

Research Article

Removal of Cr(III) from Aqueous Solution Using *Labeo rohita* Chitosan-Based Composite

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Received 18 August 2022; Accepted 10 September 2022; Published 5 October 2022

Academic Editor: Rabia Rehman

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This study focusses on the synthesis of chitosan-cellulose composite membrane derived from *Labeo rohita* fish scales (FS) for the removal of Cr(III) from aqueous solution, while chromium is a serious threat to groundwater. Waste FS are valorized to chitosan by demineralization, deproteination, and deacetylation successively. Cellulose was extracted from sugarcane bagasse using acidic hydrolysis. Chitosan-based cellulose composite porous membrane was fabricated by evaporating solvent from polymer solution in petri dish. The impact of pH, contact time, and absorbent dosage on the removal of Cr(III) from an aqueous solution was investigated. Atomic absorption spectrophotometer was used to check the Cr(III). Results showed that chitosan comprising 85% degree of deacetylation was achieved by alkali treatment, while yield was 22%. FTIR analysis confirmed the chitosan and chitosan-cellulose-based composite membrane. Morphology studies showed that the cellulose was strongly staggered and due to the chitosan, the surface of cellulose became rougher, which is good to enhance the adsorption capacity. The maximum removal 57% of Cr(III) from aqueous solution was observed at pH 6 at 60 min and 50 mg dosage of adsorbent. The minimum removal (47%) of Cr (III) was found at pH 2. These results confer that *Labeo rohita*-based chitosan-cellulose composite membrane has great potential for the removal of metals from industrial effluents.

1. Introduction

Organic pollutants such as diethyl phthalate and polycyclic aromatic hydrocarbons and inorganic pollutants like heavy metals are major threat to water resources [1, 2]. Increasing industrial activities and the subsequent discharge of untreated wastewater containing dye to aqueous environment can cause problems such as reducing the sunlight penetration and creating anaerobic conditions such as allergy

and cancer [3]. To circumvent the water pollution, low cost and environmentally friendly adsorbents are a hot topic of water treatment research. In 2020, Imran and co-workers reported the active carbon derived from pomegranate peel as green adsorbent [4]. Today, the removal of heavy metals ions such as chromium (III) from water is very important to lower the environment and human health risks. Chromium is widely used in many industrial activities such as electroplating, leather tanning, nuclear power plants, and

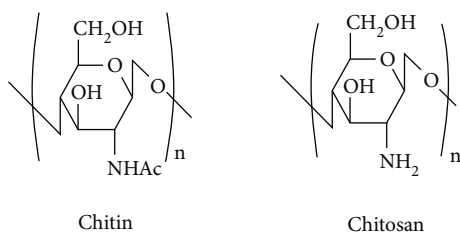


FIGURE 1: Structure of monomer of chitin and chitosan.

textile industries [5]. There is a need of hour to remove the metal ions from water using biodegradable adsorbents. Chitosan-based adsorbents are degradable and efficient to metal ions removal.

The outermost layer of the fish body consists of small, tough, and protective structures called scales that typically end up in bins and are regarded as waste in seafood restaurants, local markets, kitchens, and fish processing plants. A large amount of this waste is generated annually in Pakistan. Despite the fact that the wastes generated are biodegradable, every year, approximately 130 million (M) tons of fish wastes are produced around the world and from which 18–30 M tones were dumped. Due to large demand of oxygen, entangled substances, lipid-based components, bacteria, organic compounds, and other materials, fishery wastes are potentially harmful. The absence of proper waste management poses several environmental concerns [6–11].

Chitin (CH) is an acetylated glucosamine polysaccharide (Figure 1), in nature found second abundantly, after cellulose. The insect exoskeleton, shrimp, and other crustaceans, fungi, and fish scales (FS) are the major sources of CH. Due to its low solubility and slow degradability, CH is converted into a de-acetylated form named chitosan (Figure 2). Chitosan (CS) is a biopolymer having excellent film-forming properties, as well as antioxidant and antimicrobial properties, and is environmentally friendly. CS can be modified in the form of scaffolds, flakes, hydrogels, and films. Despite its benefits, it has some drawbacks, such as inferior mechanical, solubility in water and basic media, and thermal and permeability behavior, which restrict the use in a variety of application areas. Different studies have recorded cross-linking, derivatization, mixing with major biomolecules (lipids, proteins, peptides, and carbohydrates), natural synthetic polymers, other additives, and fillers' potential means of improving the CS characteristics [12–14].

Chitosan can serve as a metal recovering and purifying agent in the wastewater treatment. Despite the fact that chitosan has an inherent affinity and specificity for metal ions, the metals, like most biopolymers, suffer from two major drawbacks that have hampered its development for separation processes: low surface area and solubility into weak acid solutions. Chitosan is available in different forms, which are nonporous due to presence of hydrogen bonding between chitin biopolymer chains. The relatively low surface area of polymeric materials restricts access to internal adsorption sites, reducing metal-ligand adsorption ability and level [15–19].

Although there are many reports concerning chitosan membranes, little fundamental and systematical work has been done to throw light on the application of chitosan

membranes for the removal of heavy metal ions from wastewater. Compared with cellulose and its derivate membranes, chitosan membranes are capable of adsorbing toxic heavy metals as well. Thus, chitosan membrane combines the adsorption process and filtration process in one step. It may represent a feasible promising technology for the treatment of wastewater containing heavy metal ions as well as other pollutants in order to produce a high quality effluent. Therefore, it is of great importance to investigate the feasibility of such novel membrane. Chitosan nanocomposites are materials formed by physical or chemical interaction around chitosan and composites such as silver oxide, thermoplastic, or bentonite, and have applications in food, paints, and the environment [20–22].

Chromium (III) and chromium (VI) are the most common oxidation states of chromium present in natural sources, which have chemical, biological, and environmental properties that are quite different. Depending on pH, the presence of oxidizing and reducing compounds and the total chromium concentration in soil, water, and atmospheric systems, chromium (III) and chromium (VI), are interexchangeable. Chromium (III) is necessary for the proper functioning of living organisms, as well as glucose and fatty acid metabolism regulation. This mainly affects the lungs and weakens the immune system at higher doses. In humans, its effects are carcinogenic, cause allergies, and damage the kidneys, liver, and gastritis. Chemical precipitation, adsorption, ion exchange, and reverse osmosis are all methods for removing chromium and aqueous solutions that included other trace compounds [17, 23–25].

Adsorbents are extremely efficient, but they are also extremely costly, and they are usually having finished treatments or specific industrial effluents which are the only options. When the concentration is increased (greater than 500 mg/l), fluid extraction processes are being used to appreciate specific solutes (high value added, corporate strategy, or exceptionally harmful metals): Those certain methods have such a massive environmental disadvantage in terms of diffusion or disintegrating losses [26–30]. Existing approaches, on the other hand, face a number of difficulties. Biodegradable and renewable low cost biosorbents are very required as these would have least impact on environment. A large quantity of fish scale generates annually in Pakistan. Fish scales can be converted into chitosan which has wide applications in biomedical field and in nonmedical field. Unlike the commercially available chitosan and cellulose, de-acetylated fish scale (chitosan) is proposed to fabricate into composite porous membrane with cellulose.

This study focuses on the extraction of CH and its conversion into chitosan (CS) and composite membrane. The main objective of this study is to extract chitosan from fish scale waste and to prepare fish scale chitosan based-cellulose composite membrane. These prepared membranes were characterized and were also used for removal of chromium from aqueous solution.

2. Materials and Method

Distilled water was used for solution preparation; scales of the Labeo rohita fish Labeo were collected from a local

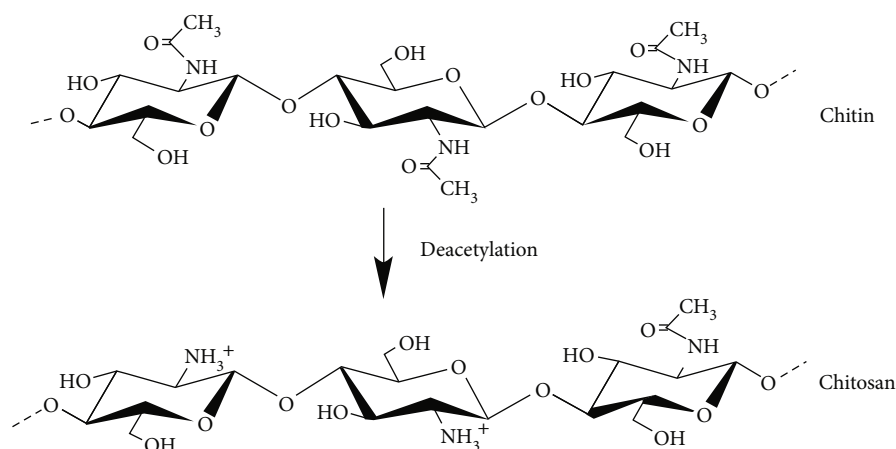


FIGURE 2: Deacetylation of chitin to chitosan.

market (Pakistan); HNO_3 , NaOH , and HCl were purchased from Sigma-Aldrich; and cellulose extracted from sugarcane bagasse was donated. Acetic acid for membrane preparation and chitosan solubility was purchased from Sigma-Aldrich. A pH meter, FTIR spectrometer (Bruker Alpha 2 with platinum ATR), atomic absorption spectrometry (AAS), and scanning electron microscope (SEM) were used for characterization.

2.1. Extraction of CS. Scales of the *Labeo rohita* fish (known in Pakistan as Rohu) were collected from various business sectors in Lahore and brought to the lab for CH extraction. Meat and other materials are removed and thoroughly washed with water. Samples were dried for three days in the sunlight after washing. FS were weighed both before and after drying.

Demineralization is performed in an acidic medium with 2 percent hydrochloric acid at room temperature with a solid-to-solvent ratio of one five (weight/volume) for sixteen hours to remove organic matter such as calcium carbonate (CaCO_3). Filtrate was also cleaned until it was pH neutral and then dried in the sun [31]. This process involves soaking dried fish scales in 4 percent sodium hydroxide at room temperature for twenty hours with a solid-to-solvent ratio of 1 : 5 (w/v). The residue was washed and dried in the sun until it was pH neutral. Chitin is converted to chitosan in this step by dipping it in 4 percent sodium hydroxide for 20 hours at 60 degrees Celsius. To convert chitin to chitosan, this process involves partially removing acetyl groups from the chitin structure.

2.2. Characterization of CS. The physicochemical and spectral analyses of the CS were assessed using a variety of methods and a Fourier change infrared (FTIR) spectrometer. When evaluating actual properties, consider solubility, MW, yield, ash, water, and protein content. Chemical characterization was associated to the estimation of DoD and pH. The DD and MW are the main physicochemical and organic properties of CS, as they impact numerous physico-chemical and natural properties like bioactivity, solubility hydro-philicity, cancer prevention agent action, and crystallinity [32].

Physicochemical analysis has been done to determine the properties of CS. In that study, an FTIR spectrometer (Bruker Alpha 2 with platinum ATR) was used to find the spectra of CH and CS. A frequency range of 4000 to 600 cm^{-1} was set for analysis. FTIR spectroscopy was used to investigate the parameters of CH deacetylation in a quantitative manner. It is the most common method for determining CS's DD. The literature-based baseline and calculations were used. The hydroxyl group was measured at a wavelength of 3450 cm^{-1} , while the amide group was calculated at 1655 cm^{-1} . Chitin with a deacetylation level of more than fifty percent was observed to be chitosan, which is dissolvable in acetic acid at a concentration of one percent.

2.3. Ash or Mineral Content. The ash content of 2 g of CS was determined by placing it in a preweight crucible. In a furnace, CS samples were heated for 1 hour at 800°C . Crucible was allowable to cool at 25°C . The crucible and the ashes' weights are weighed [33]. The following formula is used to calculate the percentage of ash content:

$$\text{Ash Content (\%)} = \frac{\text{Weight of ash}}{\text{Weight of sample}} \times 100. \quad (1)$$

2.4. Solubility. For CS, the source, MW, and DD all have an impact on melting. CS was dissolved in a 1 percent acetic acid solution in a test tube and centrifuged to determine its solubility. Before being weighed, solids that had not been melted were removed and dried in the oven. To calculate CS melting records, use the following formula:

$$\text{Water Content (\%)} = \frac{\text{Weight of dry sample}}{\text{Weight of wet sample}} \times 100. \quad (2)$$

2.5. Preparation of Cellulose/Chitosan Composite Membrane. 0.5 grams of chitosan was dissolved in 30 ml of two percent (volume/volume) acetic acid for 7 hours to make the nano-composite membrane extraction solution. Thereafter, solution was homogenized after the addition of 1.0 gm of nanocellulose. The chitosan-cellulose homogeneous mixture was poured into petri dish and heated in oven at 60°C for 24

hours. When the suspension was completely dry, 1N sodium hydroxide was poured into it for copolymerization and kept for twenty-four hours. Afterwards, the membrane was washed and kept in deionized for twenty-four hours to remove the remaining chemical substances. The standard solution of 100 mg L⁻¹ chromium (III) was prepared with chromium chloride hexa-hydrate. A series of purification solutions for stocks using pure water were used to prepare typical solutions for various concentrations of adsorption testing. The absorbance was monitored at 420 nm using spectrophotometer (Thermo Scientific Genesis), and the final concentration was determined using absorbance data.

2.6. Optimization of pH, Adsorbent Dose, and Contact Time.

One of the key determinants of the adsorbent top chemical is its pH. The pH range 2–10 was used to study its effect on chromium (III) exposure. To clearly understand the effect of the pH solution on the adsorption of chromium (III), the initial concentration of chromium (III) at 10 mg/l was studied for the testing of chromium (III) biosorption with a chitosan cellulose composite membrane at a dose of 10 mg per 100 ml of chromium (III) at pH 6. The effect of the cellulose composite membrane on chromium (III) adsorbing was investigated by changing the dose of adsorbent from 10 mg to 50 mg in a solution of 100 mg/l chromium (III) at pH 6. Many of the most significant changes in the adsorption process are contact time. The effect of time on chromium (III) adsorption with chitosan cellulose composite membrane was investigated with 10 mg/l of chromium (III) solution at pH 6. The contact time varied from 40 minutes to 180 minutes to determine the exposure and the measurement time.

2.7. Characterization of Chitosan-Cellulose Composite Membrane. Chitosan visibility, FTIR spectroscopy, BET location, and SEM-EDX analysis were all performed. For obtaining information about the functional groups and morphology of chitosan samples, FTIR spectra and electronic microscopy SEM scanning are both very useful.

3. Results and Discussion

CH was obtained from the FS of *Labeo rohita*. CH was obtained through chemical extraction, analyzed with FTIR spectroscopy, and then converted into CS via the deacetylation process. After that, a batch study of adsorption is performed.

The DoD and amine units present in CS can be calculated with the FTIR, by observing the effect of several parameters, including the base concentration, the temperature, and the length of the reaction, to detect a conversion reaction of CH in the CS and others. The band at 1633 cm⁻¹ indicates the presence of intermolecular forces (hydrogen bond) between the carbonyl and amine groups and the formation of α -CH (1659 cm⁻¹ single band is for β -CH). The band at 3382.85 cm⁻¹ exhibits the vibrational mode of the CO-HN hydrogen bonding. The spectral band at the wavelength of 1416.48 cm⁻¹ further confirms the presence of α -CH because this band is absent in the case of β -CH. The absence of the

β -CH state in the CH sample derived from the FS corresponds to the absence of bands at 1436 and 1659 cm⁻¹ wavelength.

FTIR characterized the procedure for de-acetylated chitosan preparation with lower environmental emissions. In low concentration alkaline conditions, the 4% deacetylation CS was made, requiring only 15 percent alkaline solution and a powder to NaOH solution ratio of one hundred CH for 1 hr. When the alkaline concentration ranged between 4% and 50%, high DoD CS is formed (up to 86%). A broad peak at about 3346.12 cm⁻¹ is representing N-H stretching. A small and slightly broad peak is showing CH₂ bending at 1412.39 cm⁻¹ along with C-O stretching at about 1016.20 cm⁻¹. A peak at ~872.63 cm⁻¹ is demonstrating C-H bending.

3.1. Degree of Deacetylation. The degree of N-deacetylation of chitin determines the DoD of chitosan. FTIR spectroscopy was used to determine DD. It was discovered that chitin with a deacetylation level off more than fifty percent can be classified as a chitosan that is solvable in one percent acetic acid. Degree of deacetylation is find by this formula.

$$DD (\%) = \frac{C_1 V_1 - C_2 V_2}{M \times 0.0994}, \quad (3)$$

where the concentration of standard hydrochloric acid aqueous solution (mol/l) is denoted by C₁. The concentration of normal sodium hydroxide solution (mol/l) is symbolized by C₂. V₁ indicates the volume of the normal hydrochloric acid aqueous solution that was used to dissolve chitosan (ml), V₂ represents the volume of normal sodium hydroxide solution disbursed during titration (ml), and M represents the weight of chitosan (g). Our product had an 85 percent degree of deacetylation.

The equation was used to calculate the percentage yield.

$$\text{Yield } (\%) = \frac{\text{Amount of chitosan obtained}}{\text{Amount of fresh fish scales used}} \times 100. \quad (4)$$

Our yield is 22.8%, indicating a high conversion of fish scales to finished product (chitosan).

3.2. FTIR Analysis of Composite Membrane. The membrane of chitosan composite has been characterized by the FTIR spectra that are showing the preparation of the chitosan composite membrane (Figure 3). The C-H stretching at about 3331.74 cm⁻¹ is shown by a broad peak. A nearly broad signal at around 2989.91 cm⁻¹ is picturing the N-H stretching. Also, a peak at about 1315.95 cm⁻¹ is showing C-N stretching. C-O stretching is shown at about 1159.73 cm⁻¹. A narrow peak at about 1029.11 cm⁻¹ is representing the C-N stretching.

3.3. Morphology of Cellulose-Chitosan Composite Membrane. The composite membrane with the highest proportion of acetic acid, cellulose, and chitosan is chosen for morphological observation under SEM in order to detect the structure of the composite membrane as shown in Figure 4. The composite membrane had a rough surface. Because static electricity as a result of this leads to the formation of an

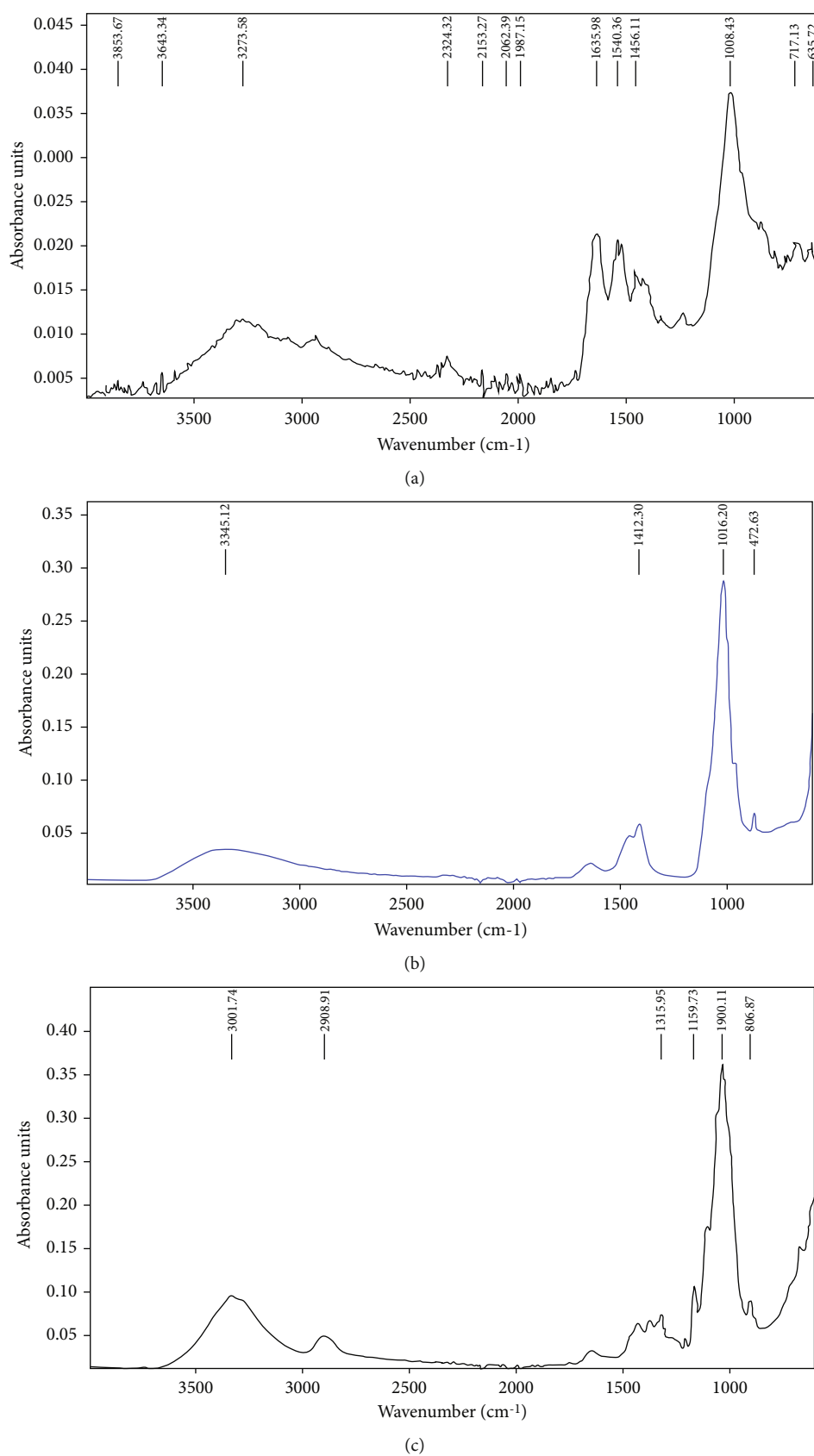


FIGURE 3: FTIR analysis of (a) chitin, (b) chitosan, and (c) chitosan-composite membrane showing the position of functional groups.

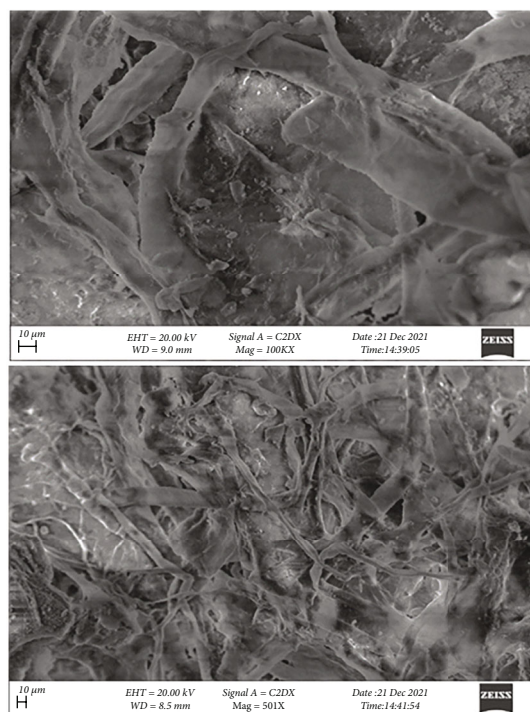


FIGURE 4: SEM analysis of cellulose-chitosan composite membrane showing the morphology.

TABLE 1: Comparison of Cr removal using different substrate/polymers.

Substrate	Cr(III) removal (%)	Reference
Polymer inclusion membrane	52	[34]
Chitosan composite	41.5	[35]
Flax straw	32	[36]
Brewery spent diatomite	71	[37]
Functionalized chitosan nanocomposites	58.24	[38]

insoluble polyelectrolyte complex between the poly-anionic cellulose and the poly-cationic chitosan, cellulose was strongly staggered and the coating of acetic acid and chitosan on the surface of cellulose, different morphology, and different roughness. The membrane had no delamination in cross-section, indicating that the components were well-matched.

3.4. Effect of pH on Adsorption of Chromium (III). The effect of pH was determined on the removal of Cr(III) using AAS parameter of absorbance. At pH 2, the absorbance of Cr(III) is 1.64. It accounts 53% removal of chromium. At pH 4, only a small difference was observed. Moving on to the pH 6, change in absorbance takes place. At pH 6, the absorbance is about 1.51. By increasing the pH, the absorbance started increasing once again. Minimum absorbance was at pH 6, and it means that maximum removal of chromium (III) has taken place. Minimum absorbance means the highest efficiency at pH 6. The highest removal of Cr (III) 57% was achieved at pH 6. It means pH 6 is the most efficient value

for the removal of Cr (III). Comparable results of Cr(III) removal using chitosan based different adsorbents have been reported (Table 1) by other researchers as shown in the table. Depending on the substrate composition and source, the adsorption capacity could be changed.

3.5. Effect of Contact Time. The effect of contact time of Cr(III) has been checked while keeping the pH value was kept at 6 and concentration 15 ml. Only contact time varying that is 40, 60, 90, 120 minutes. At 40 min, the absorbance is 0.76 and 60, 90, and 120, and absorbance is 0.43, 0.86, and 0.99, respectively. Only the time varies, and absorbance suddenly falls at different times. Minimum absorbance was observed at 60 min. It means that the optimized conditions for removing Cr (III) from aqueous solution are contact time of 60 minutes and pH 6 under this experimental setup.

3.6. Effect of Dosage. The effect of dosage on Cr(III) removal while keeping the optimized conditions of pH 6, contact time of 40 minutes, and concentration 15 ml was investigated. Only the dosage, which varies between 10 and 50 mg, has been different. The absorbance of 10 mg is 0.513, while that of 20, 30, 40, and 50 mg is 0.349, 0.135, 0.149, and 0.026, respectively. Overall, a decreasing trend of absorbance has been observed, and minima is found at 50 mg dosage of adsorbent (Figure 5). It means the maximum removal was observed while using 50 mg adsorbent.

Polymers are important materials in today's civilization. Polymers have altered agricultural productivity and food technology over the last 60 years, improved health care via the development of effective medical gadgets and equipment, decreased fuel consumption through the manufacture of lighter cars, and increased aircraft performance. Natural polymers, often known as bio-based materials, can be extracted from nature via physical or chemical techniques. Silk, wool, deoxyribonucleic acid (DNA), cellulose, and proteins are examples of naturally occurring polymers. Foods, fabrics, papers, woods, adhesives, and pharmacy are just a few of the industries that use these polymers [39].

Chitosan-based nanoparticle composite materials are progressively being examined as an alternate solution biosorbent in water treatment, using materials, iron oxide, hematite, and bimetal to adsorb toxic metals and coloring agents from wastes. Chitosan-coated magnetite nanoparticles (CMNP) have been prepared and used as a strong antibacterial agent to eliminate organic pollutants and microbes from water [26].

In order to avoid water pollution, heavy metals must be removed from wastewater. The effectiveness of chitosan-coated carbon in removing chromium (VI) and lead (II) from aqueous solutions was demonstrated in this study. Carbon, potassium, calcium, magnesium, aluminum, silicon, and chlorine were identified as constituents of the adsorbent by (EDX), while agglomeration of the adsorbent particle was revealed by scanning electron microscopy (SEM). Batch adsorption experiments were carried out to investigate the removal efficiency under various conditions and contain large numbers, catalyst concentration, stirring speed time, and grain size which are all factors to consider [40].

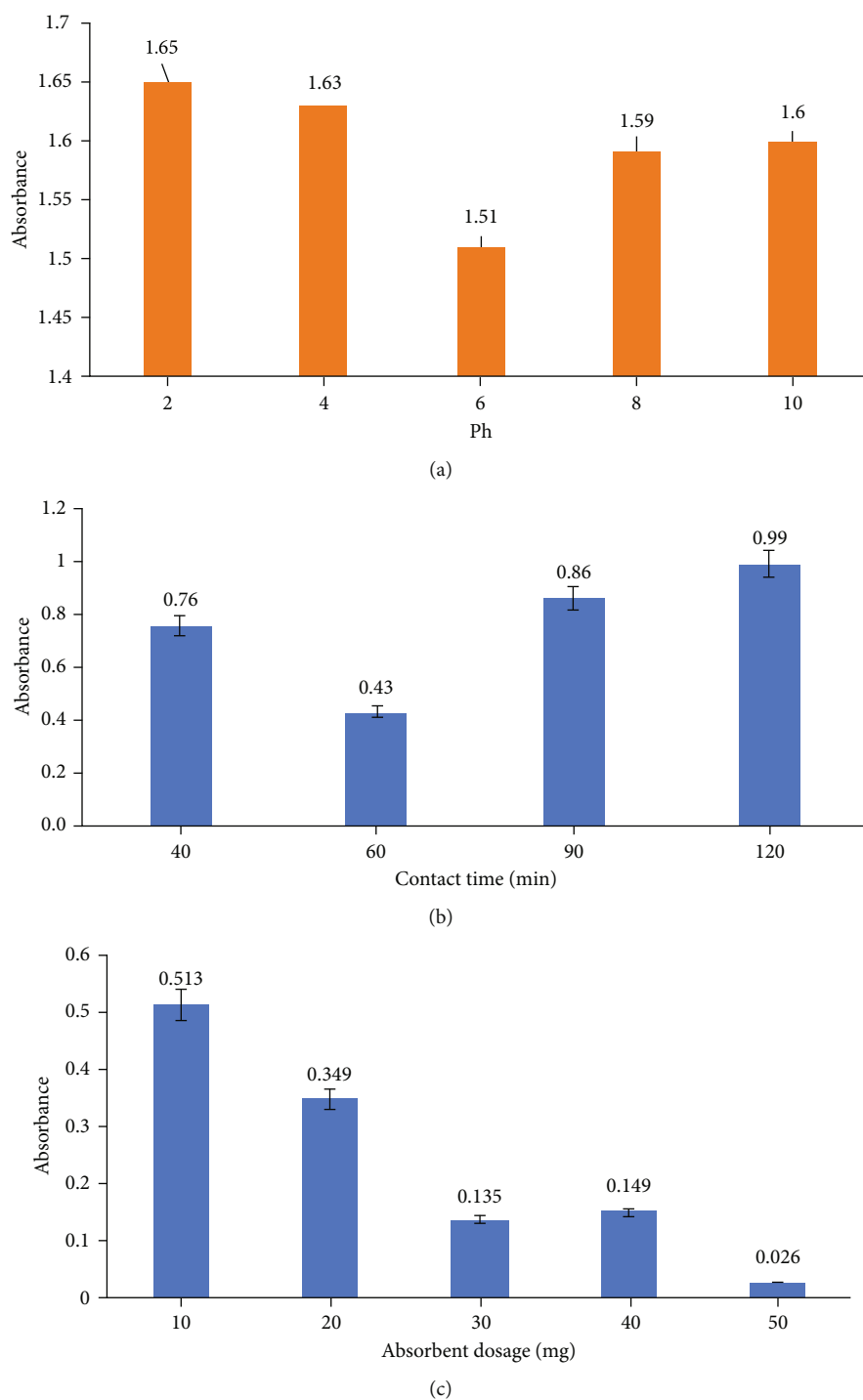


FIGURE 5: Optimization parameters for the removal of Cr from aqueous solution on the basis of (a) effect of pH, (b) effect of contact time, and (c) effect of adsorbent dosage.

3.7. Recent Advances in Chitosan Composites for Wastewater Purification

3.7.1. Nanochitosan-Based Adsorbents. The nanochitosan-based materials have been proved to be highly efficient due to compatibility, nano-size, higher surface area, structural defects, and porous nature. The nanochitosan could be a potential material for the treatment of wastewater. They sur-

pass micro-sized chitosan components of adsorbent rates and abilities.

3.7.2. Aminated Chitosan Nanomaterials. Adsorption efficiency and specificity of physisorption are enhanced by amination of nano-sized chitosan components. Because the -OH group found in chitosan are known to be capable for contaminant microbes, modifying agents such as diamine,

hexanediamide, diethylenetriamine, and others have been used to increase the –hydroxy groups [20].

3.7.3. Chitosan Nanocomposites. Carboxylation, amination, electrostatic particle combinations, hydroxyapatites, multi-walled nanotubes, magnetite, and other techniques have been used to adjust chitosan nanomaterials. They are used to remove chromium (6+), ferric ion, zinc ion, cupric ion, and among other contaminants.

3.7.4. Chitosan–Hydroxyapatite Nanocomposites. Hydroxyapatite materials have been suggested as potential defluoridation materials. Some studied have been employed it as fluidized beds in columns for continuous treatment system, but due to granules form of the adsorbent, higher pressure cannot be applied. In heavy metal adsorption, organic polymer composites made of (n-HAp) and chitin and chitosan are of notice. In one of the studies, the Cr(VI) adsorption of the chitin and chitosan-based nHAp–modified nanocomposites was tried.

4. Conclusions

Fish scale-based chitosan composite membrane as biosorbent was prepared for the removal of chromium (III). Solution casting method was used successfully to fabricate the composite membrane. FTIR and SEM results confirmed the composition of membrane with rough surface composite. *Labeo rohita* scales yield 22% of chitosan having 85% degree of deacetylation. The maximum removal of 57% Cr(III) was recorded at optimal pH 6. Optimal adsorbent dosage was found 50 g, while contact time was observed 50 min. On the basis of results, it concludes that fish scale waste-derived chitosan composite membrane is a promising low cost and environmental friendly biosorbent for Cr(III) removal from wastewater.

Data Availability

Data will be available on demand.

Conflicts of Interest

The authors declare no competing financial interests.

Acknowledgments

The authors express their gratitude to Princess Nourah bint Abdulrahman University Researchers Supporting Project (Grant No. PNURSP2022R156), Princess Nourah bint Abdulrahman University, Riyadh, Saudi Arabia. The authors extend their appreciation to the Deanship of Scientific Research at King Khalid University, Saudi Arabia, for funding this work through the Research Groups Program under grant number R.G.P.1: 255/43.

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