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Research paper

The effectiveness of cement lime to reduce detergents content in domestic wastewater

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Abstract

The content of detergent in the domestic wastewater which is disposed directly to the river has been cause inhibition in transfer of oxygen mass into water. The Ca ions can be used to reduce activity of detergent in the domestic wastewater. The Ca ions will bind Na ions and phosphate compound in the detergent through precipitation reactions. The granular media from cement lime was used as filter media to release of Ca ions. The aims of the research were to find the composition of cement lime which is capable to release Ca ion which capable to reduce detergent activity. Jar test experiments have been conducted to find the optimum composition of lime cement media in reducing detergent concentration in domestic wastewater, the composition of lime cement with a ratio of 1:1 to 6:1. Furthermore, the optimum composition of lime cement medium was used as a filter medium to treat domestic wastewater. The filter is operated with a continuous flow. The result showed that the composition of lime - cement media 6:1 was able to reduce detergent concentration up to 88.65 % with initial concentration 122.6 mg/L.

Keywords: *Ca Ions; Cement; Detergent; Lime; MBAS; Na Ions.*

1. Introduction

Water is essential for socio-economic development and for maintaining healthy ecosystem. As population increases and development calls for increased allocations of groundwater and surface water for the domestic, agriculture and industrial sectors, the pressure on water resources intensifies, leading to tension, conflict among users and excessive pressure on the environment. In general, the enhancement of detergent in the domestic wastewater will increase the concentration of COD and BOD [1]. Disposal of domestic wastewater directly to the environment has destroyed the ecosystem of rivers and lake. Due to the detergent compound has inhibited oxygen transfer from the air to the water. Generally, the content of detergent compound in the domestic wastewater is not easy to remove. Many methods have been developed to reduce detergent content in wastewater. In general, detergent compound consists of NaDBS (Sodium Dodecyl benzene sulfonate) and STP (Sodium Tripoli Phosphate).

Detergents are synthetic cleaning media consisting of compounds that are capable of releasing dirt, oil, and killing useful bacteria. Detergent solutions contain the main ingredients of Surface Active Agent (surfactants), builders, fillers and additives. The builder functions to increase the efficiency of the washers from surfactants by deactivating minerals that cause water hardness. Four categories of builders are Sodium Tripoli Phosphate (STPP), nitrile tri acetate (NTA) & ethylene diamine tetra acetate (EDTA), zeolite and citrate acid. Sodium citrate was utilized as a builder, but it has some disadvantages [2], [3]. It is considerably more expensive than STPP (twice as much at that time) and does not perform as well in removing calcium and magnesium ions. This lower performance is least marked at very low temperatures.

Nitrile tri acetate (NTA) & ethylene diamine tetra acetate (EDTA), Both of these chemicals are effective at abstracting calcium and magnesium ions and NTA in particular can largely replace STPP as a builder. However, it does not buffer as strongly as STPP and is less effective as a particle disperser. The main problems with NTA are that there has been some evidence that it is carcinogenic and its great strength in combining with metal ions has caused fears that heavy metals in sewage sludge may be taken up and hence mobilized [2], [4]. This could then result in peak concentrations of heavy metals in rivers and lakes being above regulated level [2], [5] argue that this latter risk is not significant, but these environmental concerns have resulted in both EDTA and NTA being excluded.

The effect caused by detergent in water is the formation of a film layer that can interfere with the transfer of oxygen into the water [6]. In addition, other influences that occur include the presence of white foam on the surface of the water, physical and chemical changes, and the occurrence of eutrophication. The higher the detergent content in the waters, the lower the level of oxygen supply in the waters. This will affect the process of respiration in aquatic biota [7].

Surfactants have a function to reduce the surface tension of the water so that it can release dirt that attaches to the surface of the material [8]. This occurs because of the different properties between the constructing group of surfactants, namely the hydrophobic group and the hydrophilic group [6]. Hydrophobic has non-polar properties that cannot dissolve in water, oil, and fat. The hydrophobic function is binding to impurities. Hydrophilic has polar properties that can dissolve in water, reducing surface tension between impurities and the material to be cleaned.

The classification of surfactants based on their hydrophilic structure is 4 types. Anionic surfactant, the hydrophilic group has a negative charge. This type of surfactant is the most commercial surfactant, because the price is cheap and the net power is good. Examples of anionic surfactants are ABS (Alkyl Benzene Sulfonate), DBS (Dodecyl Benzene Sulfonate). ABS is the type most often used because it has good clean power and is relatively not affected by hardness [3], [6]. But ABS has the disadvantage of being difficult to degrade by microorganisms in the waters. Cationic surfactant, the hydrophilic group has a positive charge. This type of surfactant is often used as a disinfectant in hospitals. For example, trimethyl ammonium chloride [9]. Nonionic surfactant, the hydrophilic group has no charge. An example for nonionic surfactant is Alcohol Ethoxylates. Amphoteric surfactant, the hydrophyte group can be negatively or positively charged where the charge depends on PH. If PH is high, it is negatively charged and if the low pH is positively charged [10]. An example is Alkyl betaines.

According to the research of Kurniati (2009), the element $Ca(OH)_2$ is an alkaline earth class when reacting with HDBS (Hydrogen Dodecyl Benzene Sulfonate). HDBS is one type of anionic surfactant that is most often used by detergent producers because of its lower cost and good clean power [6], [11]. The chalk mechanism when binding to surfactants will form salt deposits (DBS). The reaction is presented as follows:

$$2HDBS + Ca(OH)_2 \rightarrow Ca(DBS)_2 + 2H_2O \quad (1)$$

Equation 1 can be explained, a water sample added by $Ca(OH)_2$ in the form of powder will experience a decrease in surfactant because DBS ions bind to metal ions Ca^+ by forming salt deposits. Anion Ca $(OH)_2$ binds to cations of HDBS compounds to form $2H_2O$. However, the addition of excessive Ca $(OH)_2$ will result in a poor reduction in surfactant concentration. Detergent compounds can be removed through the precipitation process using Calcium ion. Research by Sumarno et al., 1996, showed that 5 mg/L Ca^{2+} ions were able to precipitate detergent concentrations in the wastewater [12]. Izidin (2001), in his paper stated that precipitation techniques using $Ca(OH)_2$ solution was able to reduce the concentration of detergent up to 75.5% [13]. Precipitation of detergent using CaO powder generally was carried out by coagulation-flocculation method and followed sedimentation or filtering process. This process is not easy doing by civilians or laundry entrepreneurs. Therefore, it is necessary to search an appropriate technology which simple in operation.

The filtration process with grained media containing Ca elements feasible to develop as appropriate technology. Artificial granular media from lime-cement mixture is predicted be able to bind Na-DBS and STTP compounds in precipitate form. The purpose of this research is to find the composition of lime-cement that able to release ion Ca, and binding detergent compound in the domestic wastewater. The performance of artificial media will be tested as filter media for reducing the content of detergent compound in the domestic wastewater.

2. Materials and method

The research was carried out on a laboratory scale with a batch and continuous process. Research started by making the material of lime - cement mixture with ratio of lime: cement (1- 6):1. The aggregate of lime-cement molded in cubical form with dimension (1 x 1 x 1) Cm. The best lime-cement composition, was selected by salting test reaction in batch process using Jar test apparatus. The Jar test experiment was carried out with the same weight of media and wastewater volume. The media with the higher ability in reduction of detergent compounds will be selected as an artificial media for domestic wastewater treatment. This first experiment will be using wastewater from laundry activities and wastewater from the drainage. Wastewater from laundry activities was selected to represent water with high detergent content. The result from the first experiment will be analyzed to determine the best composition of lime - cement media. Selected media will be used in the second experiment as a media filter. The filter will be operated continuously with the variable of contact time i.e. 6, 7 and 8 hours. Material of artificial media consist of lime powder and Portland cement. Jar Test equipment used to determine the best composition of artificial media. Plexiglas tube was used for filter column. The unit filtration consists of filter column and selected artificial media.

2.1. Experiment for determination lime - cement ratio that can reduce detergent

The making of lime-cement media was carried out using lime powder (CaO) and Portland cement. Determination of lime and cement requirements based on ratio by weight ratio. The desired total mixture of lime and cement for this preliminary test is 100 grams, so the need for lime and cement in each ratio is as follows:

- For 1:1, 50 grams of lime and 50 grams of cement are needed
- For 2:1, 66.67 grams of lime and 33.33 grams of cement are needed
- For 3:1, 75 grams of lime and 25 grams of cement are needed
- For 4:1, 80 grams of lime and 20 grams of cement are needed
- For 5:1, 83.33 grams of lime and 16.67 grams of cement are needed
- For 6:1, 85.7 grams of lime and 14.3 grams of cement are needed

Performance of artificial media was tested using Jar Test method. Jar Test was operated for media with different ratio of lime - cement, and same volume of wastewater. Experiments were carried out with variations in speed and specific mixing times. Mixing speed is used for determining the gradient value in the coagulation - flocculation process to form precipitate of CaDBS. During the experiment, the concentrations of Detergent, COD, TSS before and after the experiment were measured for evaluating of the cement-lime media performance. The results of Jar Test experiment were controlled using similar wastewater without additional of artificial media.

Wastewater which contain surfactant is prepared in 6 beaker glass with volumes 1 L. Artificial media with different compositions, and the same weight added to the glass beaker containing waste water and then slowly stirring. Stirring speed arranged using a paddle rotation at 30-40 RPM for 2 hours. Furthermore, sample of wastewater taken every 30 minutes to be analyzed the reduction of surfactant concentration. The measurement results of changes in surfactant concentration were analyzed use of graph method [14][15] to determine the best lime-cement composition. The composition of lime - cement selected which results in the greatest decrease in the concentration of surfactant.

2.2. Design and operation of filtration

The filter operation was operated under a continuous system. The process to be used was adsorption, where the lime-cement media acts as an adsorbent [16]. This process is related to Ca^{2+} release ions and binds to HDBS-ions. In addition to media variations, discharge variations were used in this study. Calculation of debit can be seen in Table 1.

Table 1: Aerobic Filter Design Criteria [17]

Parameters	Unit	Value
OLR	COD/m^3.days	< 5-6
HLR	m^3/m^2.hours	< 2
td	hours	6-10

The variation of discharge that enters the filter was calculated to plan variations in residence time according to design criteria (6-10) hours. The discharge entering the filter calculation was planned that the filter dimensions are 15 x 15 cm and the filter height is 65 cm. Then the filter volume is 0,0146 m3.

- Reactor 1 with td = 6 hours,

  Q = V / td = 0.0146 m3/6 hours = 6.75 x 10-7 m3/s hours = 40.6 mL/minutes

- Reactor 2 with td = 7 hours,

  Q = V / td = 0.0146 m3/7 hours = 5.80 x 10-7 m3/hours = 34.8 mL/minutes

- Reactor 3 with td = 8 hours,

  Q = V / td = 0.0146 m3 / 8 hours = 5.06 x 10-7 m3/hours = 30.4 mL/minutes

Variation of discharge was carried out to determine the ability of the media to reduce surfactant during the specified time. Fig. 1 is a filter sketch used in the main research. The pump head used is 3 meters.

2.3. Testing of lime - cement granular as filter media

The cement-lime aggregate with a certain composition, then tested its characteristics and performance as a provider of Ca ions. Filter was operated using flows of wastewater continuously and then samples taken periodically for measuring of detergent concentration. Monitoring was done at some time to measure changes in the concentration of detergents, COD, TSS and to observe the change of media physically. The results of measurements of changes in detergent concentration, COD, TSS were analyzed to evaluate the feasibility of cement-lime aggregates as a filter media for detergent reduction in domestic wastewater.

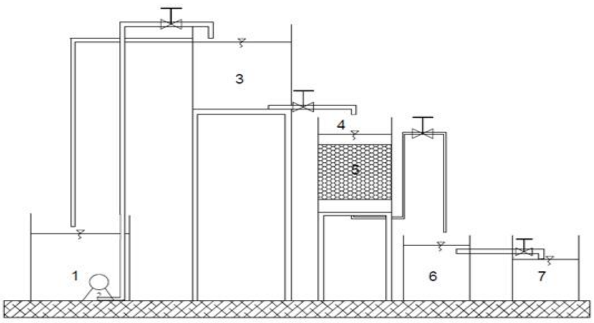

Fig. 1: Filter Sketch.

Where:
1) Holding Tank
2) Submersible pump
3) Influent Tank
4) Filter Tank
5) lime-cement filter media
6) Sedimentation Tank
7) Effluent Tank

3. Results and discussion

Raw influent (untreated laundry rinsing water) parameters such as COD, BOD, pH, TSS, anionic active surfactant (as Methylene Blue Active Substances) was analyzed in the laboratory and are shown in Table 2. Based on Table 2, the measurement results show that the concentration of detergent is very high, beyond the content of detergent in domestic wastewater in general.

Table 2: Characteristic of Laundry Wastewater

Parameter	Concentration (mg/L) Sample 1	Sample 2
Detergent as MBAS (mg/L)	140.56	199.62
COD (mg/L)	1570	1600
BOD (mg/L)	660	675
TSS (mg/L)	460	220
pH	7.08	7.1

3.1. Determination of the best composition of lime - cement media

The optimum of composition lime - cement media was determined by making mixed material with a ratio of lime - cement i.e. 1:1, 2:1, 3:1, 4:1, 5:1, and 6:1. The results of an artificial media to decrease concentration of detergent showed in Table 3 and Fig. 2.

Table 3: Concentration of Effluent Detergent for Ratio of Lime Cement Variation

Contact time (minutes)	Detergent concentrations at influents (mg/L)	Ratio of lime : cement 1:1	2:1	3:1	4:1	5:1	6:1
		Effluent Concentration (mg/L)					
30	199.62	195.29	192.34	193.33	190.40	183.87	126.04
60		188.21	184.24	182.03	177.40	173.20	78.84
90		157.69	153.49	148.46	145.10	128.33	54.94
120		138.49	130.85	114.07	101.91	95.62	22.65

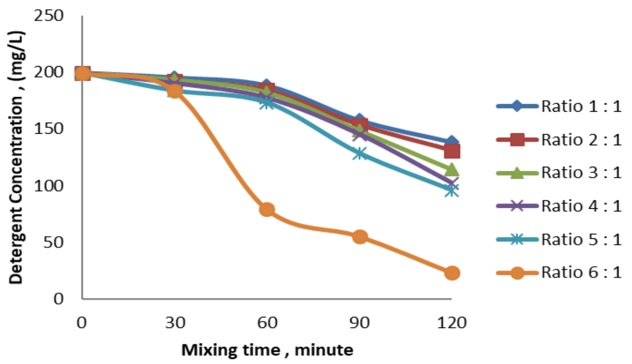

Fig. 2: Results Test the Media of Lime: Cement in Decrease Detergent Concentration.

Data in Table 3 was obtained from Jar Test experiment and at every 30 minutes' samples took to be analyzed the change of its detergent concentration. Detergent concentration in the sample was analyzed after settled for 30 minutes. This settling time for reduction of CaDBS was done follow results of research by Kurniati (2009). Fig. 2 shows that all media with variety ratio of lime - cement was able to reduce the concentration of detergent. The test results show that the stirring time has an effect on decreasing the concentration of detergent. Results shows that longer the contact time the greater the decrease in concentration of detergent.
Based on Fig. 2, ratio of 1:1 can reduce surfactant concentrations up to 30.62%, a ratio of 2:1 can reduce surfactant concentrations to 34.45%, ratio of 3:1 can reduce surfactant concentrations up to 42.85%, ratio of 4:1 can decreasing surfactant concentration up to 48.94%, ratio of 5:1 can reduce surfactant concentrations up to 52.10%, ratio of 6:1 can reduce surfactant concentrations to 88.65%.
Fig. 2 was also explaining that the higher the lime content in the media, the greater ability to decrease detergent's. As explained earlier that the function of cement in the formation of artificial media aggregates as a binder of lime powder, so the lower the cement content in the media, media will more easy to release Ca ion. Media with a lime-cement ratio of 6:1, results in a decrease in the concentration of the largest detergent. It showed that ratio of

lime - cement 6:1 was easy released Ca ions into the water and then occur detergent binding reactions to form Ca-DBS precipitates. At this ratio, the cement content contributes quite well as a binder, which is demonstrated by violence from the media.

3.2. Change of the pH water from the Batch process experiment

The release of Ca ions, during experiment has caused a change in pH water. Changes in pH of the water after the stirring process indicate that the media of cement lime affected the speed of pH increase. The results of measuring pH changes are explained using the graph in Fig. 3.

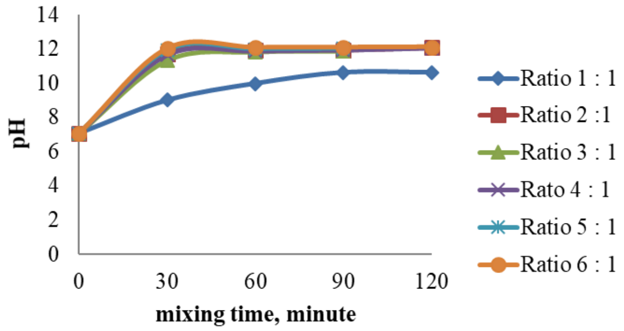

Fig. 3: Trend of Changes in PH at Various Lime: Cement Ratios.

At stirring for 30 minutes, the pH of water has increased sharply for all lime: cement ratios. Furthermore, the increase occurs gradually, this shows that the release of Ca ions occurs instantly from the beginning of stirring to 30 minutes. The cement bond has an effect on the release of Ca ions. In cement lime material with a ratio of 1:1, the increase in pH is relatively low compared to materials that have higher lime content. The highest pH value achieved by the media with a ratio of 1:1, after stirring for 120 minutes, reaches its maximum point at pH 10.64. Fig. 2 also explains the increasing pH gradually. For the ratio of cement lime 2:1 to 6:1, the increase of pH value after stirring for 60 minutes, is relatively almost the same. The increase in pH is relatively constant after stirring 60 minutes, it can also be estimated that the concentration of Ca has reached the point of saturation.

3.3. The performance of filter with cement lime media

Research on the performance of media filters is carried out in 2 (two) stages. The first stage, the filter was tested using original wastewater from laundry activities and the second stage, the filter was operated using laundry waste water that diluted use tap water. This is intended to obtain detergent concentration nearing the quality of domestic wastewater at river water or drainage. Research on the performance of cement lime media filters was carried out by monitoring changing detergent concentrations at influents and effluents of the filter. Monitoring is carried out by taking samples of wastewater after it is estimated that the process is in a steady state condition.

The Filter was operated with continuous flow at contact time of 6, 7 and 8 hours. The results on COD reduction using of lime - cement filters are described in Fig. 4. Decreasing detergent concentration in wastewater will be followed by a decrease in COD concentration, where a decrease in COD concentration indicates a decrease in organic compounds in wastewater. Decreasing the concentration of detergent in wastewater will be followed by a decrease in COD concentration, where a decrease in COD concentration indicates that there has been a decrease in organic compounds in wastewater [18]. Detergents, which contain organic compounds in the structure of DBS (Dodecyl Benzene Sulfonate). The results of the study of COD reduction in cement lime filters are described in Fig. 4. Decreasing the COD concentration of wastewater in the filtration process is very large. The amount of COD reduction is 63% with td 6 hours, 80% with td 7 hours, and 81% with td operating 8 hours. The increase in COD reduction percentage is in line with the large decrease in detergent concentration. The greater the decrease in detergent concentration, the COD of wastewater will also decrease with a significant amount. Research on the performance of cement lime media filters at the second stage using laundry wastewater which diluted. Dilution is carried out as much as 10 times intended to obtain detergent concentration close to the quality of domestic wastewater in general. The quality of wastewater after dilution is presented in Table 4.

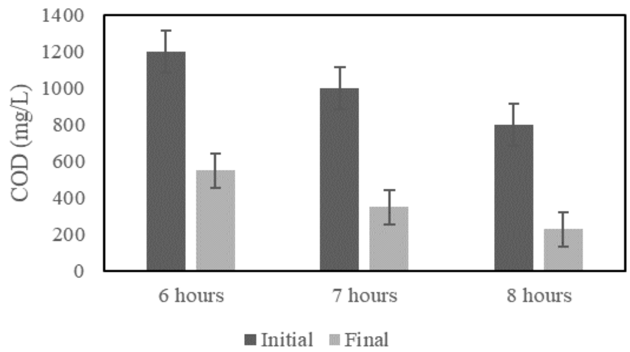

Fig. 4: Decreasing (COD) on Lime-Cement Media Filters.

Table 4: Characteristic of Wastewater Before and After Dilution

Parameter	Before dilution	10 times dilution
pH	7.7	7.6
TSS (mg/L)	460	60
COD (mg/L)	1570	200
BOD (mg/L)	660	84
Detergent (mg MBAS/L)	140.58	17.78

Performance test of cement lime media filter with selected media composition, with diluted wastewater carried out with 8 hours contact time. Waste water is flowed continuously, sampling effluent water filter is done on day 2. Taking on day 2, it is intended that the contact time for 8 hours has been exceeded and the effluent quality is estimated to have reached a steady state. Furthermore, sampling was carried out every 10 minutes for 120 minutes, to see the stability of the effluent quality of the cement lime media filter. The research data is shown in Table 5. The results of filtration using the diluted wastewater, with monitoring time every 10 minutes for 120 minutes, obtained an average value of 3.5425 ± 0.234. The concentration of detergent in the filter effluent was relatively stable with a deviation of 0.234 mg / L or 6.62%. The average detergent removal was 80.1%, it was not much different from the study using origin wastewater, where detergent reduction reached 81%.

Table 5: Results of Filtration Using Diluted Wastewater

Sampling time (minute)	Detergent (mg MBAS/L)
0	17.78
10	3.69
20	3.47
30	3.25
40	3.62
50	3.48
60	3.56
70	3.26
80	3.89
90	3.9
100	3.69
110	3.52
120	3.18
Average	3.5425
Std Deviation	0.234

Furthermore, filtration was continued for 5 working days, by taking samples every 1 hour to test the performance stability of the filter. In this study, the parameters measured included the final pH value, reduction in TSS, COD and detergent as MBAS. The results showed that the pH value approaching the pH value in the batch test using the Jar test, averaging pH 12.45 ± 0.02 with a confidence level of 0.17.

Performance evaluation of filtration using diluted wastewater, for five days of measurement and sampling for 7 hours a day, showed detergent reduction ability was quite stable. The average daily detergent concentration in effluents was (3.5 ± 0.25) mg MBAS / L. The average detergent reduction was 80.3% from the initial concentration of 17.78 mg MBAS / L. It can be concluded that the filter performance in detergent reduction is in the range of 80%. The filtration process was able to reduce the COD concentration by 87.5% from the initial concentration of 200 mg / L to (24.91 ± 2.34) mg / L. The reduction in COD in this process is caused more by a decrease of detergent contain in wastewater. Total Suspended Solids (TSS) in wastewater was composed of organic and inorganic compounds. The filtration process has been able to reduce TSS by 79.4% from the initial concentration of 60 mg / L to (12.34 ± 1.13) mg / L. Results of filtration using lime – cement media for 5 days' measurement is shown in Table 6.

Table 6: Results of Filtration Using Lime Cement Media for 5 Days' Measurement

Sampling time (hour)	pH	Detergent (mg MBAS/L)	COD (mg/L)	TSS (mg/L)
0	7.6	17.78	200.0	60
1	12.44	3.60	32.0	14,8
2	12.42	3.52	26.4	12,8
3	12.43	3.63	24.8	12,4
4	12.47	3.69	25.2	11,6
5	12.46	3.51	22.8	11,6
6	12.48	3.34	21.2	11,2
7	12.47	3.18	22.0	12,0
Average	12.45	3.50	24.91	12,34
Std Dev	0.02	0.25	2.34	1,13
% Std Dev	0.17 %	7.20%	9.40%	9,13%
% Total Removal		80.3%	87.5%	79.4%

4. Conclusion

Research shown that the best composition of lime - cement was at ratio of 6:1. The media was able to decrease surfactant up to 88.65%. Application of granular calcium - cement as filter media shows that contact time effect on the reduction of detergent in the wastewater with initial concentration of detergent 122.7 mg MBAS/L. The performance of the cement lime media filter with selected composition shown that the longer of contact time was increase removal of detergent, otherwise the initial concentration of detergent has no effect on filter performance. Filtration operations with initial detergent concentration of 122.7 mg MBAS/L and 17.76 mg MBAS/L resulted similar decreasing of detergent i.e. 80.7 mg MBAS/L and 80.3 mg MBAS/L respectively. The filtration process can reduce COD by 81.3% from the initial concentration of 800 mg/L. The performance of the filter is able to reduce the initial concentration of detergent, COD and TSS is 80.3%; 87.5% and 79.4%, from the initial concentration of detergent 17.78 mg MBAS/L; 200 mg COD/L and 60 mg TSS/L.

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