mending in splash, gel and dressing. [11,12]. It is utilized as a help of medicaments or to control drug discharge [13], considering the biodegradability, low poisonousness, physiological dormancy, antibacterial properties, hydrophilic person, gel shaping properties, partiality for proteins and mucoadhesivity [14]. Chitosan and its subsidiaries have been widely read up for drug conveyance and other biomedical applications due to their:

1. Biocompatibility and low poisonousness.

2. Cationic properties.

3. Conceivable plan in nanoparticles or in gels. [15]

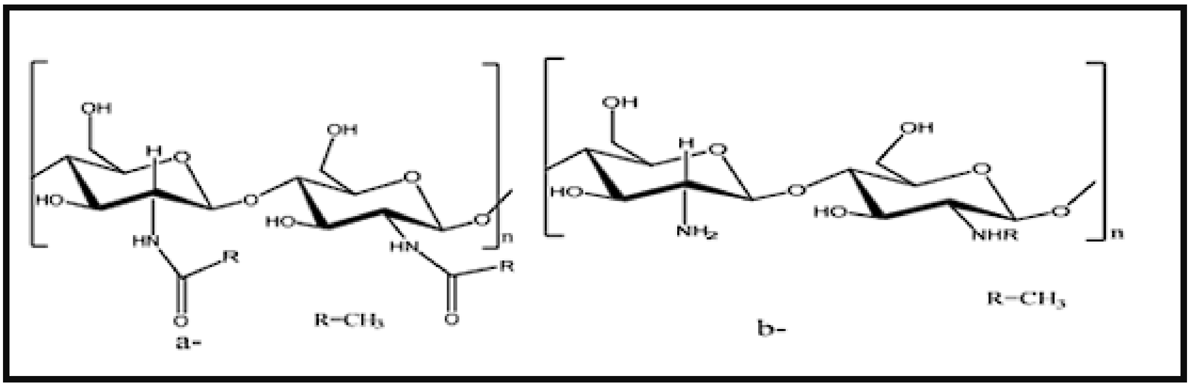

Figure 1. Structure of (a) chitin and (b)chitosan polymers

Industries including textile, paper, dye synthesis, food, printing, leather, and plastics use dyes extensively. Numerous colors can directly destroy aquatic life forms since they are harmful to certain types of creatures. Therefore, creating a competitive and sustainable effluent management strategy for the dyeing sector has always been a key responsibility for environmental preservation. Reverse osmosis, membrane separation, oxidation or ozonation, photochemical degradation, coagulation and adsorption, and membranes are some of the traditional physicochemical techniques for eliminating dyes from wastewater [16, 17].

Methyl Orange Dye (MO) is one of the dyes most frequently used in the textile industry. It is also used in titrations as a pH indicator. Its characteristics and chemical structure are presented in Fig. (1-3), respectively. MO dye can be removed from solutions using a variety of approaches, some of which include sophisticated oxidation processes. coagulation-flocculation, electrochemical degradation, ultra-filtration, and photocatalytic degradation. However, as previously said, the methods on the above list have drawbacks such complexity, high operating costs, and time-consuming unit procedures. Due to its low operating costs, indifferent sensitivity to toxicants, and ease of design and operation, adsorption is a technology that is recommended above these other approaches for mitigating MO [18].

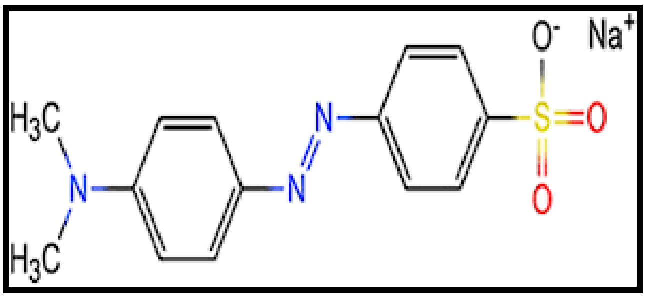

Figure 2. structure of Methyl Orange Dye

Methodology

2.2 Extraction of chitin polymer

2.2.1 Collecting Shrimp Shells

Dry shrimp shells are collected from the local market. They are washed by water several times and dried under the sun with dry air blown over them, which took 3 hours. Then, they are grinded by an electrical mill, and become ready to be used for the extraction of chitin.

Figure 3. show (A) shrimp shells (B) shrimp shell powder

2.2.2 Acid Treatment

To remove minerals and their salts, 75g of the powder sample was mixed mechanically for 24 hours at room temperature with 750 ml of a 4% v/v hydrochloric acid solution. After filtering and repeatedly washing the leftover powder in distilled water to eliminate any remaining hydrochloric acid until pH = 6-7, it was allowed to dry fully [19–21].

2.2.3 Base Treatment

To get chitin powders, 75 ml of a 10% sodium hydroxide solution was added to the powder and mechanically agitated for three hours at 90°C to remove all protein. The powder was then filtered and repeatedly washed with distilled water to remove any remaining sodium hydroxide, and dried [19–21].

2.3 Deacetylation of Chitin to Chitosan

In order to get a higher degree of deacetylation and, thus, improved solubility of chitosan, the extracted chitin is converted to chitosan using the deacetylation process. A solution of 60% sodium hydroxide (200 mL) is combined with 13 g of dry chitin. For almost three hours, the mixture was heated to a temperature of 120 oC.After filtering and washing, the sample was brought to pH 7. following the sample's washing and drying. After that, the samples were allowed to dry outside [56]. The resulting chitosan was supposed to be creamy-white in color.

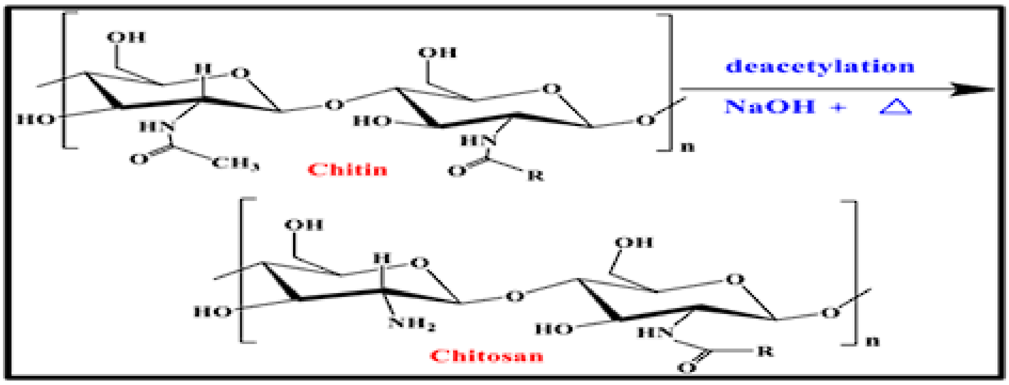

Figure 4. Deacetylation reaction of chitin to chitosan

2.4 Preparation of Chitosan Polymer (CS) Membrane

A 100 ml 1% acetic acid solution containing 10 mg of chitosan polymer was used to prepare 100 ppm of CS membrane [22]. The mixture was then vacuum-filtered using a cellulose nitrate membrane filter as a substrate (pore size: 0.22 µm).

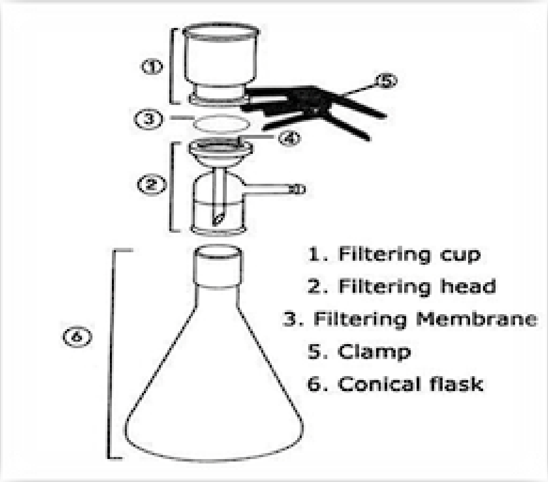

Figure 5. Show Vacuum Filtration Pump

2.5 Preparation of Stock Solution of Methyl Orange Dye(100 ppm)

A stock solution of Sodium-4-(4-dimethylamino phenyl diazenyl) benzenesulfonate dye (MO) C14H14N3SO3Na (Mwt = 327.34 g/mol) was prepared by dissolving 10 mg of the MO dye in deionized water into beaker, transferred quantitatively to volumetric flask (100 mL), filled up to the mark with deionized water. The working standard solutions were prepared by serial dilution of stock solution.

2.6 Determination wavelength maximum (λ max) of MO by UV- visible Spectrophotometer

The absorption spectrum of MO dye was obtained by UV-Visible spectrophotometer, the maximum absorption wavelength of MO dye was λ max = 463 nm and as shown in Fig. (6).

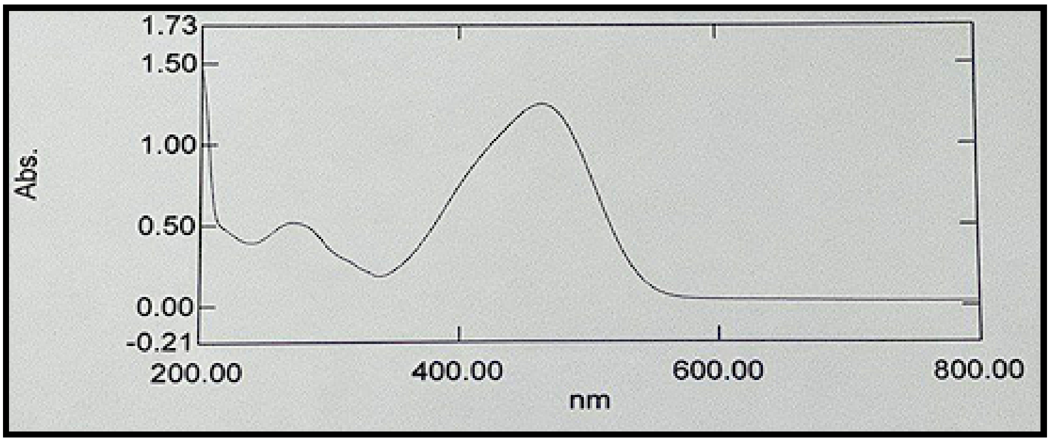

Figure 6. Absorption spectrum of MO dye

2.7 Separation of MO Dye by Chitosan Membranes

Prepared (5, 10, 15 and 20 ppm) solutions of MO dye in 25 mL as standard solution, absorbance at λmax= 463 nm measured by using UV-Vis Spectrophotometer. Added each solution of MO dye solutions to CS membrane , filtered by using the vacuum measured at the same wavelength.

Results and discussion

3.1 Infrared Spectrum of Chitin Polymer

When IR is used to verify the extracted chitin, the resulting spectrum is displayed in Figure (7). The chitin structure's distinctive carbonyl amide I group is stretched, resulting in a maximum at 1553.16 cm-1 and a sharp peak at 1666.20 cm-1 that are connected to the N-H amide II bond [23, 24]. Furthermore, a strong, broadband peak at 3431.22 cm-1 in the spectrum is jointly attributed to a stretching of hydroxyl groups (-OH) and a nitrogen group (-NH). The methylene groups' aliphatic C-H bond stretching peak is located at 2876.50 cm-1. The two peaks, corresponding to amide II C-N and C-O-C stretching, are located at 1375.55 cm-1 and 1307.63 cm-1, respectively [25].

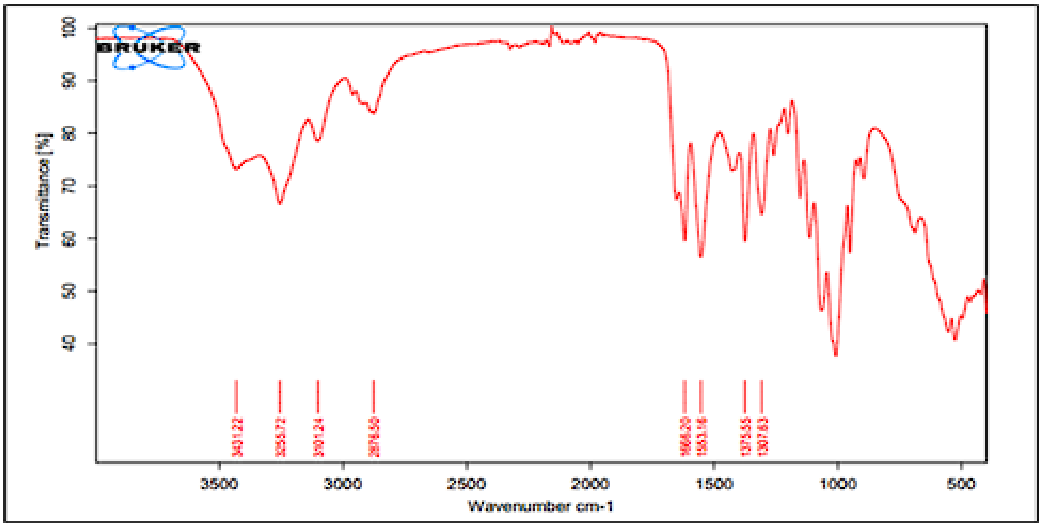

Figure 7. IR spectrum of extracted chitin from shrimp shells

3.2 Infrared Spectrum of Chitosan Polymer

IR spectroscopy is also used to analyze chitosan, which is chitin in its deacetylate state. The resultant spectrum is displayed in Fig. (8), The region of amide I is the first region seen in the infrared spectrum of chitosan. It primarily demonstrates the absence of this peak or the presence of a very weak peak at 1619 cm-1, suggesting a high degree of deacetylation process.Furthermore, owing to hydrogen bonding and (-OH) stretching and sharing with the stretching vibration of the

(-NH2) group, the spectrum displays broadband with a peak at 3356.01 cm-1. C-H stretching is the cause of the band at 2875.50 cm-1 [25, 26]. The deacetylation process is further confirmed by the emergence of an active band at 1141.7 cm-1, which is assigned to the (C-N) stretching bond.

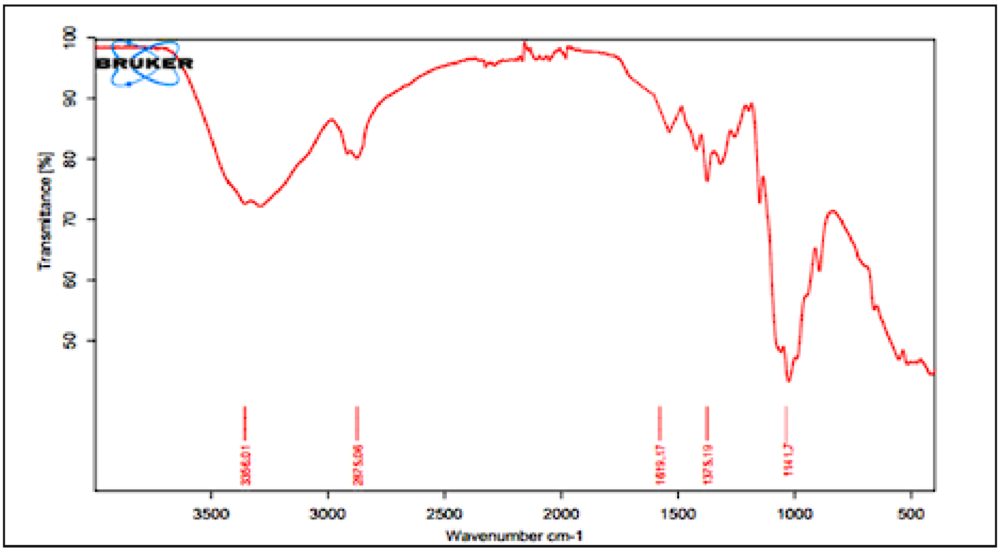

Figure 8. IR spectrum of extracted chitosan from shrimp shells

3.3 Applications of Chitosan Polymer (CS) Membrane to removal Methyl Orange Dye from aqueous solutions

As seen in Fig. (9), the experimental data indicates that the chitosan membrane removes 93,95,89,85% of the MO dye from solutions containing (5,10,15, and 20 ppm). Equation (1) yields the removal rate (%R) as follows:

%R = (Ci – Ce)/Ci × 100% .... (1)

Where: Ci (ppm) is the initial adsorbate concentration, Ce (ppm) is the dye concentration after separation, and %R removal rate is [27].

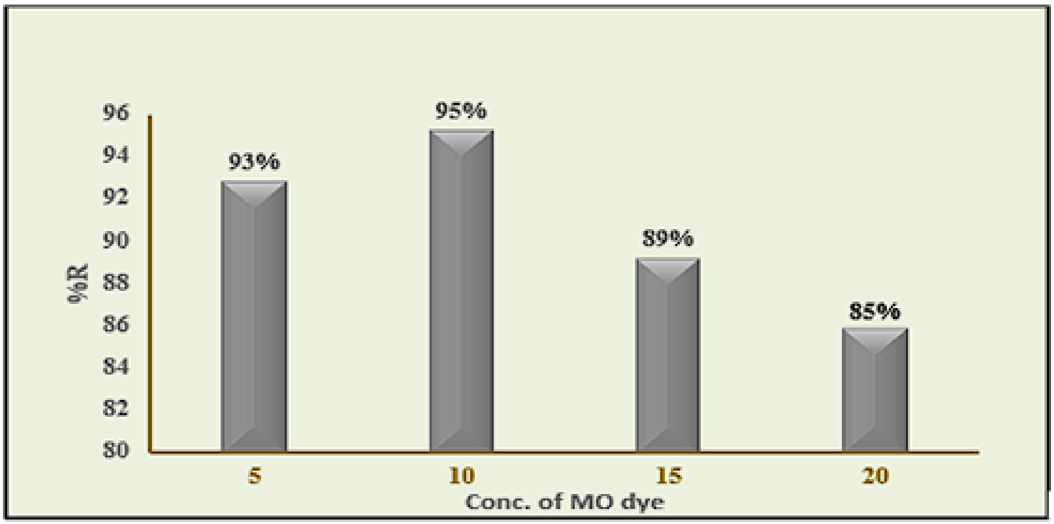

Figure 9. Removal rate of MO dye by chitosan membranes

We observe that the dye removal rate with membranes made from natural chitosan polymer is excellent and highly efficient, as shown in Fig. (10). The mechanism analysis revealed that the membrane removes dyes primarily by size exclusion, electrostatic interaction, hydrogen bonding, and physical sieving.

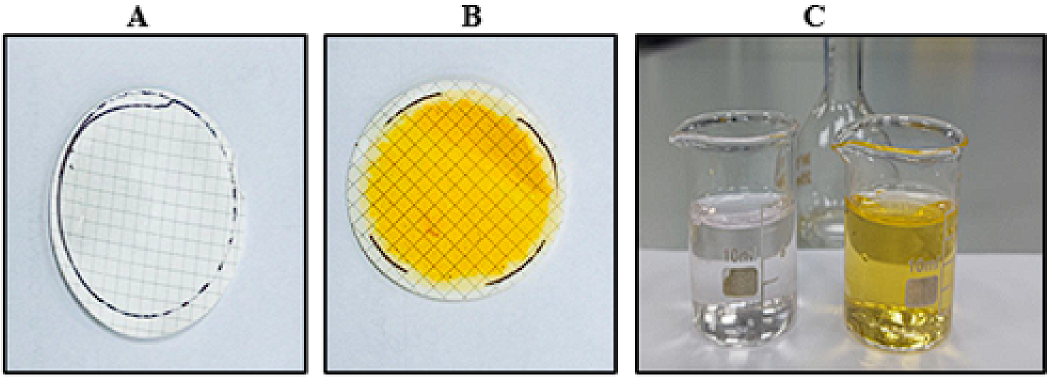

Figure 10. CS membrane (A, B) before and after separation of MO dye respectively (C) Solution of MO dye before and after separation by CS membrane

Conclusion

Chitosan polymer membranes are very effective in removing toxic dyes from aqueous solutions, such as methyl orange, with a very high removal rate.

Abbreviations

MOMethyl Orange Dye

CSChitosan Polymer

IRInfrared spectroscopy

UV-VisUltraviolet-Visible Spectroscopy

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