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THE EFFECT OF VARIATIONS OF CHITOSAN BIOCOAGULANTS FROM MUJAIR (*Oreochromis mossambicus*) FISH SCALE WASTE IN REDUCING VEHICLE WASH WATER POLLUTION

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ABSTRACT

Car wash services in Indonesia are becoming increasingly popular in urban areas. One of them is a vehicle washing business in Kuta Raja District, Banda Aceh. However, vehicle washing services not only increase regional income, but also produce vehicle washing liquid waste which can reduce environmental quality. So it is necessary to process liquid waste, one of which is by using tilapia fish scale chitosan. This research aims to determine the value of the best coagulant dose of chitosan mass in reducing COD, TSS and Phosphate pollutants in vehicle washing waste. The dose determination method is carried out by varying the dose to 10 mg/L, 20 mg/L and 30 mg/L for each with a combination of fast stirring at 120 rpm for 30 minutes and slow stirring at 90 rpm for 40 minutes. The results of the study showed that the best dose for reducing COD parameters was the use of a dose of 20 mg/L, then the best mass for reducing TSS parameters was the use of a dose of 30 mg/L and the effectiveness of reducing COD levels were 81.53%, then the reduction in TSS levels was 88.11%. . In phosphate there is an increase in concentration with each dose given. The addition of chitosan to COD, TSS and Phosphate depends on the optimum dose found in vehicle washing wastewater. Thus, processing vehicle washing liquid waste using tilapia fish scale chitosan using the flocculation-coagulation method is able to reduce the concentration of the parameters.

Keywords : Chitosan, Tilapia Fish Scales, Vehicle Washing, Water Treatment.

ABSTRAK

Layanan cuci mobil di Indonesia semakin meningkat di perkotaan. Salah satunya di Kecamatan Kuta Raja, Banda Aceh. Jasa pencucian kendaraan tidak hanya meningkatkan pendapatan daerah, tetapi juga menghasilkan air limbah pencucian kendaraan yang dapat menurunkan kualitas lingkungan. Hal ini memerlukan pengolahan air limbah, salah satunya dengan penggunaan kitosan sisik ikan mujair. Penelitian ini bertujuan menentukan nilai dosis koagulan terbaik massa kitosan dalam penurunan polutan COD, TSS dan Fosfat pada limbah pencucian kendaraan. Metode penentuan dosis dilakukan dengan memvariasi dosis masing-masing 10 mg/L, 20 mg/L dan 30mg/L dengan kombinasi pengadukan cepat 120 rpm selama 30 menit dan pengadukan lambat 90 rpm selama 40 menit. Hasil penelitian menunjukkan bahwa dosis terbaik untuk penurunan parameter COD adalah penggunaan dosis 20 mg/L lalu massa terbaik untuk penurunan parameter TSS adalah penggunaan dosis 30 mg/L serta efektivitas penurunan kadar COD sebesar 81,53% lalu penurunan kadar TSS sebesar 88,11%. Pada fosfat terjadi kenaikan konsentrasi dari setiap dosis yang

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diberikan. Penambahan kitosan terhadap COD, TSS dan Fosfat tergantung pada dosis optimum yang terdapat pada air limbah pencucian kendaraan. Dengan demikian, pengolahan air limbah pencucian kendaraan dengan menggunakan kitosan sisik ikan mujair dengan metode flokulasi-koagulasi mampu menurunkan konsentrasi pada parameter.

Kata kunci : *Kitosan, Sisik Ikan Mujair, Pencucian Kendaraan, Pengolahan Air*

Introduction

Car wash services in Indonesia are mushrooming in urban areas. As the population increases, the need for vehicles also increases, and the relatively high number of vehicles provides opportunities for the emergence of vehicle cleaning services or commonly called doorsmeers (Hargianintya et al, 2018). Based on the results of an interview from one of the sources who works in a vehicle washing business in Kuta Raja District, Banda Aceh has 60-70 vehicle consumers every day and this business operates 24 hours.

According to Andina's research (2020), vehicle washing services not only encourage economic growth and increase regional income, but also produce motor vehicle washing water waste which can reduce environmental quality. Vehicle washing services require a lot of water. One four-wheeled vehicle requires around 240-600 liters of pure water. Clean water used in the washing process will become waste which is then released into the environment. Vehicle washing wastewater contains high TSS and COD values. Kusumawardani et al (2019), also added that waste water from washing motor vehicles usually contains sticky dirt (soil/dust), detergent scum (surfactant) and oil from vehicle polish.

The high quantity of vehicle washing waste causes more and more water bodies to be polluted. Therefore, the coagulation and flocculation processes using natural coagulants require treatment to reduce the levels of contaminants analyzed, namely COD, TSS and phosphate levels. According to Putri et al (2015), the coagulation-flocculation process can remove particles that settle easily (colloids), through placing the coagulant into raw water followed by fast stirring (coagulation) and slow stirring (flocculation) causing clumping of the particles. The colloid can then be largely separated in the sedimentation process. Coagulants in the coagulation-flocculation process have the effect of accelerating the formation of larger, stronger and more stable flocs. In this research, chitosan was used as a coagulant where the coagulant came from tilapia fish scales.

Tilapia fish is one of the fish in freshwater waters that is easy to live and reproduces relatively quickly compared to other freshwater fish. Tilapia fish are omnivorous fish. Tilapia fish in their natural habitat live in various freshwater waters such as lakes, reservoirs, estuaries, lakes, ponds and rivers. Maintaining tilapia fish with good quality water, namely water that is not too abundant, not cloudy, not polluted by waste and chemicals and poisons (Fadhylah N, 2019). According to Bija et al, (2021) The use of tilapia fish scale chitosan is carried out through proximate analysis to determine water content, ash content, fat content, protein content and carbohydrate content. A material can be processed into a compound product that is beneficial for human life if the percentage of the chemical components in it is known.

Chitosan can be extracted from fish scales because it contains chitin (Azis et al. 2017). Researchers Ifa et al (2018) said that chitosan generally dissolves in organic acid solvents in the pH range of 4-6.5. Chitin and chitosan are widely used in modern industry. All chitin and chitosan derivatives can be used in industry, agriculture, pharmaceuticals, cosmetic medicine, waste water treatment and biotechnology. Chitosan has an active group that will bind to microbes so that chitosan is also able to inhibit microbial growth. This research aims to determine the value of the best coagulant dose of chitosan mass in reducing COD, TSS and Phosphate pollutants in vehicle washing waste using fish scale chitosan, namely tilapia fish.

Methods

The tools used in this research include a Pyrex beaker, GP-45BE oven, spatula, 18 ONE water bath, Sojikyo electric scale, Pyrex Erlenmeyer, OPPO A39 stopwatch, Pyrex measuring cup, HI 9813 Multiparameter thermometer -5, Pyrex measuring flask, Daihan Scientific magnetic stirrer, cup, Panasonic blender type MX-GX1061, Prestige-21 FTIR IR spectrophotometer, Messgerate model S6S test jar, Patraproduk 100 mesh sieve, 18 ONE brand jerry can and furnace .

The materials that will be used in this research include 3 kg of tilapia (*Oreochromis* mossambicus) fish scales, 500 mL of motor vehicle washing waste. Aquades, $MnSO_4$ 1 mL, alkali iodide 1 mL, H_2SO_4 1 mL, ($Na_2S_2O_3$) 0.023 N, $MnSO_4$ 1 mL, mixed solution of $K_2Cr_2O_7$ – H_2SO_4 1.5 mL, mixed solution of Ag_2SO_4 – H_2SO_4 3.5 mL, HCl 1 N, H_2SO_4 1 N, CH_3Cl_3 1 N NaOH 1 N and CH_3COOH 1%.

The scale cleaning process refers to research by Bija et al (2020), the scale cleaning process can be done by preparing 3 kg of tilapia fish scales each, then washing the fish scales until clean, then drying the fish scales in the sun, after that they are smoothed and sifted using a 100 mesh sieve.

The deproteination process refers to research by Bija et al (2020), in this process the fish scales are first washed and then dried under the sun for 24 hours. Then grind the dried fish scales using a blender until they become powder. Then the powder is weighed and put into an Erlenmeyer. Then 2% NaOH solution was added with a ratio of solid: solvent = 1:10. Then heated and stirred using a magnetic stirrer for 1 hour at a temperature of 60^oC – 70^oC. Then filtered using filter paper until a precipitate is obtained.

The demineralization process refers to research by Bija et al (2020), the sediment resulting from deproteination is mixed with distilled water until the pH is neutral. After that it is dried. Then the dried sediment was put into an Erlenmeyer. Then 1 N HCl solution was added with a solid:solvent ratio = 1:10 for 2 hours at room temperature. Then filtered using filter paper until a precipitate is obtained.

Degree of Deacetylation In this degree of deacetylation process referring to research by Bija et al (2020), the precipitate resulting from demineralization is mixed with distilled water until the pH is neutral. Then dried until chitin is obtained.

After that, the chitin was put into an Erlenmeyer, then 50% NaOH solution was added. The mixture of chitin and NaOH solution was heated at 121^{o}C for 1 hour with a solid: solvent ratio = 1:10 so that the result was slurry and filtered. Then the precipitate was washed with distilled water and then neutralized using HCl solution. After that, it is dried until chitosan is formed. Next, the chitosan obtained was analyzed using the FTIR spectrophotometer method to determine the Degree of Deacetylation (DD). To determine DD, the line method by Moore and Robert is used, as shown in equation (1). The samples were pelleted in KBr powder and then the spectrum was determined (Hanafi et al, 1999).

$$\% \text{ DD} = 1 - \left(\frac{A1655}{A4350} \text{ x } \frac{1}{1,33} \right) \text{x } 100\ \%$$

Information :

A : log (PO/P) = absorbance

A1588 : Absorbance at a wavelength of 1588 cm-1 for group absorption amide/acetamide (CH_3CONH^-)

A3410 : Absorbance at a wavelength of 3410 cm-1 for group absorption hydroxyl (OH^-)

Results and Discussion

The yield produced in each process experienced a decrease in the weight of the initial raw material which was thought to be influenced by the chitosan manufacturing process itself. Chitosan is a product that goes through a deproteination, demineralization and deacetylation process so that many mineral components or other organic materials and proteins in the raw material for tilapia fish scales are dissolved in HCl and NaOH solutions and result in a lower final weight of chitosan (Susanti and Ani, 2020) . In this study, the result of the deproteination process after weighing was 14.33 gr. Next, in the demineralization process, the process of removing minerals found in tilapia fish scales such as calcium carbonate ($CaCO_3$) and phosphorus using HCl solvent. When the demineralization process was complete and weighed, the weight was 6.54 g. The final stage in obtaining chitosan is the deacetylation process. In this process, the acetyl group in chitin will be removed to become an amine group. The gradual chitin deacetylation process had no effect on the yield of chitosan. According to Nadia et al (2014), the high and low yield of chitosan obtained is influenced by the length of the reaction process and the reaction temperature. Making a chitosan solution to be used as a coagulant refers to Bija et al (2020), 1.8 grams of chitosan in 100 mL CH_3COOH. The results of the FTIR test for fish scale chitosan can be seen in Figure 1.

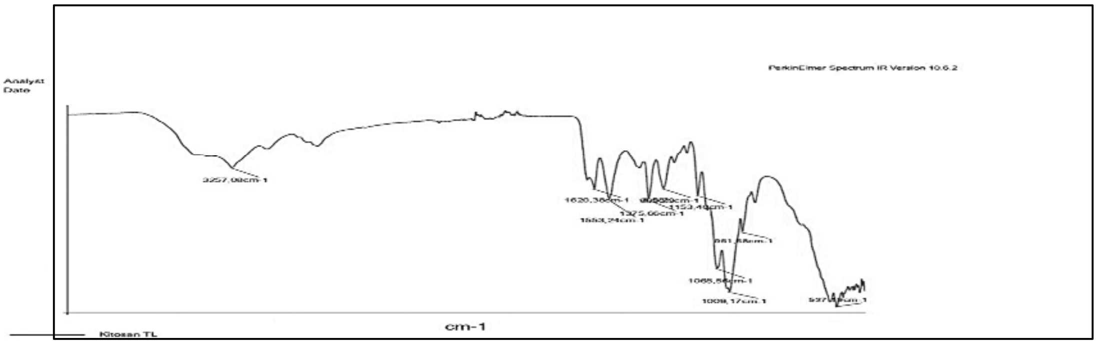

Figure 1.FTIR results from tilapia fish scales

The chitosan that has been formed is identified using FTIR to examine the functional groups on the chitosan and calculate the degree of deacetylation (DD) of the chitosan. The DD results will show that the acetyl group can be removed from chitin which will produce chitosan. The less acetyl groups in chitosan, the stronger the interaction between ions and hydrogen bonds of chitosan. In this study, the deacetylation degree of 75% was found. According to Rahayu and Purnavita (2007), the degree of deacetylation for chitosan in general is around 60-100% for chitosan that undergoes complete deacetylation.

A 500 mL wastewater sample with a mass variation of 10 mg/L chitosan biocoagulant was tested using a jar test with rapid stirring at 120 rpm for 30 minutes. Then slow stirring was carried out at a speed of 90 rpm for 40 minutes. After that, deposition was carried out for 30 minutes. Then do the same thing for varying doses of 20 mg and 30 mg. After that, measure the Chemical Oxygen Demand (COD), Total Suspended Solid (TSS) and Phosphate samples.

The measurement data only represents the water quality at the time of collection and at the point of collection. Therefore, water collection using the grab sampling technique is aimed at water bodies whose quality is relatively stable against seasonal changes and changes in the water body. The results of initial testing of parameters before processing can be seen in Table 1.

Table 1. Initial Test Results

No	Parameter	Unit	Quality standards	Analysis results
1	COD	mg/L	180	129.86
2	TSS	mg/L	60	142.86
3	Phosphate	mg/L	2	1.136

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The test results of vehicle washing wastewater before the processing process in Table 1 show that the COD and Phosphate parameters meet the established quality standards. From the initial test results, only TSS exceeded the established quality standards. This is due to the presence of residue from the vehicle washing process so that what experiences significant changes is the TSS level. After carrying out the initial testing, there were factors that did not meet the quality standards of Regulation of the Minister of the Environment of the Republic of Indonesia Number 5 of 2014 concerning Waste Water Quality Standards for Soap, Detergent and Vegetable Oil Products Industrial Businesses and/or Activities, namely TSS. However, COD and Phosphate concentrations will also be treated because if vehicle washing waste water is always discharged into water bodies without any processing, it can pollute the environment. Therefore, it is necessary to carry out processing to minimize the concentration of waste content by using chitosan from tilapia fish scale waste as an adsorbent medium. After each processing has been carried out, it is continued by measuring the reduction results obtained after processing vehicle washing wastewater using tilapia fish scale chitosan, which can be seen in Table 2.

Table 2. Yield Reduction After Processing

Chitosan Mass (mg/L)	rpm	COD (mg/L)	TSS (mg/L)	Phosphate (mg/L)
Quality standards		180	60	2
Before Processing		129,86	142,86	1.136
After Processing				
10	120/90	68,25	73	20,90
20	120/90	24,48	40	18,62
30	120/90	49,97	17	8,32

Each additional dose of coagulant must also be at the optimum limit in order to reduce the parameters to the maximum. Yuniarita et al, (2022) stated that excessive increase in chitosan will maintain the stability of pollutant deposits and reduce flocculation efficiency. This is due to the additional load of organic material in the wastewater. The changes that occur after processing vehicle washing wastewater can be seen in Figure 2.

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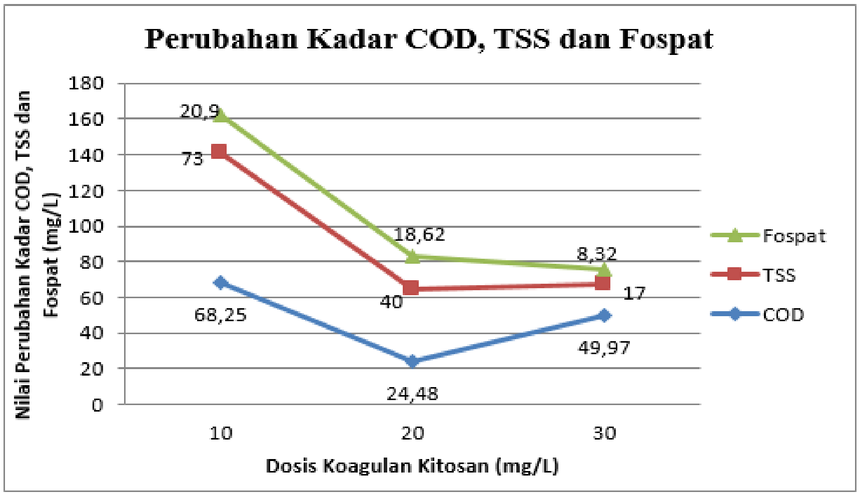

Figure 2. Graph of Changes in COD, TSS and Phosphate Levels

The effect of adding a dose of chitosan coagulant on reducing COD (Chemical Oxygen Demand) levels was obtained from the results of laboratory analysis of samples before treatment and samples after treatment with the addition of chitosan coagulant which can be seen from Table 3.

Table 3. Results of Reducing COD Levels

Chitosan Mass (mg/L)	QualityStandard (mg/L)	Before Procescing (mg/L)	After Processing (mg/L)
10	180	129,76	68,25
20			24,48
30			49,97

A graph of the results of decreasing COD levels after processing can be seen in Figure 3 below:

The effect of adding a dose of chitosan coagulant on reducing TSS (Total Suspended Solid) levels was obtained from the results of laboratory analysis of samples before treatment and samples after treatment with the addition of chitosan coagulant which can be seen from Table 4 and Figure 4.

According to Yuniarita et al (2022), fish scale chitosan coagulant is effective in reducing TSS concentrations. If a coagulant dose has exceeded its optimum limit, then in the ion binding process there will be an excess of positive charge contained in the biocoagulant. In terms of TSS parameters, a low coagulant dose will also result in a low decrease in TSS concentration. On the other hand, if the dose given is correct, it will provide maximum results in reducing TSS concentrations. Another factor that influences the flocculation coagulation process is the stirring speed. The optimal stirring speed will also influence the physical properties of the particles that cause TSS. The size of the TSS in waste water is influenced by vehicle contaminants that are carried in the water when the vehicle washing process is carried out, the more vehicle contaminants there are, the higher the TSS, this of course will also affect the color of the waste water, because TSS is proportional to color (Hadiwidodo, 2008).

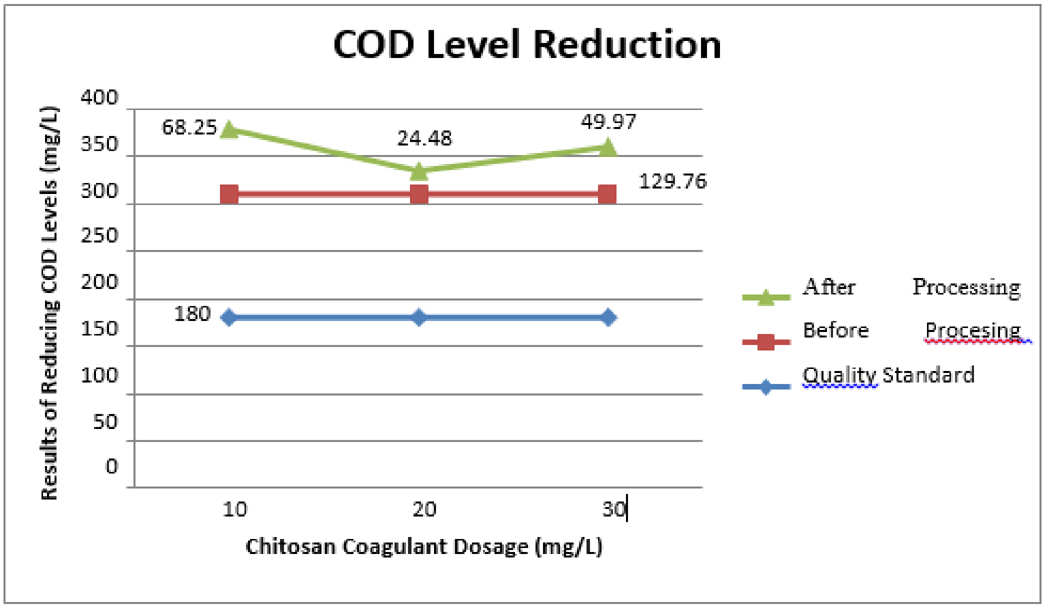

Figure 3. Graph of Changes in COD Level

Table 4. Processing Results of Adding Chitosan Coagulant

Chitosan Massa (mg/L)	Quality Standards (mg/L)	Before Treatment (mg/L)	After Treatment (mg/L)
10	60	142,86	73
20			40
30			17

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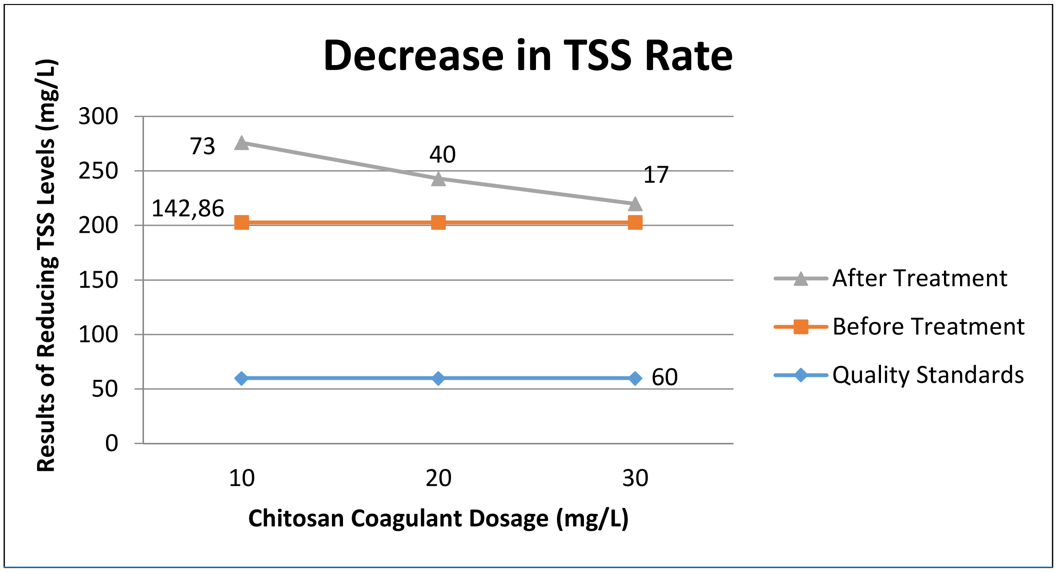

Figure 4. Results of Reducing TSS Levels

According to Mutakhabbibatillah et al (2022), chitosan coagulant is also able to reduce the TSS value because chitosan contains positively charged amino groups so that chitosan is polycationic and the positive charge on the chitosan coagulant binds to the negative charge on the colloid, so that it forms flocculent particles. The active groups in chitosan come from the nitrogen atom in the amine group (NH_2) and the oxygen atom in the hydroxyl group (-OH) which has free electrons that are able to bond with protons or metal ions, forming a complex. There is the presence of hydrogen interactions which result in chitosan being able to dissolve in organic waste and having a higher ability to bind with proteins from the waste. In this way, TSS levels in vehicle washing wastewater can be reduced.

The effect of adding a dose of chitosan coagulant on reducing phosphate levels was obtained from the results of laboratory analysis of samples before treatment and samples after treatment with the addition of chitosan coagulant which can be seen from Table 5 and Figure 5.

Table 5. Results of Increased Phosphate Levels

Chitosan Coagulant Dosage (mg/L)			After Processing (mg/L)
10			20.90
20	2	1,136	18.62
30			8.32

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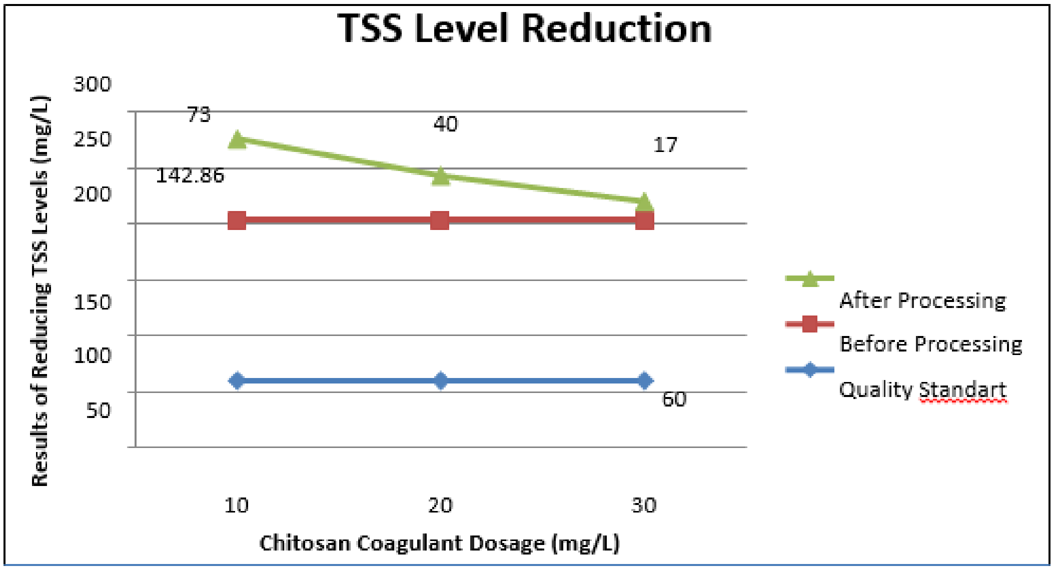

Figure 5. Graph of Results of Increasing Phosphate Levels

It can be seen from the graph above that the increase in phosphate levels in the processing of motor vehicle washing waste is very significant. This is because a coagulant dose that has exceeded its optimum limit will experience a decrease in concentration. However, what happens to the Phosphate parameter is that the dose given has not reached its optimum limit. If continued to a higher dose it is possible to reduce the Phosphate concentration. According to Bija et al (2020), another factor that also influences is the low dose of chitosan used. Providing the correct coagulant dosage in wastewater treatment can affect the reduction in phosphate values.

The phosphate level at each coagulant dose received a high phosphate value. The phosphate concentration in washing wastewater can be influenced by temperature during the adsorption process. The higher the temperature, the greater the phosphate concentration, conversely, the lower the temperature, the lower the phosphate concentration. This is caused by the slowing of the adsorption rate as the temperature increases. According to Syauqiyah et al (2020), adsorption is an exothermic reaction, therefore the level of adsorption generally increases as the temperature decreases. In general, increasing temperature causes a reduction in adsorption capacity (Jannatin, 2016).

Adsorbant molecules have greater energy than the adsorbent, causing the adsorbant energy to escape from the surface, so that the adsorption capacity decreases. The higher the pH, the greater the phosphate concentration and vice versa. The alkaline pH in wastewater is caused by polyphosphate in detergents and NaOH. The highest concentration of phosphate absorption will occur when the water pH is the highest or alkaline. Alkaline solutions can adsorb anions through the ion exchange process. According to Ristiana et al (2009), absorption of phosphate concentrations depends on high pH. The adsorbent functional group tends to be positively charged at high pH so it tends to accept phosphate ions resulting in increased phosphate absorption.

Conclusion

The best dose variation for reducing COD parameters is using a dose of 20 mg/L then the best mass for reducing TSS parameters is using a dose of 30 mg/L. The effectiveness of reducing COD levels was 81.53% and then reducing TSS levels was 88.11%. Meanwhile, the Phosphate parameter after processing experienced a very significant increase. The increase and decrease in COD, TSS and Phosphate levels were influenced by chitosan doses that had not reached the optimum limit and were also influenced by fast and slow stirring.

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