Recycling of Chitosan-Source Waste to Remove Heavy Meta Ions from Polluted Water

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ARTICLE INFO | **ABSTRACT**

Ion exchange resins, which are essential for water purification, have seen a major increase in use over the past 20 years due to industrial expansion. They are used to remove heavy metals, which are one of the most widespread pollutants, considering that these notoriously toxic metals can end up in ecosystems via several pathways. The chemical structure of chitosan extracted from the shrimp shell was confirmed by Fourier transform infrared (FTIR) and Proton nuclear magnetic resonance (1H-NMR) characterization. It was used as an ion exchange material for the removal of heavy metal ions Fe(III), Cd(II), and Pb(II) from their aqueous solutions in polluted water treatment, and the samples were tested by flame atomic absorption. The analytical study started by exploring the influence of pH (2, 4, 6, and 8) on the removal process by chitosan resin in a batch system. The obtained results revealed that as the pH of the analyzed ion solution increased, the removal efficiency for ions also increased. The highest removal efficiencies were obtained at pH 8 for the investigated Pb(II) and Fe(III) ions, ranging from 94.62 to 96.0, respectively, and 99.98% for Cd(II) ions at pH 6.

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1. Introduction

Water is one of the most important natural resources for the support of all types of life, food security, economic growth, and welfare. It cannot be replaced in many uses and is costly to ship, but to de-pollute is a blessing to the world from Mother Nature [1]. The quality of drinking water is declining because of increasing population, agricultural practices, and industrialization. Therefore, better water management is required, along with a strategy for preventing water pollution and supplying pure water [2]. Water pollution is caused by two types, points and non-points, as shown in Table (1). A pipe connecting to a factory, oil from a pipeline, and waste from industry are all examples [3]. Point contamination is caused by urban and commercial drainage effluent, as well as drain leaks, and it mostly affects the surrounding lands. Non-point source causes, on the other hand, are those that arise from a variety of sources and the number of ways contaminants enter groundwater or surface water through a variety of unidentified sources. Industrial pollution, municipal trash, and so on are examples. Waste that has traveled hundreds or even thousands of miles in one region frequently has an impact on the environment. This is referred to as "cross-border contamination." One example is radioactive waste that travels across oceans from nuclear power facilities in neighboring countries, and hence, causes soil and water pollution [4].

Table 1: Point source and non-point source [3].

Point Source	Non-point source
Wastewater effluent (Municipal and industrial)	Runoff from agriculture
Runoff and leachate from disposal sites	Runoff from pasture
Runoff and infiltration from animal feedlots	Runoff from abandoned mines
Runoff from mining sites, oil fields	Runoff from building establishment sewers
Runoff from construction	Activities on land that generate impurities

One of the most common pollutants is heavy metals, which are released into a variety of environments, particularly aquatic ones. Notably, these infamous toxic metals can enter ecosystems through several different channels, especially industrial polluted water, and mineral weathering, along with improper management of underground waste disposal, making water bodies their sinks for accumulation [5]. Heavy metals are capable of causing some potentially fatal

impacts in both people and animals, even at low doses. Because of this, heavy metal pollution has become a serious problem for both the natural system and public health on a global scale. The supplied drinking water may be contaminated by lead and cadmium from tubing, fittings, soldering, and home plumbing systems. In humans, the blood, central nervous system, and kidneys are all affected. Lead is the most common source of exposure for children and pregnant women [6]. Contaminated water is the leading cause of infectious diseases (e.g., amoebiasis and malaria, cholera, dysentery, paratyphoid fever, typhoid, and jaundice). According to the World Health Organization (WHO), one-sixth of the world's population (1.1 billion people) lacks access to safe drinking water. Polluted water from businesses, agriculture, and families is polluting the atmosphere. Arsenic, fluorides, nitrate, pesticides, and petrochemicals are just a few examples of the toxic contamination in our water that is hurting the organisms that live there and, consequently, our bodies. The type and location of chemicals thrown into water determine the repercussions (urban areas are highly polluted). Pollutants like lead and cadmium are eaten by minor species [7,8]. Recently, a lot of attention has been paid to creating polluted water treatment systems that are more efficient, less expensive, and long-lasting while also not risking human health or the environment, to develop alternative and cost-effective water and wastewater technologies to remove various sources of pollutants from water [9]. In an attempt to remove or minimize the aforementioned threat, in this work, two different resins are used as ion exchangers. The scientific community has focused its efforts on the removal of heavy metal ions through the application of the most highly specified technologies of ion exchange resins. Therefore, this study is concerned with recycling chitosan extracted from the shrimp shell waste trying to be used to improve environmental hygiene in addition to reducing the amount of solid trash.

2. Experimental

2.1. Materials
Iron (III) chloride, Cadmium (II) nitrate, and lead (II) nitrate were purchased from GCC and used as sources for heavy metal ions in pollutant samples.

2.2. Collecting Shrimp Shells
The shrimp shell waste was collected and cleaned several times with tap and distilled water before drying in the air. Then, they are ground in an electrical mill to prepare them for the extraction of chitin.
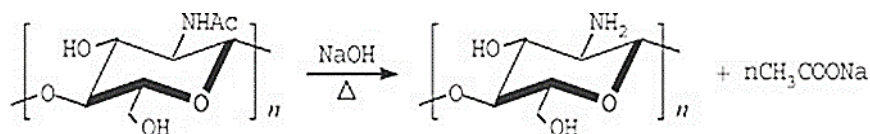
2.2.1. Extraction of chitin

After weighing 150 g of the powdered shrimp shell, 1500 mL of a 4% HCl solution is gradually added, and the powder is mechanically agitated for roughly 24 hours at room temperature to remove minerals and their salts. The remaining hydrochloric acid is filtered out of the residue powder and rinsed many times with distilled water. The powder is mixed mechanically for 16 hours at 90 °C with 1500 mL of a 10% sodium hydroxide solution to remove all proteins. The mixture is cooled down to ambient temperature, filtered and washed several times with distilled water to remove residual sodium hydroxide, and dried at room temperature to get chitin powder [10-12].

2.2.2. Deacetylation of chitin to chitosan

Deacetylation of chitin to produce chitosan is usually achieved by hydrolysis of the acetamide groups with concentrated NaOH at high temperatures. This reaction is generally carried out under heterogeneous conditions [13]. Thirty grams of dry chitin was combined with 350 mL of 60% sodium hydroxide solution and charged in a three-neck round-bottom flask equipped with a condenser, mechanical stirrer, and thermometer. The content was heated and maintained between 90 and 100 °C for approximately 12 hours, after which it was allowed to cool at room temperature. The sample was filtered, continually washed with 50 mL of 50% NaOH, and then again washed with distilled water to preserve the chitosan. The vacuum desiccator is used to dry the sample. Finally, chitosan white powder was obtained. Scheme 1 illustrates the deacetylation process of chitin to chitosan.

Scheme 1. Deacetylation reaction of chitin to chitosan.

The degree of deacetylation is one of the most important parameters that distinguish chitosan, and it is directly related to the quality of chitosan, which is required for the current target of application [14]. The simplest method among many different methods for determining the degree of deacetylation of chitosan is measured by the absorbance baseline method using infrared

spectroscopy [15,16] and it depends on the calculation of the absorbance ratio of certain bands according to the following equation [17,18]:

$$DA = \frac{A1655}{A3450} x100/1.33 \ldots\ldots\ldots\ldots.1$$

Where DA is the degree of acetylation, A_{1655} is the absorbance of the band at a wavelength of 1655 cm^{-1} due to amide, and A_{3450} refers to amine absorbance at a wavelength of 3450 cm^{-1}. Then, DD, the degree of deacetylation, is equal to DD = 100 – DA, and it was found to be equal to 92.1.

2.3. Analytical Study

The batch approach was used to examine the circumstances that would be most favorable for the bonding of metals to the prepared resins. Investigations were carried out at different pHs.

2.3.1. Preparation of standard solutions

Standard solutions with various concentrations of the element ions (Fe(III), Cd(II), and Pd(II)) were prepared by diluting 1000 ppm stoke solutions of their salts to 50 ppm. $FeCl_3.6H_2O$, $Cd(NO_3)_2.4H_2O$, and $Pb(NO_3)_2$ were the salts of these elements employed. The pH was controlled by dilute solutions of 0.01 N nitric acid and 0.01 N ammonia [19].

2.3.2. Study the effect of the pH on the resin by batch method

A 0.1 g of each of the prepared resins was treated with 25 ml of previously prepared aqueous solutions of Fe(III), Cd(II), and Pd(II) in pH ranges of 2, 4, 6, and 8 [20]. Each bottle containing resins was left at room temperature for an hour of shaking (175 rpm/min) after being filtered. The remaining concentrations of the elements were measured with a flame atomic absorption spectrometer after the filtrate was collected in 50-mL plastic bottles.

3. Results and Discussion

3.1. FTIR Characterization of Chitin and Chitosan Resin

Infrared spectroscopy is used to characterize chitin and chitosan. Their FTIR spectra were recorded from the Shimadzu 8400S FTIR spectrometer in Japan. The main target is to detect the conversion of chitin acetyl groups to chitosan amino groups and to get valuable information about the vibrational origin of the amide, carbonyl, and alcoholic groups of chitosan.

3.1.1 The infrared spectrum of chitin

The FTIR spectrum of chitin is exhibited in Figure 1. It shows a clear, broadband peak at 3443 cm^{-1} which is assigned to hydroxyl groups (-OH) and a (-NH) stretching. The peak at 2926 cm^{-1} was assigned to aliphatic C- H bond stretching of methylene groups, and at 1315 cm^{-1} due to C-N stretching. The stretching of the carbonyl amide I group appears as a sharp peak at 1660cm^{-1} and a peak at 1558 cm^{-1} related to the N-H amide II bond, and at 1035 cm^{-1} indicates C-O-C stretching [18-20], and Table 2 briefs the main peaks and their assignment.
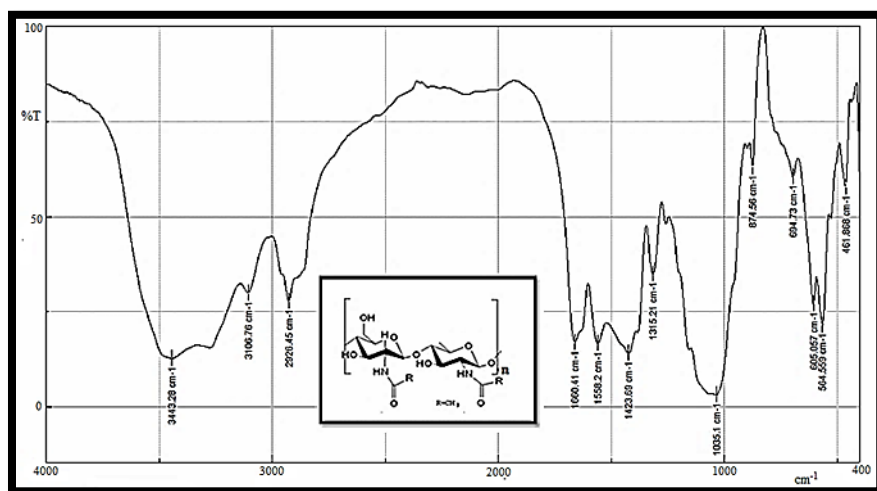

Figure 1: FTIR spectrum of extracted chitin from shrimp shells.

Table 2: The major IR bands of chitin and their assignment.

Functional Group	Assigned Bond	Wavenumber (cm^{-1})
-OH, -NH	O-H, NH	3443
-CH$_2$-	CH	2926
-CO-O-	C=O	1660
-NH II	N-H	1558
-C-C-N	C-N	1315
-C-O-C	C-O	1035

3.1.2 The infrared spectrum of chitosan

Figure 2 shows the FTIR of the extracted chitosan, and the essential assigned peaks are listed in Table 3. The first region observed in the FTIR spectrum of chitosan is the region of amide I, and it shows mainly the disappearance of this peak or leaving a very weak peak present at 1647 cm^{-1}, giving the impression that a high degree of deacetylation (DD) process takes place, and this is very true since the determined DD is found to be equal to 92.1 as measured by the IR method [20, 21]. In addition to that, the spectrum exhibits broadband with a peak at 3417 cm^{-1} due to the stretching and sharing of the OH group with the stretching vibration of the NH group. The band at 2924 cm^{-1} is due to C-H stretching [22, 23]. Also, the appearance of an active band at 1419 cm^{-1} assigned for the C-N stretching bond verifies the deacetylation process. The absorption bands around 1064 cm^{-1} and 875 cm^{-1} correspond to the vibration of C-O-C bonds and confirm the bonding of the monomers through β-glucosidic linkages [22,24].
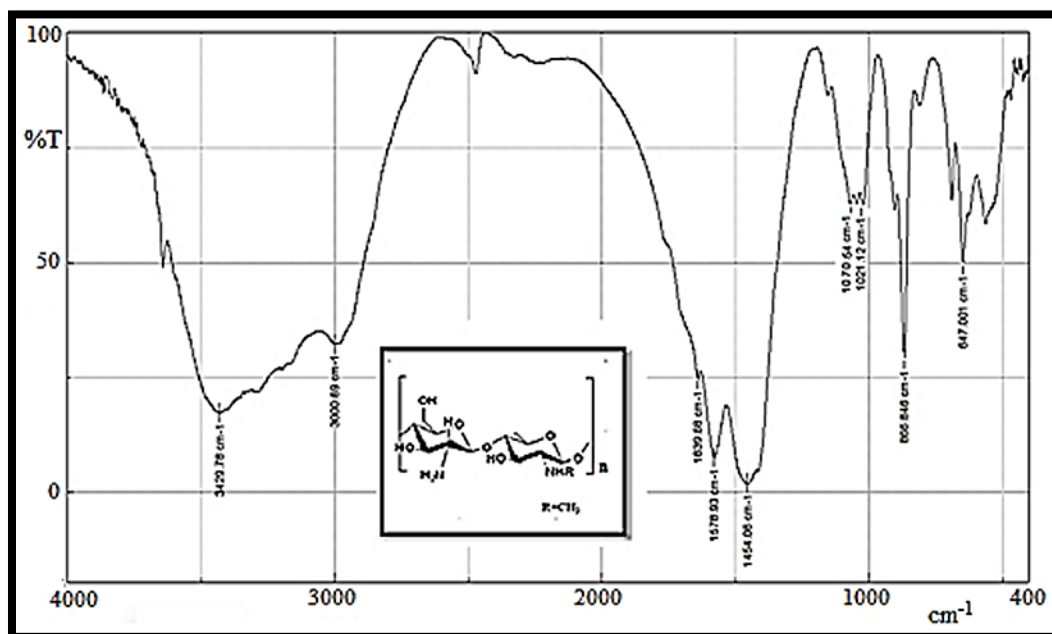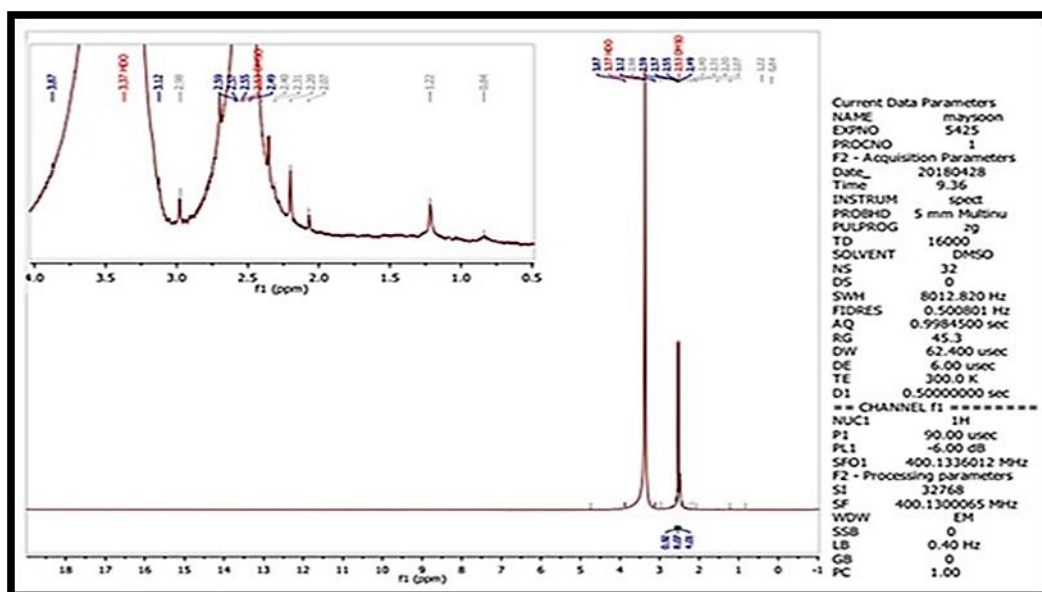

Figure 2: FTIR spectrum of chitosan.

Table 3: The major IR bands of chitosan and their assignment

Functional Group	Assigned Bond	Wavenumber (cm^{-1})
-OH, -NH	O-H, N-H	3429
-CH$_2$-	CH	3000
NH$_2$ I	N-H	1639
-NH II	N-H	1578
-C-C-N	C-N	1454
-C-O-C	C-O	1070

3.2 Characterization of Chitosan by 1H NMR

The 1H NMR spectroscopy technique was also used to confirm the structure of chitosan resin. It was recorded by the INOVA 500 MHz ™NMR Spectrometer (USA) using deuterated DMSO as solvent. Figure 3 shows the 1H-NMR spectrum of chitosan. The chitosan proton peaks area appeared at 4.6 ppm (H-1 of the glucosamine ring), 3.1 ppm (H-2 of the glucosamine ring), 3.1-3.8 ppm (H-3, H-4, H-5, H-6) [26]. As well as the presence of the peaks at displacement 2.5 ppm attributed to the protons in the DMSO solvent.

Figure 3: 1H-NMR spectrum of Chitosan.

3.2. Assessment of chitosan resin by batch method

Chitosan attracted researchers to be used as an ion exchange resin due to its chemical structure and polymeric properties. The presence of an amine group made chitosan more appealing to metal ions, while the presence of a hydroxyl group increased chitosan's ability to bind to metal ions at high pH values, while protonation of amine groups and their derivatives induces electrostatic repulsion of metal ions at low pH [27]. The effect of different pH values, which are 2, 4, 6, and 8, respectively, on the ion exchangeability of extracted chitosan resin was studied, and the results are shown in Table 4 and Figure 4. It was noticed that the Pb(II) ion had a low efficiency (35.78%) at pH 4 (32.11 ppm) and a high efficiency (94.62%) at pH 8 (2.69 ppm) (Table 4 and Figure 4). The results showed that Cd(II) had the highest efficiencies, and it reached its maximum at pH 6 (99.98%). The Fe(III) ion also showed high efficiencies at all pHs, and it reached its maximum at pH 8, but they were less than in the case of Cd(II). This can be explained by the differences in atomic diameter between Cd(II) which has a larger atomic diameter compared to Fe(III).

Table 4: Batch efficiency of chitosan towards various metal ions at different pH.

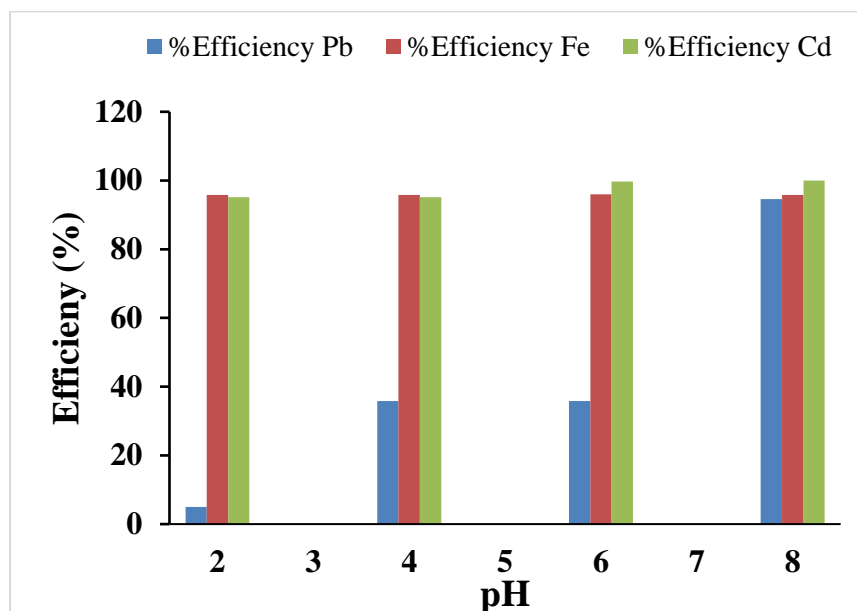| pH	Initial Metal Ions Conc. (ppm)	Pb(II) (ppm)	%Efficiency Pb(II)	Fe(III) (ppm)	%Efficiency Fe(III)	Cd(II) (ppm)	%Efficiency Cd(II)
2	50	50	0	2.08	95.84	2.45	95.10
4	50	32.11	35.78	2.03	95.94	0.16	99.68
6	50	32.11	35.78	2.08	95.84	0.01	99.98
8	50	2.69	94.62	2.00	96.00	0.08	99.84

Figure 4: Effect of pH on the efficiency of chitosan toward different metal ions.

4. Conclusions

Chitosan extracted from the recycled shrimp shells was successfully used as an ion exchange resin in terms of removing metal ions Fe(III), Cd(II), and Pd(II) from polluted water sources in a batch system. The highest removal efficiency was obtained with the Cd(II) ion at 99.96%, while Fe(III) and Pb(II) were at 94.62% and 96.0%, respectively. The findings demonstrated that Cd(II) had the best efficiency, which peaked at pH 6 (99.98%). The efficiencies of the Fe(III) ion were similarly very high at all pHs, peaking at pH 8, but they were lower than those of Cd(II). This can be explained by the fact that Fe(III) has a smaller atomic diameter than Cd(II), which has a larger atomic diameter that it seems is much preferable to exchanging with the chitosan resin.

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إعادة تدوير نفايات مصدر الكيتوسان لإزالة أيونات المعادن الثقيلة في معالجة المياه الملوث

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المستخلص:

تلعب راتنجات التبادل الأيوني الآن دوراً مهماً في معالجة المياه، وقد زاد استخدامها بشكل ملحوظ مع التطور الصناعي على مدار العشرين عاما الماضية حيث يتم استخدامها لإزالة المعادن الثقيلة التي تعد واحدة من أكثر الملوثات انتشاراً، مع الأخذ في الاعتبار أن هذه المعادن السامة الضارة يمكن أن ينتهي بها المطاف في النظم البيئية عبر عدة مسارات. تم تحضير الكيتوسان المستخلص من قشور الروبيان وتم التأكد من تركيبه من خلال التشخيص بتقنية FTIR. استخدم راتنج الكيتوسان كمبادل أيوني في معالجة المياه الملوثة لإزالة أيونات المعادن الثقيلة (II) Cd و (II) Pb و (III) Fe . تم اختبار العينات عن طريق الامتصاص الذري للهب. بدأت الدراسة التحليلية بدراسة تأثير الدالة الحامضية (2 و 4 و 6 و 8) على عملية الإزالة بواسطة الكيتوسان المحضر. كشفت النتائج التي تم الحصول عليها أنه مع زيادة الدالة الحامضية للمحلول الأيوني الذي تم تحليله ، زادت كفاءة إزالة الأيونات أيضا. تم الحصول على أعلى كفاءة إزالة عند الدالة الحامضية 8 لأيوني (II) Pb و (III) Fe التي تم فحصها ، والتي تتراوح من 94.62 و 96.0 على التوالي و 99.98٪ لأيون (II) Cd عند الدالة الحامضية 6.

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