Contents list available at CBIORE journal website

Journal of Emerging Science and Engineering

Journal homepage: https://journal.cbiore.id/index.php/jese

Research Article

Optimisation of chitosan as a natural flocculant for microplastic remediation

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Abstract. The objective of this study is to determine the optimal concentration of chitosan for microplastic remediation using the coagulation-flocculation method. The chitosan concentrations employed in this study include 10, 20, 30, and 40 ppm. The process of coagulation was conducted for one minute, with a rotational speed of 120 rpm. The process of flocculation was performed for 30 minutes with a rotational speed of 60 rpm. The findings of the study indicate that chitosan demonstrates a high efficacy in microplastic removal, resulting in a removal rate of 68.3%. Furthermore, the research findings indicate that the optimal concentration of chitosan for microplastic remediation was determined to be 30 ppm. The concentration of chitosan has a direct impact on the pH, TDS, COD, and BOD values. In general, an increase in chitosan concentration leads to a drop in pH and TDS values; conversely, an increase in chitosan concentration results in a rise in COD and BOD values.

Keywords: Flocculation, Coagulation, Microplastic, Chitosan, Water pollution

Received: 8th Oct 2023; Revised: 18th Dec 2023; Accepted: 20th Dec 2023; Available online: 26th Dec 2023

1. Introduction

The growth of industrial and residential zones has the potential to contribute to increasing pollution levels. In the absence of concurrent efforts to conserve natural resources, this can result in a decline in environmental quality and adversely affect various forms of life. The potential consequence of the discharge of pollutants into rivers, subsequently leading to their entry into the marine ecosystem, is the occurrence of water pollution. Various forms of trash contribute to pollution, including but not limited to plastic, metal, textiles, paper, and other discarded materials that find their way into the marine environment, subsequently transforming into marine debris (Ayuingtyas et. al., 2019).

The quantity of plastic garbage in Indonesia has undergone a notable escalation, primarily due to the impact of shifting millennial lifestyles. Plastic pollution arises from diverse origins, encompassing packaging (37%), buildings and construction (21%), automobiles (8%), electrical equipment (6%), as well as medical and other sources (28%) (Gall et. al., 2015). Plastic packaging is currently in significant demand, primarily for single-use purposes. Insufficient management and failure to adhere to circular economy principles in handling plastic trash can result in substantial environmental risks, including the contamination of marine biota and the degradation of coral reefs. These consequences can have far-reaching implications for marine ecosystems (Eriksen et. al., 2014).

Microplastics refer to plastic garbage that has a diminutive size, typically measuring less than 5 mm in diameter. The existence of microplastic debris within aquatic ecosystems poses significant challenges because of its composition of enduring, possibly hazardous, carcinogenic, and habit-forming substances. The presence of microplastic debris has the potential to infiltrate the food chain, thereby exerting adverse effects on both human health and the environment (Kristiningsih, 2020). The proliferation of microplastics in global marine ecosystems has resulted in significant negative consequences for both the natural environment and human well-being. In the field of microplastic removal, it is commonly seen that three distinct approaches are employed, namely filtering, biodegradation, and coagulation-flocculation (Par et. al., 2021).

One approach to reducing microplastic pollution involves employing a remediation technique that utilises the inherent properties of naturally occurring coagulants, which are widely accessible in the environment. The role of the coagulant in the coagulation-flocculation process is to expedite the aggregation of larger, more robust, and enduring flocs. One naturally occurring coagulant that can be used for microplastic coagulants is Chitosan. According to a study (Manurung, 2011), the application of chitosan has been found to enhance the sedimentation rate, decrease turbidity, and augment the density of sediment generated during waste processing.

The Beringin River, located in Mangunharjo Village within the Tugu District of Semarang City, serves as a conduit for various industrial, residential, and coastal activities. The Mangunharjo Coastal Area, in particular, is utilised by local inhabitants for fishing,

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https://doi.org/10.61435/ijred.2023.7
ISSN: 3026-0183/© 2023.The Author(s). Published by CBIORE

fish farming, and industrial endeavours, thereby supporting their livelihoods. The community activities conducted in Mangunharjo Village have both direct and indirect implications for the aquatic environment of the Beringin River.

Based on the aforementioned background information, the efficacy of the coagulation-flocculation approach for remediating microplastic pollution in water systems was investigated in this study. The coagulant employed in this study is chitosan. The objective of this study is to determine the most effective concentration of chitosan for the remediation of microplastic pollution.

2. Materials and Methods

In this research, the study population consisted of the Beringin River water in the Mangunharjo sub-district, Mangkang Wetan sub-district, and Wonosari sub-district, as well as the Ngaliyan sub-district in Semarang city. River water samples were collected on April 15, 2022, at 10:00 Western Indonesian Time (WIB). Before collecting a water sample, the flow of the river was collected in order to determine the number of the sample, as indicated in Table 1. This investigation involved the selection of two sampling stations based on the observations of river flow discharge. Sampling point 1 was conducted in the Mangunharjo sub-district, Mangkang Wetan sub-district, whereas point 2 was conducted in the Wonosari, Ngaliyan sub-district, Semarang city (Figure 1).

The present study involved the implementation of a coagulation-flocculation procedure utilising a naturally occurring coagulant, specifically chitosan. Chitosan was dissolved in hydrochloric acid (HCl) to establish an acidic environment, thereby inducing the transformation of chitosan into a cationic polymer. This modified form of chitosan can be effectively employed as a coagulant or flocculant agent. Chitosan works by creating a film or localising enzymes that facilitate the coagulation of particles. Afterwards, 500 ml of the sample was combined with Chitosan solution to coagulate and flocculate the microplastics.

The concentrations of chitosan employed in this study were 10, 20, 30, and 40 parts per million (ppm). The stirring speed employed during the coagulation process (fast stirring) was set at 120 revolutions per minute (rpm) for 1 minute. Subsequently, proceed with the flocculation procedure, employing a slow stirring motion at a speed of 60 rpm for 30 minutes. Subsequently, the floc settled down for two hours in order to facilitate proper sedimentation of the floc particles. The coagulation-flocculation procedure employed in this study pertains to the standard SNI 19-6449-2000.

The parameters evaluated in this study encompassed the characteristics of river water subsequent to and preceding treatment, specifically biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), and pH. BOD analysis was carried out using the respirometric test method. COD analysis was carried out using the UV-Vis spectrophotometry method. Both BOD and COD refer to 5210 B 23rd Edition 2017 American Public Health Association. TDS analysis was carried out using TDS & EC meter (hold). pH analysis was conducted utilising an Ohause digital pH meter. Afterwards, the acquired data is analysed and processed into a bar chart utilising Microsoft Excel software. The X-axis represents the independent variable, while the Y-axis represents the dependent variable.

Table 1. The number of samples according to the river's flow.

Debit (m^3/s)	Number of Samples
<5	1
5 - 100	2
>150	3

Figure 2. Sampling location

3. Result and Discussion

3.1. Characteristics of Beringin River Water

Table 2 presents a comparison between the properties of Beringin River water before treatment and the standard values for class III river water as defined by PP No. 22 of 2021. The results indicate that All the characteristics of the Beringin River meet with standards except for the COD value, which is above the acceptable threshold (>40 mg/L).

Table 2. Characteristics of Beringin River water before treatment.

Parameter	Berinin River Water Characteristics	Standards
BOD (mg/L)	4.742	<6
COD (mg/L)	51.05	<40
pH	8.13	6-9
TDS (mg/L)	134	<1000

3.2. pH value

Table 3 displays the pH values of the Beringin River water before and after the coagulation-flocculation process using chitosan. The pH of the Beringin River water before treatment was measured to be 8.13, indicating an alkaline character. Subsequently, the water from the Beringin River, after the treatment process, exhibited a pH level within the neutral range for samples treated with chitosan concentrations 20, 30, and 40 ppm, with recorded values of 7.54, 7.50, and 7.62. Conversely, samples treated with a chitosan concentration of 10 ppm displayed an acidic pH level of 4.49. Among all the samples examined, it was observed that only the samples treated with a concentration of 10 ppm chitosan failed to fulfill the prescribed standards for class III river water quality as defined by PP No. 22 of 2021.

Table 3. pH value of Beringin River before and after treatment.

Chitosan concntration (ppm)	pH		
	Before treatment	After treatment	Standards
10	8.13	4.49	6-9
20		7.54	
30		7.50	
40		7.62	

3.3. Total Dissolved Solid (TDS)

Table 4 displays the changes in TDS within the Beringin River water after treatment. The TDS value in Beringin River water exhibited a decline, starting from an initial measurement of 134 mg/L to subsequent measurements of 125, 126, 127, and 133 mg/L, after the implementation of coagulation-flocculation using chitosan at concentrations of 10, 20, 30, and 40 ppm, respectively. All of the TDS measurements acquired comply with the prescribed river water quality criteria as outlined in PP No. 22 of 2021.

Table 4. TDS value of Beringin River before and after treatment.

Chitosan concntration (ppm)	TDS (mg/L)		
	Before treatment	After treatment	Standards
10	134	125	<1000
20		126	
30		127	
40		133	

3.4. Biological Oxygen Demand (BOD)

The BOD levels in Beringin River water samples increased after coagulation-flocculation with chitosan, as shown in Table 5. BOD of the Beringin River water, initially measured at 4.74 mg/L, showed a rise to a range of 15.84-21.19 mg/L. The increase in BOD levels results in the BOD values of the treated Beringin River water samples exceeding the maximum acceptable level outlined in PP No. 22 of 2021, precisely 6 mg/L.

Table 5. BOD value of Beringin River before and after treatment.

Chitosan concntration (ppm)	BOD (mg/L)		
	Before treatment	After treatment	Standards
10	4.74	15.84	<6
20		16.33	
30		12.64	
40		21.19	

3.5. Chemical Oxygen Demand (COD)

The COD measurement indicates the quantity of oxygen required for the oxidation of both organic and inorganic substances. An increase in the COD value of water is indicative of a higher concentration of organic contaminants present in the water. The data shown in Table 6 demonstrates a notable reduction in COD values subsequent to the application of chitosan treatment at concentrations of 10 and 20 ppm. Nevertheless, the application of chitosan at concentrations of 30 and 40 ppm resulted in an elevation of COD levels. The COD levels in the water of Beringinbayan River, both before and after treatment, fail to reach the regulatory standards established by PP No. 22 of 2021.

Table 6. COD value of Beringin River before and after treatment.

Chitosan concntration (ppm)	COD (mg/L)		
	Before treatment	After treatment	Standards
10	51.07	40.09	<40
20		50.61	
30		53.35	
40		66.28	

3.6. Microplastic removal

Microplastics are a type of contamination that arises from an excess of plastic trash. Microplastics are plastic particles that have a diameter of less than 5 mm (Andrady, 2011). Table 7 illustrates the reduction in microplastic concentration subsequent to the implementation of coagulation-flocculation using chitosan. The decline in microplastic concentration is linear with respect to the concentration of chitosan. The treatment with a chitosan concentration of 40 ppm exhibited the most significant reduction, specifically 6.3 mg/500mL, whereas the treatment with a chitosan concentration of 10 ppm showed the least reduction, specifically 4.2 mg/500mL. Regarding microplastics in water systems, there are currently no quality standards.

Table 7. Microplastic concentrations of Beringin River before and after treatment

Chitosan concentration (ppm)	Microplastic (mg/500mL)		
	Before treatment	After treatment	Removal
10	10.6	6	4.2
20	10.5	4.4	6.1
30	10.1	3.2	6.9
40	10	3.7	6.3

3.7. The impact of coagulation-flocculation on pH value

The data shown in Figure 2 illustrates a notable decline in pH levels observed in the Beringin River water both before and after the treatment process. The observed decline in pH can be attributed to the utilisation of hydrochloric acid (HCl) as a solvent for chitosan. Nevertheless, the observed pattern in the pH of the sample after treatment demonstrates a positive correlation with the increasing concentration of chitosan. This phenomenon occurs due to the polycationic nature of chitosan, which facilitates the binding of hydrogen ions (H^+) in aqueous solutions, resulting in an elevation of the pH level (Suptijah et. al., 2008).

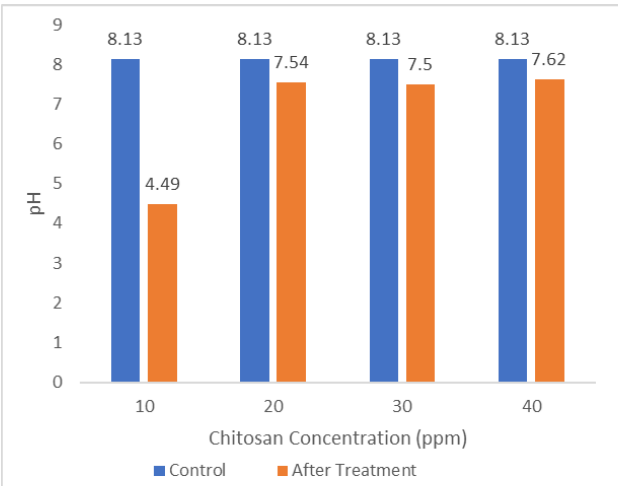

Figure 2. pH of samples before and after coagulation-flocculation using chitosan

3.8. The impact of coagulation-flocculation on TDS

The TDS value of the water sample collected from the Beringin River exhibited a decrease after the coagulation-flocculation process involving chitosan, as shown in Figure 3. The observed decrease can be attributed to the ability of chitosan to effectively bind both organic and inorganic contaminants present in the water samples. This finding demonstrates that chitosan possesses favourable coagulation properties, rendering it a viable substitute for natural coagulants. Nevertheless, it is observed that the TDS values of the water samples after treatment have a positive correlation with the concentration of chitosan employed. This increase is possible because chitosan can dissolve into a dissolved organic substance. The overutilisation of chitosan has been found to result in a notable increase in the TDS value.

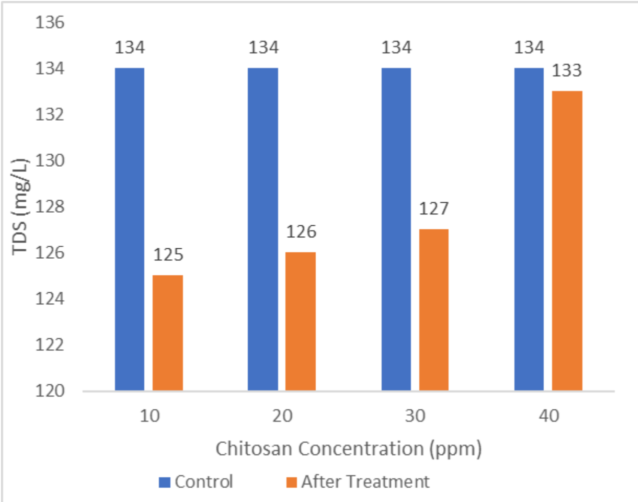

Figure 3. TDS of samples before and after coagulation-flocculation using chitosan

3.9. The impact of coagulation-flocculation on BOD

According to Figure 4, there was a significant increase in BOD levels, with values increasing from 4.74 ppm before treatment to a range of 12.64-21.19 ppm after treatment. The increase in BOD measurements may arise due to the presence of dissolved chitosan, which augments the organic content within the sample, hence causing a higher oxygen demand for the oxidation of organic substances. The findings shown here are consistent with the study conducted by Hendrawati (2016), which posited that the utilisation of chitosan bio coagulant could lead to an elevation in the organic load present in samples, thereby resulting in higher levels of BOD.

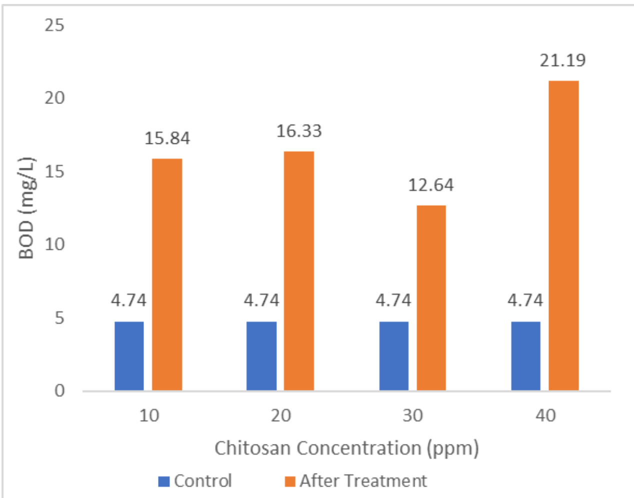

Figure 4. BOD of samples before and after coagulation-flocculation using chitosan

3.10. The impact of coagulation-flocculation on COD

The COD test indicated a decline in COD levels in samples treated with chitosan at concentrations of 10 and 20 ppm. In comparison, an elevation in COD levels was seen in samples treated with chitosan at concentrations of 30 and 40 ppm (see Figure 5). A reduction in COD levels may be observed as a result of the coagulation-flocculation process, which leads to the removal of colloidal organic components present in the sample. On the other hand, the observed elevation in COD levels can be attributed to the excessive application of chitosan beyond its optimal concentration, resulting in the inhibition of floc formation. The inhibition of floc formation occurs due to the increased presence of cations, which increase the electrostatic forces responsible for the bonds of macro flocs. Consequently, these increased forces disrupt the bonds established during the coagulation process.

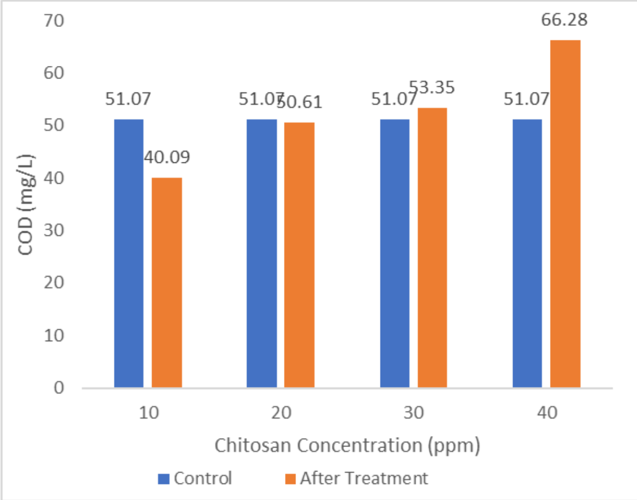

Figure 5. COD of samples before and after coagulation-flocculation using chitosan

3.11. The impact of coagulation-flocculation on microplastic removal

The data presented in Figure 6 demonstrates a positive correlation between the concentration of chitosan (ranging from 10-30 ppm) and microplastic removal. In coagulation-flocculation, however, with a chitosan concentration of 40 ppm, the microplastics removal decreased. The results indicate that the most effective concentration of chitosan for the coagulation-flocculation process of microplastics is 30 ppm. The efficiency of chitosan as a natural coagulant or flocculant for the coagulation-flocculation process of microplastics is demonstrated by the achieved microplastic removal rate of 68.3%.

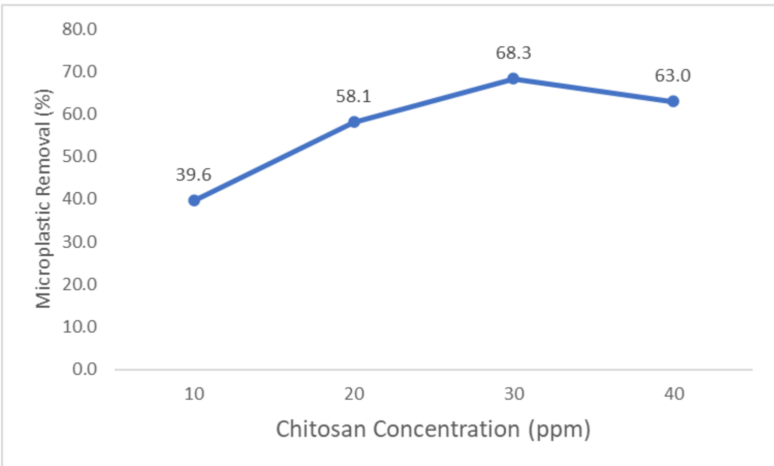

Figure 6. Microplastic removal after coagulation-flocculation using chitosan

4. Conclusion

Microplastic pollution is an urgent environmental concern that necessitates prompt resolution. The small sizes of microplastics pose a significant problem in effectively managing this form of waste. The coagulation-flocculation process represents a feasible strategy for addressing the issue of microplastic pollution. In this work, chitosan, a natural coagulant-flocculant, was used. The findings of the study demonstrate that chitosan exhibits a high efficacy in the flocculation of microplastics, resulting in a removal rate of 68.3%. Furthermore, the research findings indicate that the optimal concentration of chitosan determined in this study was 30 ppm. The concentration of chitosan has a direct impact on the values of pH, TDS, COD, and BOD. In general, an increase in chitosan concentration is associated with a decrease in pH and TDS values. Conversely, an increase in chitosan concentration is linked to an increase in COD and BOD values.

Acknowledgment

The authors would like to acknowledge the Center of Biomass and Renewable Energy (C-BIORE) for facilitating and supporting the research.

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