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Crab Chitosan-Based Sponge as an Adsorbent for Oil and Grease in Wastewater from an Automotive Repair Shop

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Wastewater from processes carried out in automotive repair shops contains oils, detergents, greases and other chemical products that are mostly discharged directly into the sewage system without prior treatment. Thus, this research determined the efficiency of the sponge from crab chitosan for the reduction of oils and greases from the wastewater of an automotive repair shop. The extraction of chitosan from crab exoskeletons occurred by demineralization, deproteinization and chemical deacetylation. The sponges were elaborated with chitosan concentrations of 5, 10 and 15 mg/mL, obtaining oil and grease removals of 75.26% with the highest concentration used and at pH 3.8. In addition, parameters such as BOD5 and COD had reduction values of 63.15 and 59.51%, respectively. Finally, it is concluded that the chitosan sponge is a viable option for future wastewater treatment research.

1. Introduction

Water pollution from wastewater discharges is a growing concern on a global scale, arising from the high rate of population growth and inadequate treatment of water resources (Ayme E, et al., 2022; Barrientos C. et al., 2022; Esquivel R. and Castaneda-Olivera, 2022). According to Yee-Batista (2013), untreated wastewater accounts for 70 % in Latin America. On the other hand, the OEFA (2014) mentions that in Peru approximately 2,217,946 m^3 of wastewater are generated per day, which are discharged into the sewage network, and only 32 % of them are treated. In the city of Lima, Peru, approximately 1,202,286 m^3 of wastewater is generated per day and discharged into the sewerage network, and only 20.5 % of this is treated.
For Vargas R. (2017), wastewater from processes carried out in car repair shops that use oils, detergents, greases and other chemical products is mostly discharged directly into the sewage system without prior treatment and exceeds the maximum admissible values established by the Peruvian Ministry of Housing, Construction and Sanitation by Supreme Decree N° 010-2019-VIVIENDA, affecting not only the ecosystem but also the infrastructure, networks and wastewater treatment plants. Similarly, Maroto A. and Rogel Quesada (2004) consider lubricating oil waste as a substance that is difficult to biodegrade and is classified as hazardous waste by the regulations established in the Basel Convention.
Currently, there are many remediation techniques for oil-contaminated waters that vary in cost and effectiveness. These techniques include the use of chemical dispersants, mechanical tools (skimmers and booms), synthetic sorbents and in situ burning. However, their use can be expensive, harmful to marine life and lead to secondary pollution (Bidgoli et al., 2019). Many biological and physicochemical treatments such as the fungus *Phanerochaete chrysosporium*, the strain *Serratia marcescens* SA30 and the natural zeolite-packed column have been used for the removal of oils and greases, indicating that the aerobic biological process can be disrupted by the excessive amount of oils and greases that reduce the rate of oxygen transfer (Fulazzaky et al. 2022). According to Guilcamaigua A. et al. (2019), the use of natural adsorbents (bioadsorption) such as rice husks are products of high value as an alternative for the treatment of industrial wastewater with high contents of oils and greases.

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Environmentally, this research contributes to the strengthening of water resource management strategies through the use of a sponge, a process that does not generate pollution and increases water availability for other uses of social and natural relevance. Socially, it provides a circular economy process for water polluted by automotive activity, benefiting the urban community in improving their habitat and quality of life. It also contributes to the management promoted by the National Water Authority (www.gob.pe/institucion/ana/institucional), for the benefit of the final disposal of water resources. In economic terms, the method proposed and developed as an alternative solution has the advantage of great accessibility and low cost. Therefore, the main objective of this research was to develop a sponge based on crab chitosan to determine its efficiency in the reduction of oils and grease in wastewater generated from an automotive repair shop, as an accessible and economical method to improve the quality of water resources.

2. Materials and methods

2.1 Study sample

For the study, 20 L of wastewater contaminated with oil and grease were collected from the engine washing area of an automotive repair shop located in the city of Lima, Peru.

2.2 Obtaining chitosan from crustacean skeleton and elaboration of the sponge

The process of obtaining chitosan from crustacean (crab) skeleton and making the sponge followed the procedure of Wang et al. (2017) and Su et al. (2017), and is shown in Figure 1.

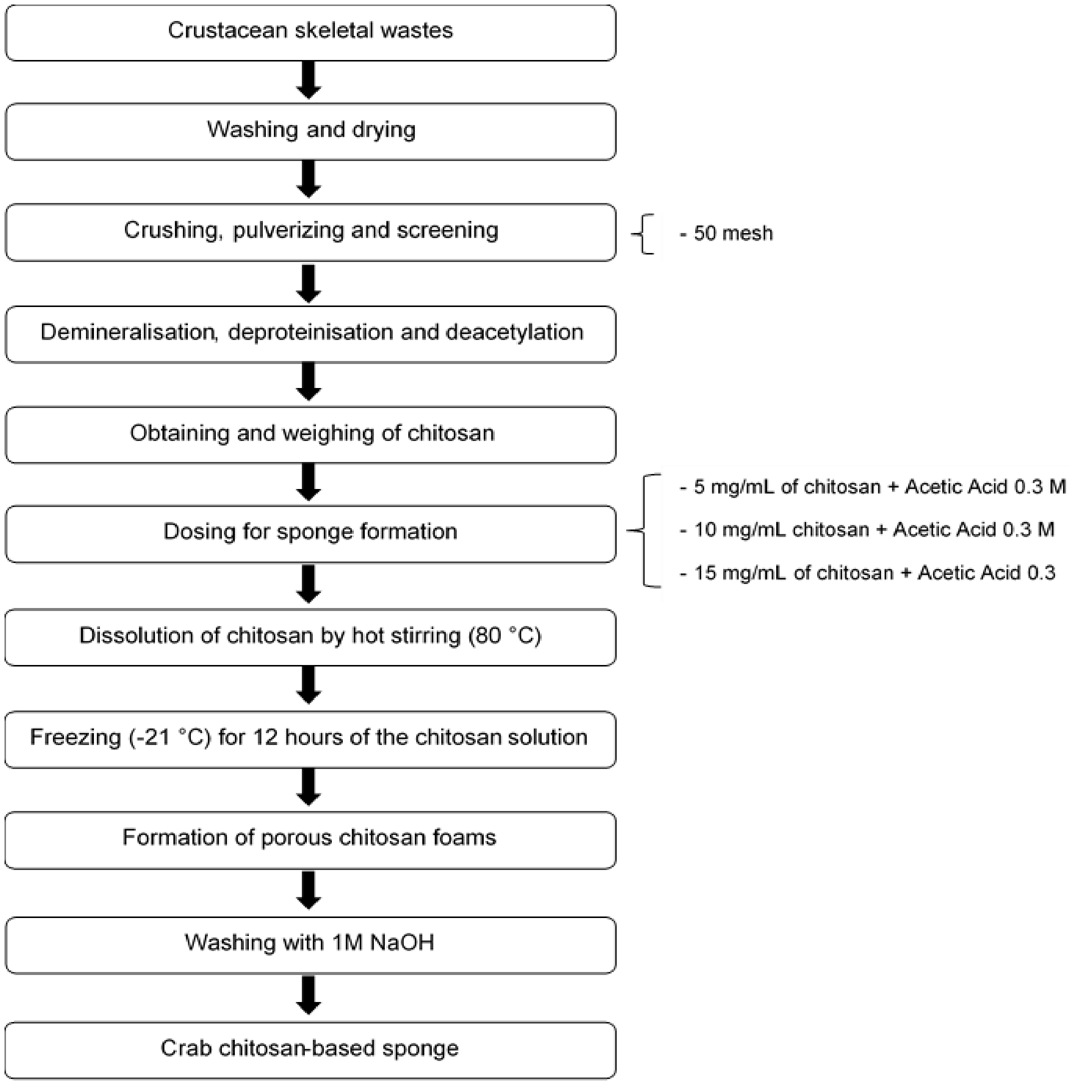

Figure 1: Flow chart for the production of the crab chitosan-based sponge

Figure 1 showed that the crustacean skeleton waste was washed, dried (35°C), crushed, pulverised and screened (50 mesh). Subsequently, the crab skeleton powder underwent demineralisation, deproteinisation and deacetylation processes:

- Demineralisation was performed with a 1.8 N hydrochloric acid (HCl) solution to remove calcium carbonate and calcium phosphate present in the crab skeleton residues, at room temperature (23 °C) for one hour with constant magnetic stirring. At the conclusion of this demineralisation procedure, the powder or sediment was filtered and washed with distilled water to a neutral pH, and then dried in an oven at 50 °C.
- The depoteinisation was carried out with 0.8 N sodium hydroxide (NaOH) solutions at 80 °C for a period of 4 hours with constant magnetic stirring. After the process time, the sediment (chitin) was filtered and washed with plenty of distilled water to remove excess base (alkali) to a neutral pH.
- Deacetylation consisted of generating the deacetylated polymer (chitosan) through a chitin derivatization reaction by hydrolysis of the acetamide groups. This reaction was carried out under very high alkaline conditions, with 13 N sodium hydroxide (NaOH) at a temperature of 150 °C for 1 h. Subsequently, the product obtained (chitosan) was carefully washed with distilled water.

Once the chitosan was obtained, the chitosan sponge was prepared. For this purpose, chitosan was used in three concentrations (5, 10 and 15 mg/mL), which were mixed with a 0.3 M acetic acid solution. Each solution was stirred hot (50°C) with a magnetic stir bar until the chitosan was completely dissolved. Then, the temperature-controlled freezing method (-21 °C) was used for 12 h to obtain the chitosan sponge. Subsequently, the sponge was washed with a 1 M NaOH solution to remove residual acetic acid. Finally, the chitosan sponge was washed with distilled water repeatedly until the pH is neutral.

2.3 Treatment of water contaminated with oils and greases using the crab chitosan-based sponge

The treatment of wastewater from an automotive repair shop was carried out with the crab chitosan-based sponge, taking into account the application conditions shown in Table 1, evaluating oils and greases, BOD5 and COD. For this, the sponge came into contact with the contaminated water as a filter medium until the volume used was exhausted, as shown in Figure 2. The volume of contaminated water used to evaluate the parameters studied was 150 mL. Each parameter was evaluated in triplicate for each treatment.

Table 1: Conditions of application of the crab chitosan-based sponge

Chitosan concentration (mg/mL)	pH	Temperature (ºC)	Contact time (minutes)
5	3.88	21	
10	3.88	21	30 to 90
15	3.88	21	

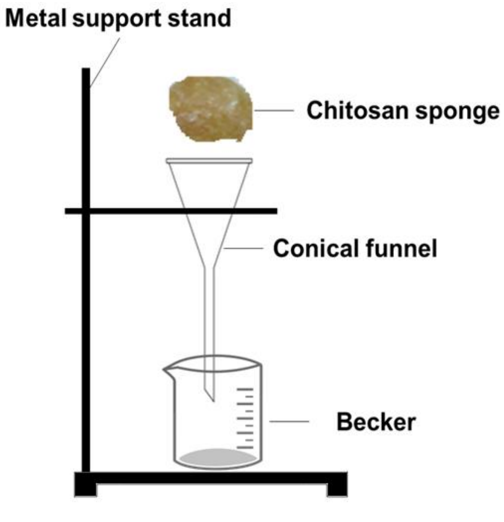

Figure 2: Schematisation of the absorption process

3. Results and discussion

3.1 Obtaining the crab chitosan-based sponge

Figure 3 shows the sponges formed from the three concentrations of crab chitosan studied.

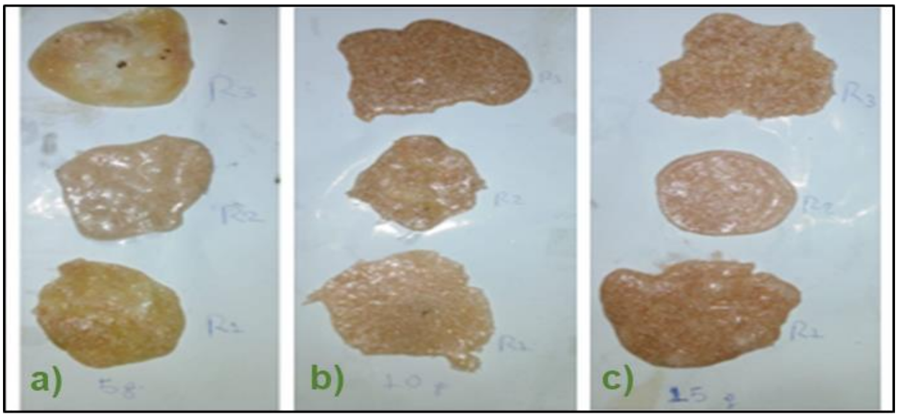

Figure 3: Crab chitosan-based sponge: a) 5 mg/mL of chitosan, b) 10 mg/mL of chitosan and c) 15 mg/mL of chitosan

The sponges formed had a diameter of 3 cm and a height of 1 cm, and they showed greater consistency and higher oil and grease reduction efficiency as the concentration of crab chitosan increased from 5 mg/mL to 15 mg/mL. Other authors such as Shi et al. (2023) constructed a chitosan and plama-based sponge to treat high-pressure arterial bleeding wounds. Jin et al. (2023) developed a chitosan antibacterial sponge combining zinc oxide (ZnO) particles and the photosensitiser chlorin e6 (Ce6) to combat multidrug-resistant bacteria and treat skin abscesses. Zhang et al. (2022) also prepared chitosan/polyvinylpyrrolidone/zein (CS/PVP/Zein) sponges that could coagulate blood significantly faster than commercial surgical gauze. In the case of Huerta L. et al., (2022), they used crab chitosan as an antimicrobial for fungi and yeasts in banana samples, and Romero-Serrano and Pereira (2020), in their review study, mentioned that chitosan has interesting scientific and industrial applications as a natural food preservative, manufacture of protective films for food packaging, synthetic bactericide, retention of nutrients in soil, improvement of crop quality and yield, adsorption of metal ions, flocculant, dye adsorbent, removal of mercury in solution and selective for removal of heavy metals by adsorption techniques.

3.2 Treatment of water contaminated

Table 2 shows the reduction values of the physicochemical parameters as a function of crab chitosan concentration. It shows that the chitosan sponge with a concentration of 15 mg/mL had a higher removal of oils and greases (75.26 %) compared to the chitosan sponges with 5 mg/mL (50.37 %) and 10 mg/mL (69.33 %). Romero-Sevilla et al. (2018) applied Cu-modified chitosan (Chitosan-Cu) and Zn-modified chitosan (Chitosan-Zn) for the treatment of tannery wastewater for the adsorption of chromium VI, obtaining removal efficiencies of 100 % at low Cr(VI) concentrations and 76 % at high Cr(VI) concentrations. Su et al. (2017) also developed chitosan sponges with large pore volume and good compression property, effectively adsorbing oily pollutants from water up to 99 %. Similarly, Tran and Lee (2017) elaborated a polyurethane (PU) sponge that had the characteristic of being superhydrophobic, porous, low dense and elastic, showing an oil-in-water separation efficiency at more than 99 %. Other researchers such as Vidales O. et al. (2010) used natural and artificial hair for the removal of greases and oils in the effluents of an automotive industry, achieving removal values of 90 %. Molina G. (2016), with the use of an artisanal filter based on beans, coconut shell activated carbon and gravel, achieved a 42.35 % removal of oils and fats from the wastewater of a car wash by 24 days of treatment. Similarly, Paitan de la Cruz & Sifuentes C. (2018) achieved maximum oil and grease removal (96.73 %) in wastewater from an equine slaughterhouse by electrocoagulation using aluminum plates as anode and cathode arranged in series.

BOD5 and COD also showed reductions in their values for the three concentrations of chitosan studied. The sponge with chitosan concentration of 15 mg/mL had the highest average reduction values of 63.15-90 % and 59.51 % for BOD5 and COD, respectively. These achieved values showed a considerable reduction of the content of organic and inorganic substances present in the polluted water.

According to the results shown above, the crab chitosan sponge was shown to have the ability to reduce the concentration of oils and greases in polluted waters, and this biomaterial can be considered a good treatment alternative due to its accessibility and low cost.

Table 2: Reduction of physico-chemical parameters with respect to chitosan concentration

Physico-chemical properties	Chitosan concentration (mg/mL)	Contact time (minutes)	Repetitions (R)	Concentration		Reduction (%)	Average reduction (%)
				Initial	Final		
Oils and greases (mg/L)	5	30	R_1	225	105	53,33	50.37
			R_2	225	112	50,22	
			R_3	225	118	47,56	
	10	60	R_1	225	65	71,11	69.33
			R_2	225	68	69,78	
			R_3	225	74	67,11	
	15	90	R_1	225	53	76,44	75.26
			R_2	225	56	75,11	
			R_3	225	58	74,22	
BOD_5 (mg/L)	5	30	R_1	843	507	39.86	39.90
			R_2	843	501	40.57	
			R_3	843	512	39.26	
	10	60	R_1	843	325	61.45	61.17
			R_2	843	330	60.85	
			R_3	843	327	61.21	
	15	90	R_1	843	307	63.58	63.15
			R_2	843	311	63.11	
			R_3	843	314	62.75	
COD (mg/L)	5	30	R_1	1253	733	41.50	41.13
			R_2	1253	742	40.78	
			R_3	1253	738	41.10	
	10	60	R_1	1253	557	55.55	56.10
			R_2	1253	548	56.26	
			R_3	1253	545	56.50	
	15	90	R_1	1253	503	59.86	59.51
			R_2	1253	508	59.46	
			R_3	1253	511	59.22	

4. Conclusions

Crab chitosan sponges were found to be effective in reducing the concentration of oils and greases in wastewater from an automotive repair shop. The sponge with a chitosan concentration of 15 mg/mL achieved an oil and grease reduction of 75.26 % for a contact time of 90 minutes. On the other hand, physicochemical parameters such as BOD_5 and COD also had considerable reductions, reaching values of 63.15 % and 59.51 %, respectively. This shows that the crab chitosan sponge is a good absorbent in the removal of oils and greases and could be used as an alternative solution that strengthens water resource management strategies. Furthermore, this material is highly accessible and inexpensive.

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