



Research Article

The effect of production parameters of crab and shrimp based chitosan on the adsorption of aluminum and lead

Zehra Özden ÖZYLÇIN¹, Azmi Seyhun KIPÇAK^{1,*}

¹Department of Chemical Engineering, Yıldız Technical University, Istanbul, 34349, Türkiye

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ABSTRACT

Heavy metals are among the most dangerous substances that cause pollution and accumulation in nature. The most bio-sensitive way to decompose these pollutants is through adsorption studies with biopolymers. In this study, chitosan, one of the most common and cost-effective biopolymers, was produced to be employed in adsorption studies of aluminum and lead, which have proven negative effects on living organisms. In the production stages of chitosan, shrimp and crab shells were reduced to three different mesh sizes and deacetylation temperatures of 60, 80 and 100 °C were used. Characterizations of the obtained shrimp and crab based chitosan are made by using Fourier Transform Infrared Spectroscopy and from the results characteristic bands of chitosan are obtained. Adsorption studies were carried out with 20 mg.L⁻¹ heavy metal solutions at different treatment times. According to the results of the adsorption studies determined by ICP–OES analysis, for shrimp and crab based products respectively, aluminum was adsorbed between 58.45% – 99.50% and 23.75% – 83.10%, and lead was adsorbed between 99.35% – 100%, and 72.80% – 92.00%.

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INTRODUCTION

Heavy metals are among the most dangerous environmental pollutants that directly threaten living organisms. Lead (Pb) is the second most toxic metal after Arsenic (As) and has no biological function in the living body. This metal, which is naturally found in the earth's crust and especially in lime-rich regions, has been processed for centuries in many industries because it can be easily shaped and alloyed with other metals [1]. As a human carcinogen, lead is generally taken into the body by ingestion. The reference blood lead

level determined by the Centers for Disease Control and Prevention (CDC) is 5 µg.dL⁻¹ [2]. Higher concentrations of lead, which is known to adversely affect the nervous system even below this level, cause growth, behavior, and cognitive problems, and give permanent damage to the cardiovascular, central nervous, excretory and reproductive systems [1, 3].

Just like lead, aluminum (Al) has no biological function in the human body and is also the third most abundant element naturally found in the earth's crust [4]. Aluminum is utilized in various industries, including construction materials, electronics, cookware, beverage cans, solid

*Corresponding author.

*E-mail address: skipcak@yildiz.edu.tr

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propellants, and dental crowns, since it is inexpensive, robust, and has a thermal conductivity sixteen times higher than stainless steel [5]. Joint FAO/WHO Expert Committee on Food Additives (JECFA) declared the tolerable aluminum amount as 2 mg/kg body weight [6]. However, an increase in the amount of aluminum in the living body can cause accumulation in the bone, parathyroid, liver, spleen, and kidney. It is stored by binding instead of calcium in the bones, and this causes osteomalacia by disrupting calcification. In addition to bone, Al is taken up by the parathyroid glands and impairs parathyroid hormone (PTH) secretion [4]. It is imperative to remove these heavy metals, which adversely affect the critical activities of plants and animals. Among the methods applied for this purpose, the adsorption has gained importance by using biopolymers with high biodegradability and obtained from natural sources.

Chitin is the most prevalent biopolymer on earth after cellulose. Chitin, which is abundant in shellfish, emerges as a high-value product in the recycling phase of wastes generated as a result of the processing of marine resources. Chitin, a natural polysaccharide, appears to have a limited applicability range due to its crystal structure and physico-chemical qualities. Chitosan is the most well-known chitin variation generated through the deacetylation of chitin. Chitosan has a wide range of applications due to its biocompatibility and degradability, as well as its antibacterial qualities and high adsorption capacity [7, 8].

In chitosan production, shrimp and crabs are generally preferred due to their high consumption rates and chitin content. Brown crab (*Cancer pagurus*) and pink shrimp (*Pandalus borealis*) are two crustaceans that are in high demand in Europe and particularly in the Mediterranean countries with their high nutritional value and distinctive taste. [9, 10].

According to Food and Agriculture Organization (FAO) report for 2021, these two crustaceans are experiencing a rapid increase in price around the world [11, 12]. Again, FAO reported shrimp was one of the most consumed fishery products with an import of over 3 million tons in 2020, while the selling price of crab reached \$62/kg. The processing of the shells of these two seashells, which have a commercial value of billions of dollars, is also of commercial importance [13, 14].

Chitosan has been used as an adsorbent for heavy metal adsorption in many studies in its simple form or with different modifications. If these studies are to be exemplified; Perumal et al. (2019) studied the adsorption of Pb, Cd, Hg, and Cr ions chitosan/gelatin hydrogel [15]. Lapo et al. (2018) studied Hg (II) and Pb (II) adsorption on chitosan-iron (III) [16]. Sharma et al. (2020) investigated the adsorption of Cr (VI), Co (III) and Cu (II) onto nano-bentonite incorporated nano-cellulose chitosan aerogel [17] and Fan et al. (2018) studied Ag, Cu, Hg, and Cr adsorption onto magnetic chitosan beads [18]. Karimi et al. (2022) examined heavy metal removal from water with nano-composite chitosan [19] and Ahmed et al. (2021) studied the adsorption of heavy metals and organic dyes with modified chitosan [20].

These studies were mostly conducted with industrial chitosan, with no regard for production factors. In this work, the influence of chitosan raw material source and particle size on adsorption was investigated in addition to adsorption duration and heavy metal type. The produced chitosan samples were examined using Fourier-Transform Infrared spectroscopy (FT-IR), and the adsorption quantities were determined using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

MATERIALS AND METHODS

Reagent

Crabs and shrimp shells were obtained as waste from a seafood restaurant in Istanbul in October 2020. The chitosan samples used in this study were obtained by the same procedure as those produced in the study of Kipcak & Ozyalcin (2020) [21]. Aluminum standard solution (traceable to SRM from NIST $\text{Al}(\text{NO}_3)_3$ in HNO_3 0.5 mol/l 1000 mg/l Al Certipur[®]) and Lead standard solution (traceable to SRM from NIST $\text{Pb}(\text{NO}_3)_2$ in HNO_3 0.5 mol/l 1000 mg/l Pb Certipur[®]) was obtained from Merck Chemicals (Merck KGaA, Darmstadt, Germany).

Chitosan Production and Characterization

The crab and shrimp shells, which were kept at -18°C in the refrigerator (1050T model; Arcelik, Eskisehir, Turkey) until the experiments, were thawed at $+4^\circ\text{C}$ before the experiment and then brought to room temperature. The shells were thoroughly cleaned and washed until the tissue fragments and flesh were removed. Finally, the shells were rinsed with distilled water from A1104 model water distiller (Liston LLC, Zhukov, Russia) and dried in a KH-45 model hot air-drying oven (Kenton, Guangzhou, China) at 45°C for 4 hours. The shells ground with the help of a grinder were passed through sieves for the desired mesh sizes of +18, -40 (1000 - 425 μm), +40, -60 (425 - 250 μm) and +60 (< 250 μm) mesh and classified into polyethylene bags.

For the deproteinization stage, the classified shells were weighed in Radwag AS 220.R2 Plus Analytical Balance (Radwag Balances and Scales, Radom, Poland) and mixed with 2% NaOH (Merck KGaA, Darmstadt, Germany) solution in a 1:10 (w/v) ratio for 1 hour at 80°C and 500 rpm on MI0102003 model hot plate magnetic agitator stirrer (Four E's Scientific, Guangzhou, China). Following the process, the shells were vacuum-filtered and rinsed with at least 2 liters of distilled water to adjust pH level. Then the shells were dried overnight in the oven at 40°C . For the demineralization process, deproteinized shells were mixed with a 2% hydrochloric acid (HCl) (Merck KGaA, Darmstadt, Germany) solution at a 1:10 (w/v) ratio for 1 hour at 80°C and 500 rpm on a magnetic stirrer. At the end of the process, the shells were vacuum-filtered and rinsed with at least 2 liters of distilled water to adjust pH level. The demineralized shells were left to dry in an oven at 40°C overnight. The product obtained after these steps is called chitin. For the conversion of the obtained chitin to chitosan, the

deacetylation stage was carried out with 30% NaOH solution at a ratio of 1:10 (w/v) for 1 hour at 500 rpm on a magnetic stirrer. To observe the effect of temperature change on the production efficiency and adsorption capability, the process was carried out at 60, 80, and 100 °C at this stage. After the process, the chitosan samples were washed with distilled water, filtered under vacuum and left to dry in an oven at 40 °C overnight. Eventually, the shells were analyzed with Fourier Transform Infrared Spectroscopy (FT-IR) to characterize the obtained bands.

The FT-IR analyses was done by Shimadzu IR Prestige-21 Fourier Transform Infrared Spectrophotometer (Shimadzu Corporation, Tokyo, Japan). The characteristic vibrations that were used in the analysis of FT-IR were at the range of 1800 – 650 cm^{-1} .

Heavy Metal Adsorption

When the end-of-production analysis was conducted, the chitosan samples produced with 80 °C deacetylation showed the greatest weight reduction. In adsorption studies, it was chosen to employ these samples, which were thought to be free of undesirable proteins and minerals. Aluminum and lead solutions at 20 $\text{mg}\cdot\text{L}^{-1}$ concentrations were prepared from the standard solutions for the adsorption processes. Adsorption times were chosen as 1, 2 and 3 hour and agitation was set to 300 rpm. A separate experimental system was set up for each of the parameters of adsorption time, heavy metal type, and chitosan raw material type and particle size.

For each system, 0.1 g of chitosan was weighed into beakers and 50 mL of heavy metal solution was added onto

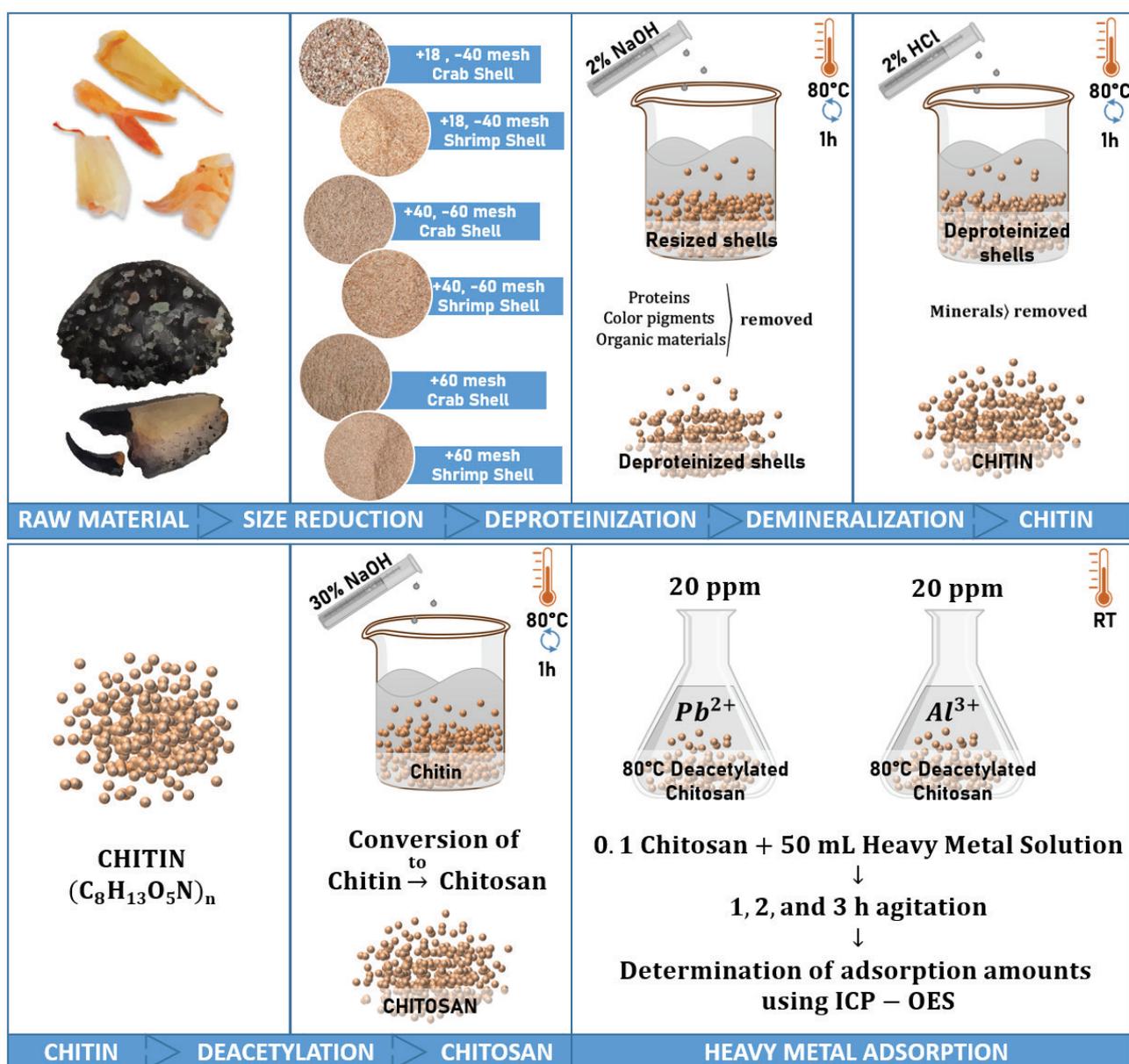


Figure 1. Summary scheme of chitosan production and heavy metal adsorption.

and agitated at 300 rpm on the magnetic stirrer. The solutions were filtered under vacuum at the end of the treatment period then the filtrates were bottled for ICP–OES analyses. Perkin Elmer Optima 2100 DV Atomic Emission Spectrometer (PerkinElmer Inc., MA, USA) was employed for the analysis. Analysis conditions were set to a power of 1.45 kW, a plasma flow of 15.0 L.min⁻¹, an auxiliary flow of 0.8 L.min⁻¹, and a nebulizer flow of 1 L.min⁻¹. A graphical explanation for the basis of chitosan synthesis and heavy metal adsorption is shown in Figure 1.

RESULTS AND DISCUSSION

Chitosan Characterization

Yield percentages of chitosan production stages were given in the study of Kipcak & Ozyalcin, 2020 [21]. FT-IR spectroscopic analysis was applied to determine the chemical structure of crab and shrimp shells, chitin, and chitosan samples that were produced. FT-IR spectra of +60 mesh crab shell, +60 mesh produced crab-base chitin, and 80°C deacetylated and +60 mesh produced crab-based chitosan were given in Figure 2, from left to right, respectively.

Similar peaks were observed in all three spectra due to similar groups. Stretching vibration peaks showing one or more C–H bonds were observed in the shell at 1400 cm⁻¹

and in the chitin samples at 1386 cm⁻¹. In the chitosan sample, a weaker peak was recorded at 1404 cm⁻¹. It can be interpreted that this is due to the acetyl group (CH₃–(C=O)) present in the shell and chitin samples, which is removed by deacetylation during conversion to chitosan. Supporting that, the peaks at 1311 and 1201 cm⁻¹, which are found in the chitosan spectrum but not in the shell and chitin spectra represent amino groups (–NH₂) as deacetylation is the process of converting acetylamino groups (–NH–CH₃–(C=O)) on chitin into amino groups.

FT-IR spectra of +60 mesh shrimp shell, +60 mesh produced shrimp-base chitin, and 80 °C deacetylated and +60 mesh produced shrimp-based chitosan were given in Figure 3, from left to right, respectively.

Peaks in the spectra of shrimp-based materials were detected to be similar to the peaks in the spectra of crab-based products. Peaks found at 1373 cm⁻¹ in the shrimp shell and 1398 cm⁻¹ in the chitin may be attributed to one or more C–H / C–N / C–O bonds. When these peaks were compared, it can be said that the stretching vibration in the C–H band of the chitin was caused by the high amount of color pigment and other materials (1200 – 1500 cm⁻¹) removed from the shell and it is consistent with the chemical structure of the chitin ((C₈H₁₃O₅N)_n). The fact that the peak observed at 1375 cm⁻¹ in the chitosan sample was weaker than the others were and the presence of peaks attributed

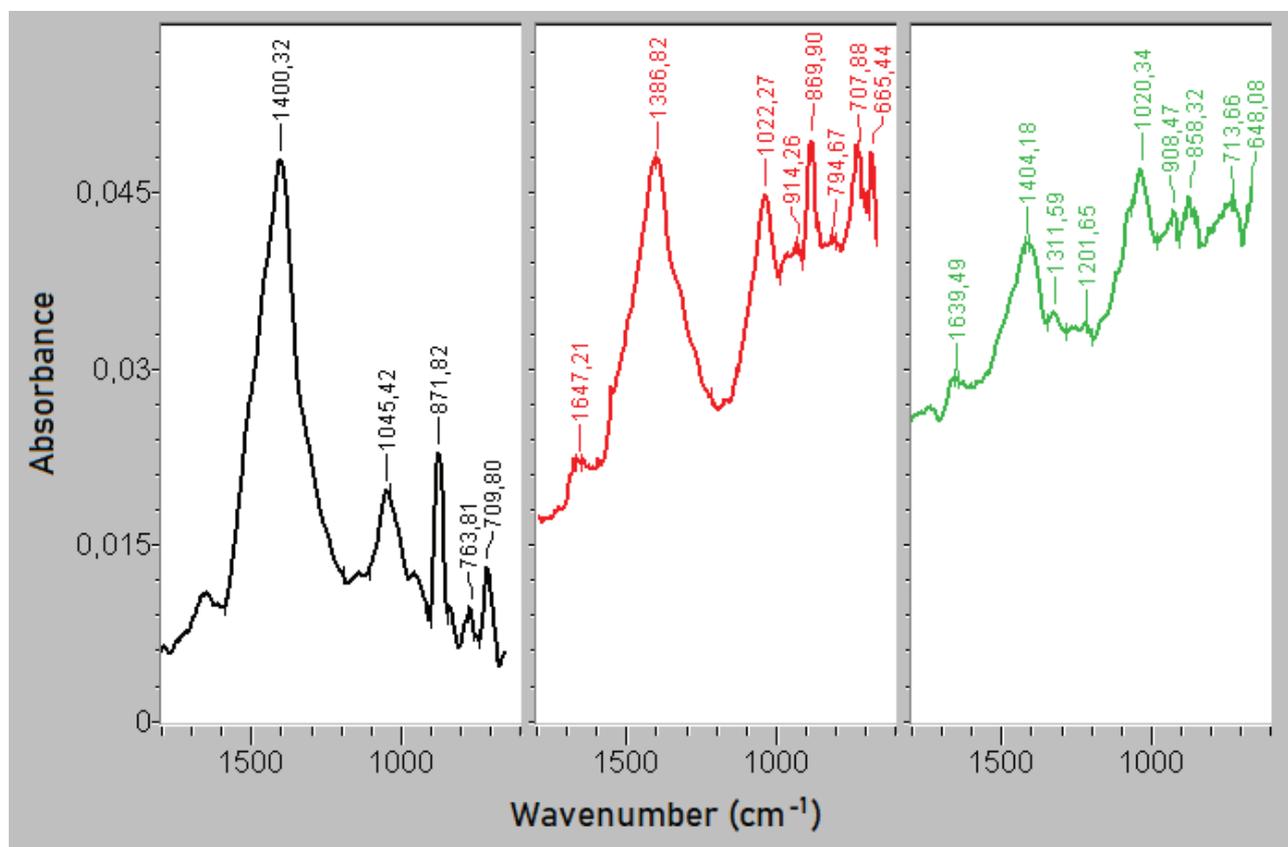


Figure 2. FT-IR spectra of crab shell (left), crab-based chitin (middle), crab-based chitosan (right).

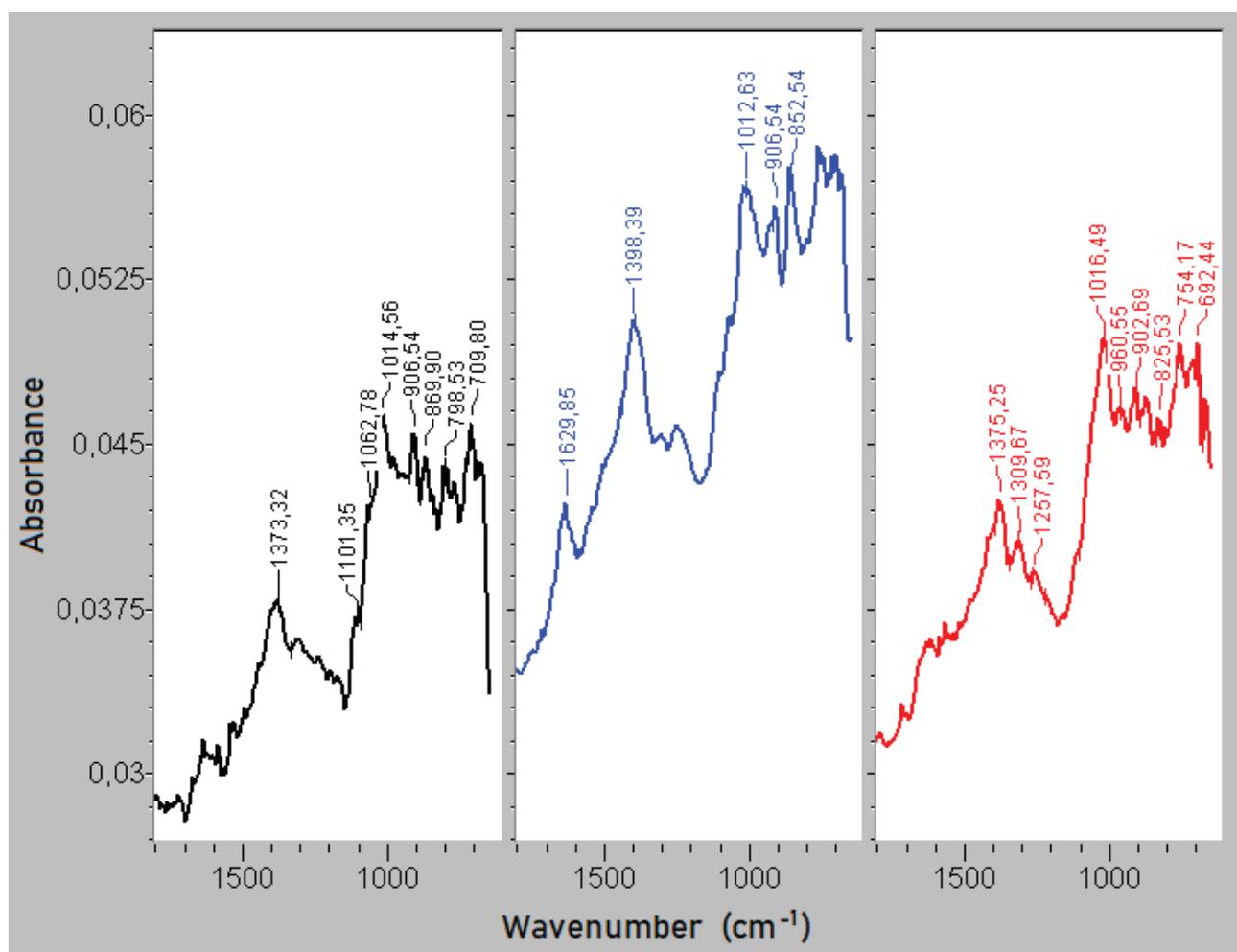


Figure 3. FT-IR spectra of shrimp shell (left), shrimp-based chitin (middle), shrimp-based chitosan (right).

to amino groups at 1309 and 1257 cm^{-1} can be interpreted as successful deacetylation. For the comparison of the chitosan obtained in this study with the literature Figure 4 is added. The peaks of 1411 (C-N); 1253 (C-O); 1057 (C-O); and 874 (C-C) cm^{-1} , was obtained in the study of Ozyalcin & Kipcak (2020). These peaks are obtained in this study at about 1404 , 1375 ; 1201 , 1257 ; 1020 , 1016 ; and 858 , 902 cm^{-1} , for crab and shrimp based chitosan respectively.

As a consequence, the bands in the spectra of the +60 mesh chitosan samples produced by 80°C deacetylation consistent with the chemical structure of chitosan ($(\text{C}_6\text{H}_{11}\text{NO}_4)_n$) as expected.

Heavy Metal Adsorption Results

For heavy metal adsorption, 80°C deacetylated samples were employed, which were purified to the highest degree possible based on their production efficiencies [21]. Final metal concentrations of aluminum and lead solutions and adsorption % are given in Table 1 and Figure 5, respectively. When the final heavy metal concentrations in the filtrate solutions given in Table 1 are examined, it is understood

that the produced chitosan adsorption process was quite successful.

Adsorption rates should be taken as inversely proportional to the metal amounts ($\text{mg}\cdot\text{L}^{-1}$) in the analysis solutions. Accordingly, when the adsorption data of aluminum is examined, it is seen that in the biggest size of +18, -40 mesh shrimp-based samples with the lowest adsorption and the highest Al^{3+} amounts, $8.310 \pm 0.420\text{ mg}\cdot\text{L}^{-1}$ (58.45% adsorption), $2.650 \pm 0.130\text{ mg}\cdot\text{L}^{-1}$ (86.75% adsorption), and $0.440 \pm 0.020\text{ mg}\cdot\text{L}^{-1}$ (97.80% adsorption) for 1, 2 and 3 hours processing times, respectively. In crab-based samples, the lowest adsorption amounts and the highest Al^{3+} were detected again in +18, -40 mesh size samples as $15.250 \pm 0.770\text{ mg}\cdot\text{L}^{-1}$ (23.75% adsorption), $15.250 \pm 0.790\text{ mg}\cdot\text{L}^{-1}$ (23.75% adsorption), and 15.250 ± 0.770 (23.75% adsorption) for 1, 2 and 3 hours mixing times, respectively. According to these data, it can be interpreted that the increase in the processing time for shrimp-based samples increased the amount of adsorption in +18, -40 mesh size samples, while the maximum metal adsorption rate was

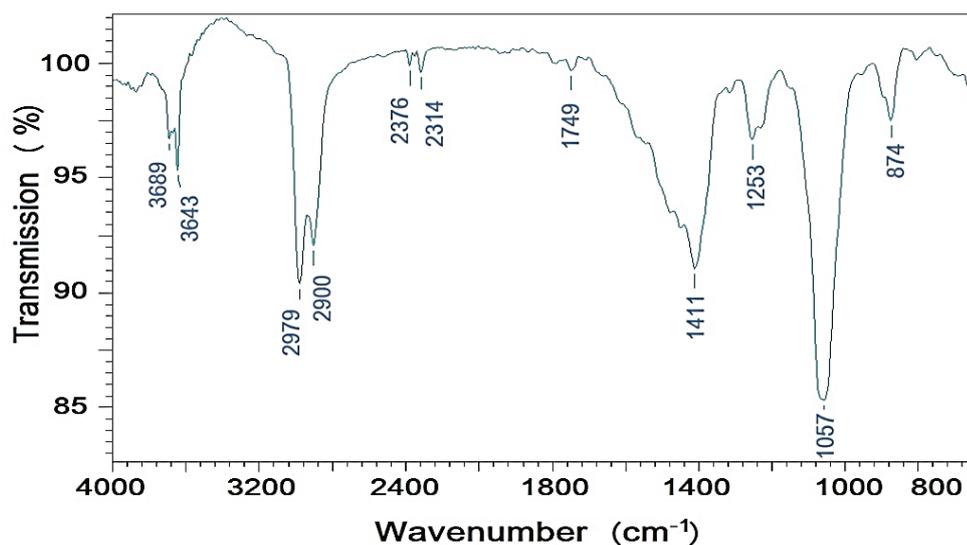


Figure 4. Chitosan FT-IR obtained from the literature [21].

Table 1. Final metal concentrations of aluminum and lead solutions

Raw Material	Mesh	Time (h)	Al ³⁺ (mg.L ⁻¹)	Pb ²⁺ (mg.L ⁻¹)
Shrimp	+18, -40	1	8.310 ± 0.420	0.130 ± 0.100
		2	2.650 ± 0.130	N.D. < 0.010
		3	0.440 ± 0.020	N.D. < 0.010
	+40, -60	1	1.080 ± 0.050	0.072 ± 0.004
		2	0.220 ± 0.010	N.D. < 0.010
		3	0.097 ± 0.005	N.D. < 0.010
	+60	1	0.200 ± 0.010	0.052 ± 0.003
		2	0.100 ± 0.010	N.D. < 0.010
		3	0.050 ± 0.003	N.D. < 0.010
Crab	+18, -40	1	15.250 ± 0.770	5.440 ± 0.290
		2	15.250 ± 0.790	4.860 ± 0.260
		3	15.250 ± 0.770	3.060 ± 0.170
	+40, -60	1	15.200 ± 0.810	5.210 ± 0.340
		2	13.190 ± 0.660	5.150 ± 0.280
		3	3.300 ± 0.170	2.810 ± 0.150
	+60	1	4.480 ± 0.230	3.860 ± 0.210
		2	3.670 ± 0.180	2.020 ± 0.110
		3	3.380 ± 0.170	1.600 ± 0.090

*N.D. refers to not detected.

reached within 1 hour in crab-based samples, and therefore the adsorption rate remained constant.

It was observed that the amount of aluminum adsorption increased for the medium sieve size +40, -60 mesh compared to +18, -40 mesh. Accordingly, the detected Al³⁺ amounts for +40, -60 mesh size, in shrimp-based samples, 1.080 ± 0.050 mg.L⁻¹ (94.60% adsorption), 0.220 ± 0.010 mg.L⁻¹ (98.90% adsorption) and 0.097 ± 0.005 mg.L⁻¹

(99.52% adsorption), and in crab-based samples, 15.200 ± 0.810 mg.L⁻¹ (24.00% adsorption), 13.190 ± 0.660 mg.L⁻¹ (34.05% adsorption) and 3.300 ± 0.170 mg.L⁻¹ (83.50% adsorption) for 1, 2 and 3 hours of processing time, respectively. As an outcome, increasing the processing time was found to have a net favorable effect on both shrimp and crab-based samples. For +40, -60 mesh crab-based samples, 3 hours of treatment time considerably increased the

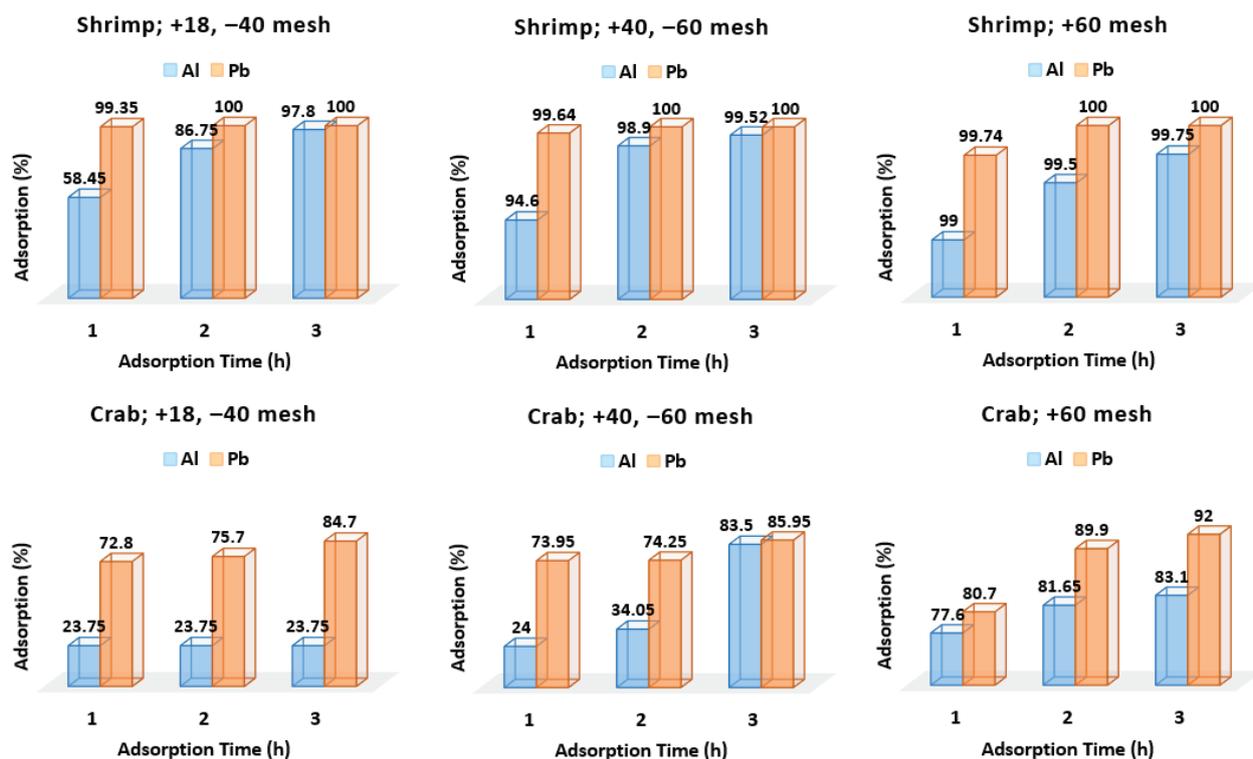


Figure 5. Aluminum and lead adsorption results.

amount of adsorption. When it comes to the smallest size of +60 mesh samples, the Al^{3+} amounts was found in shrimp-based samples as $0.200 \pm 0.010 \text{ mg.L}^{-1}$ (99.00% adsorption), $0.100 \pm 0.010 \text{ mg.L}^{-1}$ (99.50% adsorption), and $0.050 \pm 0.003 \text{ mg.L}^{-1}$ (99.75% adsorption), and was found in crab-based samples as $4.480 \pm 0.230 \text{ mg.L}^{-1}$ (77.60% adsorption), $3.670 \pm 0.180 \text{ mg.L}^{-1}$ (81.65% adsorption) and $3.380 \pm 0.170 \text{ mg.L}^{-1}$ (83.10% adsorption) for 1, 2, and 3 hours processing times, respectively. Accordingly, it was observed that aluminum was adsorbed the most by shrimp-based samples, and the amount of adsorption increased with increasing processing time and decreasing particle size.

When the adsorption results of lead were examined, Pb^{2+} amounts in 1-hour adsorption with shrimp-based chitosan were found as $0.130 \pm 0.100 \text{ mg.L}^{-1}$ (99.35% adsorption), $0.072 \pm 0.004 \text{ mg.L}^{-1}$ (99.64% adsorption) and $0.052 \pm 0.003 \text{ mg.L}^{-1}$ (99.74% adsorption) in mesh sizes +18, -40, +40, -60 and +60, respectively. After 1 hour, Pb^{2+} level was found to be undetectable for shrimp-based samples meaning that the lead adsorbs almost all the lead metal ($\approx 100\%$ adsorption) in the solution at the end of the first hour.

In the adsorption of lead with crab-based samples, the adsorption rate was found to be lower compared to shrimp-based samples. Accordingly, Pb^{2+} amounts of +18, -40 mesh crab-based samples was found as $5.440 \pm 0.290 \text{ mg.L}^{-1}$ (72.80% adsorption), $4.860 \pm 0.260 \text{ mg.L}^{-1}$ (75.70% adsorption), and $3.060 \pm 0.170 \text{ mg.L}^{-1}$ (84.70% adsorption) for 1, 2, and 3 hours of processing time, respectively. For

crab-based samples for medium sieve size +40, -60 mesh was found as $5.210 \pm 0.340 \text{ mg.L}^{-1}$ (73.95% adsorption), $5.150 \pm 0.280 \text{ mg.L}^{-1}$ (74.25% adsorption), and $2.810 \pm 0.150 \text{ mg.L}^{-1}$ (85.95% adsorption) for processing times of 1, 2 and 3 hours, respectively. The fact that +40, -60 mesh Pb^{2+} values were very close to +18, -40 mesh size can be interpreted as the difference in surface area between these two sizes did not affect the Pb^{2+} adsorption capability. However, it was seen that increasing the processing time from 1 to 3 hours increased the amount of adsorption more than the size change for both sizes. Pb^{2+} amounts of +60 mesh crab-based samples was found as $3.860 \pm 0.210 \text{ mg.L}^{-1}$ (80.70% adsorption), $2.020 \pm 0.110 \text{ mg.L}^{-1}$ (89.90% adsorption), and $1.600 \pm 0.090 \text{ mg.L}^{-1}$ (92.00% adsorption) for 1, 2, and 3 hours of processing time, respectively. From the values of Pb^{2+} in +60 mesh, unlike the other two sieve sizes, the increase in surface area was seen to increase the amount of adsorption. However, it was observed that extending the processing time results in a higher rate of adsorption than reducing the particle size.

If the effect of the parameters on metal adsorption is summarized, it has been observed that reducing the particle size and increasing the processing time have an increasing effect on both aluminum and lead adsorption. It was also determined that shrimp-based products had adsorbed higher amount of metal ions than crab-based products for each experimental set. Eventually, in a comparison of chitosan's adsorption capability for aluminum and lead heavy metals, it was clear that chitosan performed far better for

lead adsorption than aluminum adsorption. Given that aluminum adsorption rates were approaching 100%, it is reasonable to conclude that aluminum adsorption capabilities of chitosan can be improved.

CONCLUSION

In this study, aluminum and lead adsorption capability of chitosan samples produced from shrimp and crab shells were investigated. During the production stage, the shells were resized to +18, -40, +40, -60, +60 mesh and it was aimed to observe the effect of particle sizes. Chitin produced as a result of deproteinization and demineralization stages were deacetylated at 60, 80, and 100 °C, and as a result of the evaluations, it was concluded that the purest chitosan was produced from chitin deacetylated at 80 °C. For this reason, heavy metal adsorption experiments were carried out with chitosan samples produced with 80 °C deacetylations. The adsorbed heavy metal levels were estimated by ICP-OES analysis after the chitosan samples were treated in 20 mg.L⁻¹ heavy metal solutions for 1, 2, and 3 hours. For all trial sets, it was discovered that shrimp-based samples absorbed more metals than crab-based samples. The produced chitosan samples have been found to be effective adsorbents for both aluminum and lead. In general, the produced chitosan samples performed well for both aluminum and lead adsorption, however the amount of lead could not be detected in some experimental sets, leading to the conclusion that the lead was totally adsorbed, indicating that chitosan was an outstanding choice for lead adsorption. Furthermore, it was discovered that increasing the adsorption period and decreasing the chitosan particle size increased the amount of adsorption. For the future studies obtained shrimp and crab based chitosan may be applied for the industrial waste water treatment and the economic evaluations can be made.

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AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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