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Reduction of the Pollutant Load of Textile Wastewater using Chitosane as Natural Coagulant, Huancayo - 2020-2021

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Industrial effluents have high pollutant loads depending on the type of industry that generates them, which makes their treatment difficult. The textile industry consumes large amounts of water, generating large volumes of wastewater with high turbidity concentrations. For this reason, the main objective of the research was to analyse the efficiency of chitosan in reducing the pollutant load of industrial textile effluents in the city of Huancayo in the year 2020 - 2021. Tests were carried out following the guidelines of an experimental design with a pre-test, post-test, and a control group. There were 3 treatments with 160, 180, and 200 mg/L doses. An optimum efficient turbidity removal of 47.17 % was achieved at a dosage of 160 mg/L without causing variations in the effluent pH.

1. Introduction

The textile industry is considered the second most environmentally polluting economic activity due to the excessive use of water, energy, and chemical reagents in its processes (Brañez et al., 2018). Despite this, this activity has become more relevant over the years. It is projected that by 2050, 13,000 or 14,000 million people, per capita textile consumption could reach 26.2 kg/inhab/year. (Carrera, 2017) According to the results of the 2007 National Manufacturing Census, microenterprises in the industrial sector predominate in Peru, with a total of 107,334 microenterprises, followed by 3,596 small enterprises and 418 medium and large enterprises. Of which 21 % of the total are textile companies with 22,554 microenterprises, 734 small companies, and 103 medium and large companies (Ministerio de la Produccion, 2007). The volume of water used for activities, whether consultative or non-consultative, agricultural activity predominates with a total of 17,803.46 hm^3 for 2016 compared to the volume used for industry (which considers manufacturing), which in the same year represented 2,548.24 hm^3. However, the volume of water used for industry increase of 27.15 % from 1993 to 2016. (Bernex et al., 2017)The content of contaminants in industrial wastewater is variable, which is why it is necessary to include specific processes in its treatment. So, some of the typical characteristics of textile effluents are that "they have high concentrations of dyes, refractory organic pollutants, toxic compounds, inhibitory components, surfactants, chlorinated components". (Diaz et al., 2018) In addition to having large amounts of solids suspended and salt with a pH from 5 to 12 (Solis et al, 2013) representing a challenge in its treatment due to the use of chemical coagulants and flocculants that are expensive for the industry.On the other hand, there are biomass residues that have been used by countries such as China, Argentina, Ecuador, and others. (Garcia, 2017) In Peru, of the 0.58 kg of solid waste generated per person, 57.5% is organic waste that can be used either to generate energy, composting, or wastewater treatment. (Ministerio del Ambiente, 2008) As is the case in the Mediterranean Sea of Spain where to solve the invasion of the blue crab that affected the diversity of invertebrates and vertebrates and artisanal fishing, they obtained chitosan to market it and be used in different areas. (Correa-Mahecha et al., 2022) Based on references, there are significant results in the reduction of pollutants using rice husks, and wood sawdust for wastewater treatment (Huaman, 2018) also the use of banana pseudostem to adsorb crystal violet (CV) (Baharim et al., 2023) and the use of coffee extracts (Coffea Arabica) to eliminate azo dyes (Corre-Mahecha et al., 2023) In addition, there is research on the use of fruit peels for wastewater treatment and chitosan that is used in different areas such as agriculture to preserve food, in industry for weight loss, among other sectors. (Wang et al., 2017) For this, the idea of using chitosan is generated

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because it is considered biodegradable, non-toxic, easy to apply, and eco-friendly, and can reduce turbidity by 96.21 % efficiency. (Diaz et al., 2018) as well as being considered a valuable tool for the challenges of water pollution. (Mamta, et al., 2023) The following research aims to analyse the efficiency of chitosan in reducing the pollutant load of textile industrial effluents in Huancayo city in the year 2020 - 2021.

2. Materials and methods

The research was experimental with a correlational scope seeking to know the relationship or degree of association between the independent variable that is chitosan with the dependent variable which is the turbidity of the residual water. The type of experiment was pure with a pre-test - post-test design and a control group, considering three treatments with doses of 160, 180, and 200 mg/L of chitosan and realized the measurements of the turbidity and pH parameters. The population was considered the effluents generated in the textile industry and the sample was 11 litres of effluent.

2.1 Obtaining chitosan

To obtain the chitosan, the process followed by Velasco, Diaz, Ramirez and Pérez (Velasco et al.,2019) was used, which consisted of:
Cleaning and separation: with neutral soap
Drying: in a muffle for 24 hours at 60 °C
Crushed: using a mortar to a particle size of 250 mm
Demineralization: 5 % hydrochloric acid in a 1:6 ratio was added, stirred for 2 hours at a speed of 7 rpm at 40 °C. After the time was finished, the mix was washed and filtered to be baked for 24 hours at 60 °C.
Deproteinization: 3 % sodium hydroxide was added in a 1:5 ratio and stirred for 4 hours at 7 rpm with a temperature of 65 °C. The mix was washed and filtered to recover the solids.
Deacetylation: 50 % social hydroxide and distilled water were added in a 1:6:2 ratio to be stirred for 2 hours at 85 °C. To later washed, filtered, and be baked for 24 hours at 50 °C.

2.2 Preparation of the coagulant

2 grams of chitosan were weighed, and 0.5 g of 99.9 % acetic acid and 47.5 g of distilled water were added to be stirred for 30 min. After that time, it was dissolved in a 500 ml volumetric flask.

2.3 Jar test

The three treatments were added in a one-litre beaker, with the support of magnetic stirrers made a rapid mix of 3 min at 200 rpm, a slow mix of 15 min at 40 rpm, and a 30 min rest were performed. This process was carried out with three repetitions.

2.4 Removal efficiency

To define the efficiency, the following equation was considered:

$$\% \text{ efficiency} = \left(\frac{\textit{Starting value} - \text{Final value}}{\textit{Starting value}}\right) \times 100 \quad (1)$$

3. Results

The investigation had the following results:

3.1 Section headings

Based on the described procedure, 4 by-products were obtained: the ground shell, the exoskeleton after demineralization, chitin, and chitosan.

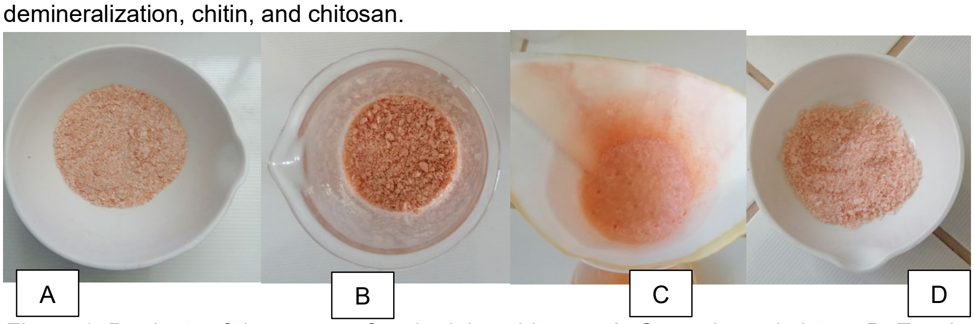

Figure 1: Products of the process for obtaining chitosan. A. Ground exoskeleton. B. Exoskeleton resulting from demineralization. C. Chitin resulting from deproteinization. D. Chitosan resulting from Deacetylation.

3.2 Control measurements

Before adding the coagulant, turbidity and pH were measured, getting values between 213 and 269 NTU, and between 7.09 and 7.34, respectively. Table 1 presents the results where NTU: Nephelometric Unit; T1: treatment 1 with a dose of 160 mg/L; T2: treatment 2 with a dose of 180 mg/L; and T3: treatment 3 with a dose of 200 mg/L.

Table 1: Control test results

		Turbidity (NTU)			pH		
Treatments		T1	T2	T3	T1	T2	T3
	I	265	264	262	7.09	7.11	7.12
Repetition	II	220	213	269	7.25	7.27	7.28
	III	234	236	238	7.31	7.32	7.34

3.3 Turbidity measurements

After the rest time, the turbidity measurements shown in Table 2 was performed, in which it is observed that in treatment 1 with a dose of 160 mg/L had a greater reduction in turbidity with a final turbidity of 125 NTU, which represents a 47.17 % reduction. Table 2 presents the results where NTU: Nephelometric Unit; T1: treatment 1 with a dose of 160 mg/L; T2: treatment 2 with a dose of 180 mg/L; and T3: treatment 3 with a dose of 200 mg/L. Figure 2 graphically shows the variations between the control and treatment results for each repetition.

Table 2: Turbidity results after chitosan application

		Turbidity (NTU)					
Treatments		C1	T1	C2	T2	C3	T3
	I	265	140	264	168	262	181
Repetition	II	220	128	213	181	269	150
	III	234	139	236	171	238	143

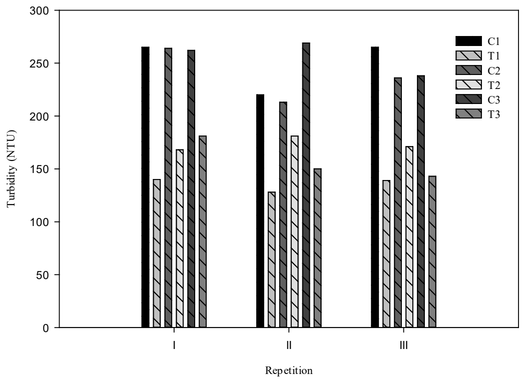

Figure 2: Results of Turbidity. Prepared with SigmaPlot 12.0 software.

To evaluate the relationship that exists between the doses of chitosan and the variation in turbidity, the "student's t-test for related samples" was carried out, in which it is considered that when $P \geq 0.05$ the data are statistically equal and if $P < 0.05$ they are statistically different. Table 3 shows the results of the test, where it is observed that for the pair C1 – T1 and C3 – T3 the P value is less than 0.05, demonstrating that there was a statistically significant difference. Otherwise for pair C2 – T2 there was no statistically significant difference because P is greater than 0.05. This evaluation was prepared through the SPSS program.

Table 3: T-test for related samples of turbidity

	CI 95%		t	df	P
	Lower	Superior			
C1 – T1	58.66874	149.33126	9.871	2	0.010
C2 – T2	-15.17201	143.83868	3.482	2	0.074
C3 – T3	50.59306	146.07361	8.862	2	0.012

3.4 Optimal dose

The removal percentages are shown in Table 4, in which it is observed that T1 in repetition I, had the highest removal percentage with 47.17 %. On the other hand, T2 in repetition II had the lowest percentage of removal with 15.02 %. With this information, it is demonstrated that there is a relationship between the dose and the percentage of removal. Table 4 presents the results where Co: Initial concentration; and Cf: Final concentration.

Table 4: Results of removal percentage according to dose

Treatments	Dose	Repetition	Turbidity (NTU)		% Removal
			Co	Cf	
		I	265	140	47.17 %
T1	160 mg/L	II	220	128	41.83 %
		III	139	139	47.55 %
		I	264	168	36.36 %
T2	180 mg/L	II	213	181	15.02 %
		III	236	171	27.54 %
		I	262	181	30.92 %
T3	200 mg/L	II	269	150	44.24 %
		III	238	143	39.92 %

3.5 pH measurements

After the rest time, the pH measurements are shown in Table 5, in which it is observed that there were no extreme pH variations. However, it was observed that between C3 and T3 in repetition II presented a wide variation and between C1 and T1 in repetition I presented a lower variation in pH. Figure 3 shows graphically the minimum variations that occurred between the control and treatment in the repetitions.

Table 5: pH results after chitosan application

		pH					
Treatments		C1	T1	C2	T2	C3	T3
	I	7.09	7.04	7.11	7.01	7.12	7.03
Repetition	II	7.25	7.03	7.27	7.11	7.28	6.96
	III	7.31	7.03	7.32	6.97	7.34	7.06

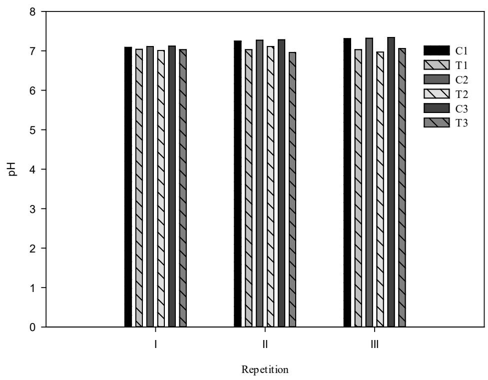

Figure 2: Results of pH. Prepared with SigmaPlot 12.0 software.

To evaluate the relationship between chitosan and the pH variation, the “student's t-test was performed for related samples” for the control tests with the treatments. To evaluate the values of P, was considered that, when $P \geq 0.05$ the data are statistically equal and if $P < 0.05$ they are statistically different. Table 6 shows the results of the test, where it is observed that all the pairs have a P value greater than 0.05, demonstrating that there is not a significant statistically difference between the control and treatment pH values.

Table 6: T-test for related samples of pH

	CI 95%		t	df	P
	Lower	Superior			
C1 – T1	-0.11303	0.47970	2.662	2	0.117
C2 – T2	-0.12088	0.52754	2.698	2	0.114
C3 – T3	-0.07526	0.53526	3.242	2	0.083

4. Discussion

The investigation entitled "Use of Chitosan as a Natural Coagulant for the treatment of effluents generated by the Textile Industry Case: Universal Textile Company" details that when using commercial chitosan, the most efficient results were with a dose of 135 mg/L at 3 % of chitosan with an optimum pH of 9, obtaining removal efficiencies of 96.21 % Turbidity, 4.78 % TSS, 82.11 % BOD5, and 82.42 % COD. (Diaz et al., 2018) On the other hand, for the investigation with chitosan, the best result was obtained with a dose of 160 mg/L at 4 % chitosan with a maximum removal of 47.7 %. The reason for the difference in removal percentages lies in the fact that the research manipulated the pH parameter up to 9 to achieve a maximized removal as shown in its results, however for the research the experiment was carried out without altering the initial pH, being close to neutral. In addition, thanks to the analysis of different pH, it is observed that having a pH of 6, they obtain a maximum removal of 42.46 %, which is like the result obtained, which was 47.7 %. Demonstrating that pH is a factor that directly affects the removal of organic load from wastewater. On the other hand, in the initial and final pH values of the cited research, there are no extreme variations, such as the present research that with the optimal dose of 160 mg/L the initial pH value of 7.09 ends with 7.04 after the treatment In addition, it is important to highlight that the aforementioned research carried out its experiment with commercial chitosan while the process of obtaining it was carried out in the present investigation, having in comparison these vary remarkably. It is necessary to compare the results with the research "Use of chitosan as a coagulant and flocculant in the treatment of wastewater from glue and paint plants", where the final pH was maintained within the limits of environmental regulations of its country of origin. It was observed that chitosan, being a cationic polymer, can function as both a coagulant and a flocculant. Therefore, pH is a very important parameter as it is one of the factors that most influence the coagulation process. (Capitillo-Maita et al., 2023) Likewise, the results are compared with the research entitled "Evaluation of the application of chitosan as a biocoagulant for the removal of turbidity in the treatment of wastewater from a lubricator" (Gonzalez, 2020) because it is another type of wastewater that can be applied. In the research cited, better results were obtained with chitosan obtained at a dose of 6 ml at 6 %, obtaining removal of 91.57 %, going from 807 NTU to 68 NTU of turbidity, maintaining a neutral pH compared to the chemical coagulant aluminum sulfate. which had a maximum removal of 71.41 % and the final pH was 4.08, observing a clear pH variance. It is important to highlight that the physical-chemical characterization of the base wastewater from the lubricator, presents a pH of 9.73, demonstrating once again that pH is one of the factors to consider for the coagulation process, affecting the removal of polluting load. For this reason, the investigation presented a reduction percentage of 47.17 %. In addition, the research shows that chitosan can be used in various types of wastewaters with different physicochemical characteristics.

5. Conclusions

It is concluded that chitosan reduces the contaminant load of textile industrial wastewater since compared to initial values of turbidity variations between 220 and 269 NTU and a pH between 7.09 and 7.34, which decreased after applying chitosan to the 4 % concentration reached turbidity values between 139 to 181 NTU and a pH between 6.97 to 7.11. The values show that the most effective treatment was the first treatment (T1) with a dose of 160 mg/L, the maximum removal of 47.17 % was obtained, going from an initial value of 265 to 140 NTU and the pH did not have extreme variations, remaining neutral for all treatments. Showing that chitosan is a good alternative to reduce the pollutant load of wastewater and to replace chemical coagulants.

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