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Antimony adsorption study of chitosan produced from *Caridea* and *Brachyura* shells

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Pandalus borealis (pink shrimp) and *Cancer pagurus* (brown crab) are among the most common used shellfishes and have significant economic value. In this study, chitosan production yields at every stage of production and heavy metal adsorption capacity of the produced chitosan were investigated. As production parameters, –40, +18; –60, +40; and +60 mesh particle size and 60, 80 and 100°C deacetylation temperatures were chosen. Besides that, adsorption was carried out for 1, 2 and 3 h in 20 ppm antimony stock solution with 80°C deacetylated 0.1 g of chitosan. Deacetylation yields are found between 60.28–93.40% for the crab and between 61.43–90.60% for shrimp shell owned chitin. Moreover, the highest adsorption was observed with –40, +18 mesh shrimp and –60, +40 mesh crab with final heavy metal concentrations as 14.14±0.32 and 13.65±0.31, respectively.

Keywords: Adsorption, antimony, chitosan, production yield, shellfish.

Introduction

Heavy metals are among the most dangerous pollutants of water resources causing serious health and environmental problems. Antimony is a heavy metal that has a wide variety of uses as a metal reinforcer in alloys and as a flame retardant in the plastics, textile and chemical industries, and is found in low concentrations in freshwater resources, seawater and soil in nature[1]. Studies have shown that the average intake of antimony from food and water for the general population is estimated at 5 μg/day[2]. However, increased rates of antimony use, and exposure can result in serious health effects such as respiratory problems, heart disease, severe vomiting, gastric ulcers and diarrhea[3]. Therefore, antimony, like any other heavy metals, must be removed from water sources. Among the wastewater treatment techniques that are becoming more diverse each day, adsorption using biopolymer as an adsorbent is a highly preferred method due to its low cost and environmental impact.

After cellulose, chitin is the most abundant biopolymer on earth. It is a protective and supportive body part of crustaceans, invertebrates, insects; cell wall of yeast and fungi. Treating chitin molecules in alkali media ensures deacetylation to obtain chitosan molecules. The component "chitosan" has come to be used to ensure sustainability for more than a half-century. Chitosan is not only the simplest and the cheapest derivative of chitin, but it also possesses, unlike polysaccharides, positively charged amino groups which repeatedly placed[4]. Chitosan is one of the most widely used groups of biopolymers and have been extensively used as an antimicrobial agent, edible film, food additive, functional foods and in water treatment, agriculture, cosmetics, biomedical and pharmaceutical materials, and enzyme immobilization. Chitosan is often obtained from sea crustaceans due to the high amount of consumption and chitin valence.

The brown crab is a large ten-legged shellfish that is perennial. Crabs live for at least 15 years and participate in fishing between the ages of 4–6[5]. Besides, pink shrimp, is one of the most abundant and most important commercial species worldwide[6]. As a result of purchasing power rising and population increasing, seafood demand is increasing all over the world. Among 300 species of shellfish, shrimp is the most well-known because of its unique color and texture. World production of shrimp was recorded nearly 3.5 million tons in 2018 and annual trade was reached to over US$ 26

million. Although not as much as shrimp, crab also had a high production rate of over 1.5 million tones with a commercial gain of US$ 4.7 million in 2018[7].

Many studies have been carried out on various heavy metal water treatments, especially with the biosorbent chitosan. Shrimp was generally used as a raw material in studies involving production due to its high availability. In most of these studies, experiments were performed with commercial chitosan and production parameters were not considered. These studies can be exemplified as follows; Wan Ngah *et al.*[8] studied a review of heavy metal and dye adsorption by chitosan composite. Ahmad *et al.*[9] studied on chitosan and cellulose for adsorption, Mohanasrinivasan *et al.*[10] adsorption efficiency and antibacterial activity of chitosan, Sarkar and Majumdar[11] optimization of biosorption with surfactant modified chitosan and Sun *et al.*[12] studied chitosan-cellulose composite biosorption. Spite of water treatment studies on antimony with chitosan are very rare, some studies can be given as follows; Sari *et al.*[13] studied antimony adsorption with chitosan-modified pumice, Lapo *et al.*[14] studied antimony removal by a chitosan-iron(III) biocomposite, and Xiong *et al.*[15] studied antimony(III) with a nano-modified chitosan.

Although heavy metal removal with chitosan has been studied for many years, the number of studies on antimony is very limited. In this study, both the effect of chitosan production parameters such as raw material, deacetylation temperature, particle size and process time on production efficiency and heavy metal adsorption were investigated. The yield was calculated for each stage of production, and chitosan formation was investigated by Fourier-Transform Infrared spectroscopy (FT-IR). In addition, the adsorption amounts were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

Material and methods

The crab and shrimp shells were obtained from a seafood restaurant in Istanbul and kept in the freezer, at –18°C. Prior to experiments, they were removed from the freezer and put in the refrigerator (1050T model; Arcelik, Eskisehir, Turkey) at +4°C to dissolve the ice. To clean the shells, firstly, the meat and the membrane were removed by using forceps and brushes, then washed thoroughly with distilled water and dried at 45°C for 4 h. The shells were ground and sieved to +60 mesh size, –60, +40 mesh size and –40, +18 mesh particle sizes.

The proteins and other organic materials are removed by treating with 1:10 (w/v) 2% sodium hydroxide (NaOH) under agitation at 500 rpm at 80°C for 1 h. Afterwards, the deproteinated shells were filtrated and washed until the solid particles have reached the neutral pH. Lastly, they were left in the oven at 40°C overnight to dry. Deproteinized shells are treated with 2% hydrochloric acid (HCl) solution with the ratio of 1:10 (w/v) under agitation at 500 rpm at 80°C for 1 h to remove minerals. The demineralized shells were filtrated and washed with distilled water until they have reached the neutral pH and dried overnight at 40°C. Chitin was obtained after these two steps and weighed to determine the amount of it. Then the chitin was converted into chitosan by removing the acetyl group with 30% NaOH solution with the ratio of 1:10 (w/v). Reactions were carried out at 60, 80 and 100°C under 500 rpm agitation for 1 h to observe the effect of the temperature on the yield. Chitosan was filtrated and washed with distilled water until it has reached the neutral pH and dried in 40°C oven overnight. Then the samples are analyzed in FT-IR spectroscopy to confirm successful production of chitosan.

Heavy metal treatment was carried out with 0.1 g of chitosan and 50 ml 20 ppm antimony solution under agitation at 300 rpm for 1, 2 and 3 h for each sample. Then the solutions were filtered to remove chitosan particles. Remaining solutions were analyzed in ICP-OES to determine heavy metal adsorption.

Results and discussion

The production of chitosan at the different deacetylation temperatures and the size of shells was investigated. The yield values which are given in Table 1 were calculated from the weighing of the shells taken before and after the experimental stages. However, up to a point, the weighing efficiency should not be perceived as chitosan formation efficiency, since the loss of more mineral and protein in the shells will provide the formation of purer chitosan.

Comparing the results between the three sizes the highest yield usually obtained with –40, +18 mesh particles in each stage. The smaller size lost more protein and organic

Table 1. Yield percentages of chitosan production stages

Mesh	Raw material	Deproteinization (%)	Demineralization (%)	Deacetylation (%, 60°C)	Deacetylation (%, 80°C)	Deacetylation (%, 100°C)
-40, +18	Shrimp	69.791	71.338	90.598	83.498	84.556
-60, +40	Shrimp	69.573	71.144	81.243	80.564	79.985
+60	Shrimp	65.338	71.998	63.525	61.426	69.357
Total	Shrimp	68.234	71.493	78.456	75.163	77.966
-40, +18	Crab	94.796	71.368	80.138	78.153	76.453
-60, +40	Crab	95.570	71.011	77.644	72.420	75.304
+60	Crab	94.016	70.285	93.401	60.279	73.948
Total	Crab	94.794	70.888	83.728	70.284	75.235

molecules. This result shows due to the increased interacted surface area the smaller size of the shells could be used for obtaining higher quality chitin and chitosan.

Shrimps have a much softer shell compared to crabs. This makes it easier to handle in chemical processes. Hence, they lose more organic matter and salt, resulting in lower production efficiency. In the deacetylation phase, it is seen that temperature change causes changes in yield values. The reason for this may be that the organic substances and salts remaining in the shells are dissolved in solution at different rates under the effect of temperature and removed by filtration. Considering these results, the lower production efficiency obtained from 80°C deacetylation can be interpreted as the purer chitosan formation.

FT-IR spectroscopic analysis was used to determine the chemical structure of chitosan. The FT-IR spectrum of chitosan obtained using the parameters of –60, +40 mesh crab-based chitosan is presented in Fig. 1.

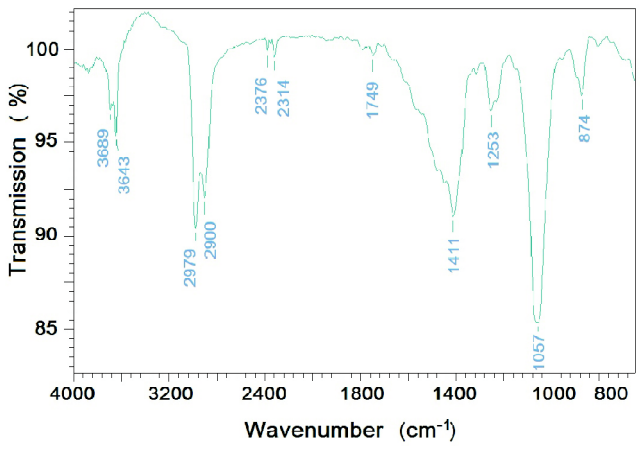

Fig. 1. FT-IR spectra of –60, +40 mesh crab-based chitosan.

According to this spectrum, the peaks at 3643 and 3689 cm^{-1} could be assigned to ν(N-H). The small peaks at 2376 and 2314 cm^{-1} could be defined as ν(C-H) which present $-CH_2$ and $-CH_3$ groups. Because of the removal of the acetyl group into the amine group due to deacetylation, the hydroxyl groups exist so the amide band is observed 1749 cm^{-1}. The peak at 1057 cm^{-1} shows ν(C-O) of alcohol. The peak at 1411 and 874 cm^{-1} in the spectra assigned to ν(C-N) vibration and ν(C-C), respectively.

Since 80°C deacetylated samples has the highest chitosan purity due to the lowest production efficiency, these samples were used for heavy metal adsorption. After stirring 0.1 g of chitosan samples in 20 ppm antimony solutions for 1, 2 and 3 h at room temperature, the final antimony concentrations were determined by ICP-OES analysis and are given in Table 2. The highest adsorption in average was observed with –60, +40 mesh size for both shrimp and crab. Reducing the particle size increase the adsorption capacity up to a point. However, as the surface pores may be damaged after

Table 2. Final concentrations of antimony stock solutions

Mesh	Stirring time (h)	Shrimp Weight (g)	Shrimp Sb (mg/L)	Crab Weight (g)	Crab Sb (mg/L)
–40, +18	1	0.1002	19.56±0.44	0.1005	17.56±0.39
–40, +18	2	0.1002	19.05±0.43	0.1010	17.53±0.39
–40, +18	3	0.1007	14.14±0.32	0.1000	15.62±0.35
–60, +40	1	0.1009	19.60±0.44	0.1004	17.94±0.40
–60, +40	2	0.1005	18.67±0.42	0.1002	16.69±0.38
–60, +40	3	0.1004	14.96±0.34	0.1002	13.65±0.31
+60	1	0.1010	18.23±0.41	0.1003	17.18±0.39
+60	2	0.1007	18.04±0.42	0.1006	16.70±0.38

this point, the amount of adsorption decreases. The adsorption ability of –60, +40 mesh particles can be interpreted in this way.

It is seen that increasing the stirring time from 1 h to 3 h increases the amount of adsorption for each size and both raw materials.

Although there are no major differences in adsorption performances between shrimp-based and crab-based products, it seems that crab-based-chitosan gives better results for almost all sizes and stirring times.

Conclusions

Chitosan production efficiency and heavy metal adsorption ability for antimony stock solution under different production parameters were investigated in this study. At the end of deacetylation, FT-IR spectroscopic analysis was used to determine the chemical structure of chitosan and the production of chitosan was confirmed as successful for each parameter. Besides, the most matching one observed as 80°C deacetylated –60, +40 mesh crab-based samples. The temperature effect on production was investigated and seen as 80°C optimum for deacetylation. In addition, the highest adsorption efficiency was observed in –60, +40 mesh sizes and it was observed that increasing mixing time increased the amount of adsorption in direct proportion.

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