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Feasibility Study of COD Reduction in the wastewater of Ethylene Dichloride (EDC) Plant in Bandar Imam Petrochemical Company

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Abstract

Output waste water control according to the standards of the Environmental Protection Agency is one of the most important commitments of industrial units, including the ethylene dichloride plant of Bandar IMAM Petrochemical Company. In this research, which was carried out from March 2017 to August 2018, we tried to reduce the amount of COD of the effluent as much as possible by increasing the efficiency of the process factors affecting the final result and with the least hardware changes in the existing operating process. For this purpose, at the beginning of the project, the amount of contamination in the existing state was determined by measuring the main parameters of the wastewater (pH, COD, TSS, OIL, EDC). Corrective actions were then carried out based on changes in operating conditions and with existing equipment, and were implemented in different stages.The final result showed that the average amount of COD in the outlet stream from the wastewater treatment system, which at the beginning of the study was 305 mg / L, was reduced to 140 mg / L (54% reduction), the reduction of other parameters was 33% for EDC, 23% for TSS, 25% for wastewater. Also, the PH and OIL parameters also have no effect on the yield and process efficiency. Proposals have been introduced to increase the efficiency of the effluent treatment system, which include setting up the flow of preheater converter into the purification tower (currently out of service).

Keywords

Wastewater Treatment, EDC, COD, Efficiency, TSS, Volume of wastewater

1. Introduction

Today, the disposal of residual wastewater from industrial processes is one of the most important problems in the world [1], which is not just for industrialized countries, but more for developing countries. The problem is more acute in these countries because they are often importers of industrial technology without having access to the technology of management and treatment of waste in that industry. Most industries are established near water sources due to the high need for water, and of course the wastewater from water consumption will be returned to that water source [2]. Sewage and wastewater from industries discharged into sewers and surface water contain many pollutants. Thus, large amounts of pollution enter the environment. Therefore, it is necessary to identify and evaluate different types of pollutants in them, provide suitable solutions for treatment or to reduce and eliminate pollutants, and this action must be performed before their discharging to surface water [3]. According to the standards of the Environmental Protection Organization, controlling the wastewater is one of the most important obligations of industrial units. In order to protect the environment and its legal and social obligations, Bandar Imam Petrochemical Company is building a central treatment plant to control the wastewater from the company within the rules and standards of the Environmental Protection Organization. Each of the production units will have a share in the production of wastewater (quantitative-qualitative) entering the treatment plant. Since the design of the treatment plant is based on the biological method, and the input to the treatment plant is specified for each of the main parameters of the wastewater (COD-TSS-OIL-PH), it is necessary to control the wastewater from each of the operating units and pre-treatment operations should be performed on the outflow. Ethylene dichloride unit is considered as one of the units with special importance in terms of the quality of wastewater. Chemicals 1,2-dichloroethaneor ethylene dichloride (EDC) are among the chemicals produced in the petrochemical industry. This material has major uses in industry including the production of polyvinyl chloride. As a product of the petrochemical industry, Ethylene D has dangerous environmental and health effects on animals and on the central nervous system (CNS) in humans. These effects include a decrease in information processing speed, flexibility, coordination speed and speech memory, and an adverse effect on visual ability [4]. The wastewater of this unit contains 1,2-dichloroethane, water and FeCL3 particles. Due to the fact that the contents of the wastewater can affect the final efficiency of treatment in terms of COD concentration, taking remedial measures is essential for improving the situation within the design of the central treatment plant to control the existing situation. So far, various methods such as the use of biological and membrane methods have been investigated [2]. However, these methods are mostly at the end of the process and sometimes “costly” or there are no required resources to implement them. Therefore, it is essential to choose a method or a set of methods which can meet the current situation in terms of equipment, have compatible facilities and its operations can be controlled and have high reliability. In the present study, the factors affecting the amount of COD in the wastewater were investigated, along with the strategies to increase the efficiency of the wastewater treatment system by improving the performance of equipment and manpower with minimal economic costs.

2. Materials and method

In order to get acquainted with the production line, performance of equipment, and status of factory wastewaters based on design conditions, as well as determining the type of required tests, points and number of samples for analysis, and analyzing the documents related to the subject, the items were reviewed. Description of the plant process such as investigating the production line, performance of equipment, relation of processes, wastewater treatment system, operational parameters affecting the project Operational reports such as a review of changes in operational parameters such as pressure, temperature, flow, and concentration Operational plans such as checking the values of operational and environmental parameters in the design and normal condition of the factory Environmental reports such as a review of reported problems and main challenges Results of measurements such as checking the current status of wastewater outflows and inlets including COD, TSS, OIL, PH . Previous actions and research such as reviewing articles and reports related to the topic and using their results to help how to choose the path and avoid repetitive activities or special attention to important issues. In order to determine the characteristics and values of the parameters as well as evaluating the performance of equipment affecting the wastewater of the plant in real conditions, the items such as the efficiency of the treatment system by measuring COD and EDC in the inflow and outflow to the wastewater treatment system, the volume of wastewaters separately both in normal and emergency situations, and the performance of process by monitoring operational parameters such as temperature, concentration, and flow were considered for evalaution. Sampling was performed according to the sample analysis instructions of Kimia Petrochemical Company of Bandar Imam, number KM-WI-1001. First, the safety equipment including a cape, plastic gloves and glasses were worn and then a glass bottle with a capacity of 250 ml was prepared. For sampling from designated sites, the outlet valve of the sampling site was opened and let the remaining material leave the tube and fresh material to enter the tube after one minute. Then, the sampling bottle was rinced twice with the liquid inside the tube to remove any disturbing substances from the bottle. After filling the bottle with the desired material, the lid was closed tightly and was taken to the laboratory. A part of samples on which the necessary analyzes should be performed as grab samples were separated from the bottles and the analyzing operation was performed. The samples which should be considered as 24-hour composite samples were poured into a 2.5 liter glass container and stored in the refrigerator after closing the lid. Operational parameters were also read by measuring devices located in the control room and operating areas. In order to obtain the best result and increase the reliability, as well as the possibility of tracking and controlling the activities, planning was performed in such a way that two-hour samples were collected in different stages, and stored in a 24-hour composite and then analyzed. This process was repeated five days a week for each step. In this way, the performance of all shift groups was monitored and the operating conditions in a working week of the working day were evaluated. After reviewing the results, processing and analyzing the data, corrective solutions with the approach of improving processes and equipment as well as improving the efficiency of human resources were reviewed and presented.

3. Findings

In order to determine the factors affecting the amount of COD in wastewater and determine the research path, the design documents of plant, especially wastewater treatment system including operational process, equipment plans and chemical flows, tables of material values in equipment and pipelines, record sheets of operation control results, operation shift books were reviewed and a diagram of the wastewater treatment area was prepared (Figure 1). Based on the results, the main purpose of the wastewater treatment system of this plant is to reduce the amount of 1-EDC from 5000 mg to 50 mg per liter (99% efficiency). Due to the fact that in the design documents of the plant, the amount of this substance, which is chlorinated from hydrocarbon compounds and is the most present substance in the composition of the inlet flow to the wastewater treatment system, one of the main factors has the greatest impact on the amount of COD in wastewater by default. In addition, the existing total suspended solid and the volume of wastewater entering the treatment plant (according to the design, the amount of inlet wastewater should be 7.5 cubic meters per hour) are other factors affecting the efficiency and control of operations in this area. First, the current status of the inflow to the treatment system was investigated and the amount of COD, EDC TSS, OIL and PH, and measurement of wastewater volume on the inflow to the treatment system were determined (Table 1).

Table 1. Specifications of inflow and outflow to the wastewater treatment system at the beginning of the study.

	PH	OIL (mg / l)	دبی پساب (m^3 / h)	TSS (mg / l)	EDC (mg / l)	COD (mg / l)
Average volume of inflow	11	12	12	421	4776	530
Average volume of outflow	10.64	8.9	12	377	459	305
Efficiency (%)		26	0	10.24	90.3	43

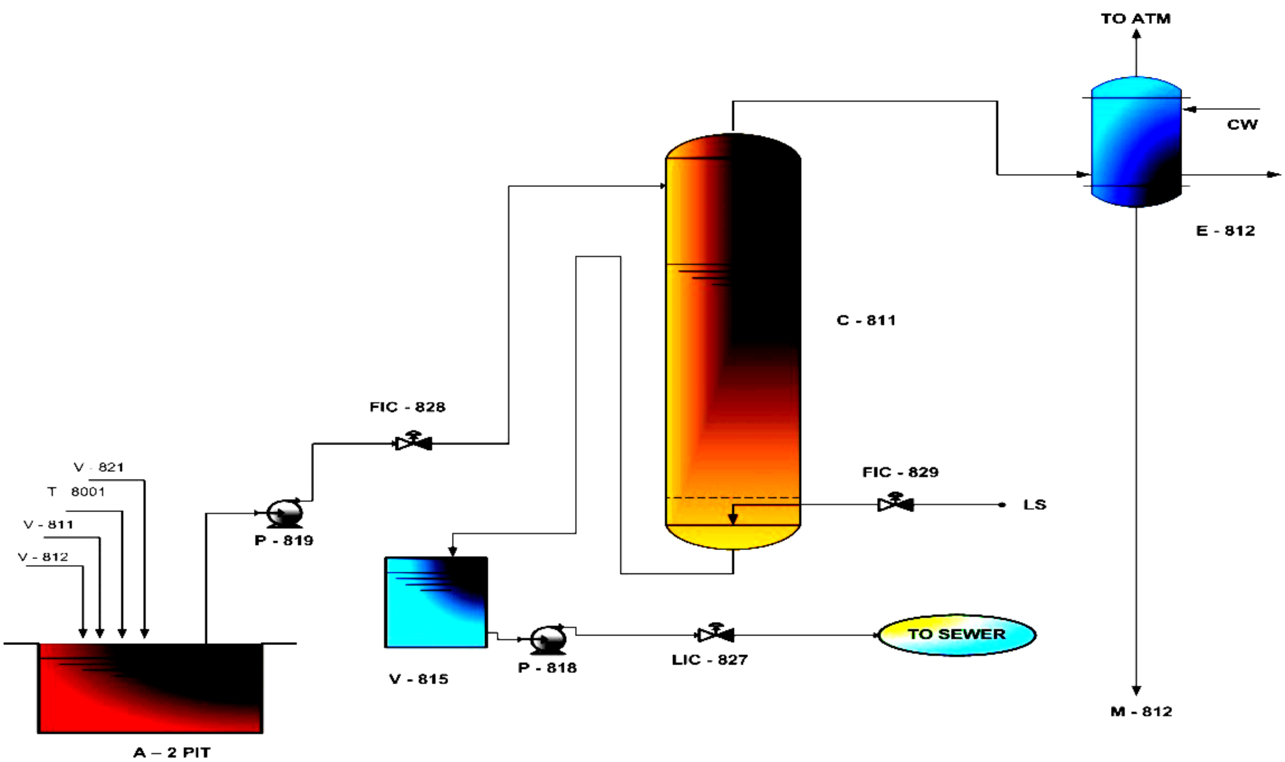

Figure 1. Diagram of treatment process of ethylene dichloride in the wastewater of plant

Determining the causes affecting COD

The main factors affecting the status of COD were identified by reviewing the results of the first stage, and monitoring the performance of equipment, reports and technical documentation as follows.

1. High amount of EDC in the inflow to the wastewater treatment tower
2. Low temperature of the inflow to the wastewater treatment tower
3. Increase in the flow rate of inflow to the treatment tower compared to the design

Corrective actions as the first stage

Corrective strategies were determined and implemented to solve the problem or reduce the effects of each of the identified causes (Table 2).

Table 2. Corrective actions defined to address the factors affecting COD (Stage One)

No.	Subject	Cause	Solution
1	High EDC in the inflow to the treatment tower.	1. Defect in the efficiency of separation operation of EDC phase from water phase in the washing area of the product. 2. Inlet of discharge lines and sampling points to the inlet tank to the wastewater treatment system.	1. Preparing instructions for operation staff on how to separate the EDC phase from the water phase in the product washing section 2. Collecting and directing the collection lines of sampling sites to the EDC recovery system and preventing them from being directed to the treatment system
2	Low temperature of inlet flow to the wastewater treatment system	1. The inflow preheater converter is broken. 2. Defect in controlling the temperature of the tower at the bottom and top	1. Repairing and reconstruction of the relevant converter 2. Installing the steam transmission line to the bottom of the tower to control the required temperature for the treatment operation until repairing or replacing the preheater converter 3. Preparing instructions for controlling the temperature of the tower at its bottom and top in order to increase the efficiency of the tower
3	Increasing the inlet flow rate to the treatment system compared to the design	1. Non-return of the overflow of tank of the third stage of washing the product to the tank of the first stage and sending it to the treatment system due to its high amount of iron	1. Controlling the amount of iron in the product and thus reducing the amount of water and sodium hydroxide for washing the product 2. Preparing instructions for controlling the appropriate operation to regulate the flow of water in the washing section

Investigating the impact of corrective actions as the first step

After performing the corrective actions of the first stage, the second stage were analyzed to measure the effectiveness of the corrective actions (Table 3).

Table3. Specifications of inflow and outflow to the wastewater treatment system after the corrective actions in the first stage

PH	OIL (mg / l)	دبی پساب (m3 / h)	TSS (mg / l)	EDC (mg / l)	COD (mg / l)	Efficiency (%)
11.4	10.5	11	400	4760	433	Average volume of inflow
10.9	9.6	11	367	360	248	Average volume of outflow
	8.6		8.3	95.4	43	Efficiency (%)

The differences between the specifications of the inflow and outflow to the wastewater treatment system at the beginning of the research and after the corrective actions are presented in Table 4.

Table 4. Comparison of the difference (reduction percentage) of inflow and outflow to the wastewater treatment system at the beginning of the research and after corrective actions

PH	OIL (mg/l)	دبی پساب (m3/h)	TSS (mg/l)	EDC (mg/l)	COD (mg/l	
-	12.5	8.3	5	0.3	18.4	Reduction percentage of inflow
-	0	8.3	2.7	21.4	18.7	Reduction percentage of outflow

Based on the results in Table 4, despite the decrease in the amount of COD and other related causes compared to the beginning of the study, the percentage of reduction and the amount of reduction of the mentioned parameters are less than that to ensure that the corrective actions are sufficient or appropriate. Therefore, the condition and performance of the equipment and processes were reviewed again, and the results related to the way of implementing new corrective actions or complete previous actions are written in Table 5.

Table 5. Supplementary corrective actions defined to address the causes affecting COD - Step Two

No.	Subject	Causes	Solution
1	High EDC in the inflow to the treatment tower.	1. Infiltration of the organic phase of the dehydration system into the inflow in the wastewater treatment system 2. Decreased capacity of the washing area of the product due to the production of alkaline sludge	1. Preventing the contents of the hydrocarbon phase of the dehydration system from entering the inlet tank of the wastewater treatment system by installing some marks on the relevant tank and preparing instructions on how to manually separate 2. Discharging and washing the tanks for washing the product and collecting the sludge contaminated with EDC and increasing their separation capacity
2	Low temperature of inflow to the wastewater treatment system	1.Preheater converter of inflow is broken. 2. Defect in controlling the temperature of the tower at the bottom and top	1. Repairing and reconstruction of the relevant converter which could not be implemented in the short term and time of the study 2. Preparing instructions for controlling the temperature of the tower at the bottom and top (100 to 102°C) in order to increase the efficiency of the tower (emphasis on accurate monitoring and implementation of this section)
3	Increase the flow rate of inflow to the treatment system compared to the design	1. Non-return of the overflow of the tank of third stage 2. Washing the product to the tank of the first stage and send it to the wastewater treatment system due to its high amount of iron.	1. Controlling the amount of iron output from the product cooling exchanger in the range of 56 to 65 mg/l (checking the corrosion of the temperature regulator of tower feed)

Evaluating the impact of corrective actions as the second step

After implementing the corrective actions of the first stage, the second step was analyzed to evaluate and measure the effectiveness of the actions, the results of which are presented in Table 6. It should be noted that the amount of OIL in the inflow and outflow of the treatment plant is insignificant and is within the authorized range of discharge to the environment or final treatment systems. Further, regarding the process studies, it has no effect on the performance of the wastewater treatment system, and accordingly was omitted from the subjects of experiments. Due to the fact that all process activities were performed from the beginning of the product to the end in an alkaline environment according to the unit design documents and the high pH had no effect on the efficiency of different parts, this parameter was removed from the analysis. Table 7 shows a comparison of the reduction percentage compared to the beginning of the project. The comparison of Tables 5 and 6 indicated that the amount of reduction in COD and other related causes is better than at the beginning of the study. Therefore, to ensure that corrective solutions can sustainably reduce the decreasing trend, as well as trying to achieve better results of the parameters of the research subject, the review of condition and performance of equipment and processes were conducted again and the results of how to implement new or supplementary corrective actions are listed in Table 8.

Table 5. Specifications of inflow and outflow to the wastewater treatment system after the corrective actions during the second step

(m^3 / h دبی پساب	TSS(mg / l)	EDC(mg / l)	COD(mg / l	
9.5	378	4728	348	Average volume of inflow
9.5	313	317	205	Average volume of outflow
-	19.1	93.3	46.7	Efficiency (%)

Table 6. Comparison of the difference (reduction percentage) of inflow and outflow to the wastewater treatment system at the beginning of the research and after the second corrective actions

(m^3 / h دبی پساب	TSS(mg / l)	EDC(mg / l)	COD(mg / l)	
21	8	1	27.5	Reduction percentage of inflow
21	17	30	32.8	Reduction percentage of outflow

Table 7. Supplementary corrective actions defined to eliminate the causes affecting COD (Third Step)

No.	Subject	Solution
1	High EDC during in the inflow to the wastewater treatment tower	1. Continuing previous actions. 2. Adjusting the ratio of caustic soda injection to the second stage of washing and thus reducing water consumption for neutralization and washing in the third step
2	Low temperature of inflow to the wastewater treatment system	1. Continuing adjusting the temperature in top and bottom of the tower 2. Repairing and cleaning the high temperature adjustment converter of the treatment tower to reduce steam injection and high temperature fluctuations in the tower
3	An increase in the flow rate of inflow to the treatment system compared to the design	1. Continuing adjusting the amount of iron in the temperature adjustment converter of feed 2. Adjusting the mixing ratio of chlorine and ethylene in the production reactor

Investigating the impact of corrective actions as the third step

After the implementation of the corrective actions of the first step, the analyses of the second step were performed to evaluate and measure the effectiveness of the actions, the results of which are given in Table 8. The comparison of the reduction percentage to the beginning of the project is given in Table 9. The results showed that the amount and percentage of COD reduction and other related causes were better than at the beginning of the study. Due to the age of this factory in its design documents, there is no limit for the amount of COD that can be compared with the success rate of the research, but achieving a 54% reduction compared to the current situation shows the effectiveness of corrective actions within the facilities. As shown in Table 10, the values of the evaluated parameters are reported comparatively at the beginning and end of the project.

Table 8. Specifications of inflow and outflow to the wastewater treatment system after corrective actions of the third step

(m^3 / h دبی پساب	TSS(mg / l)	EDC(mg / l)	COD(mg / l)	
9	351	4698	339	Average volume of inflow
9	289	305	140	Average volume of outflow
25	17.6	93.5	58.7	Efficiency (%)

Table 9. Comparison of the difference (reduction percentage) of inflow and outflow to the wastewater treatment system at the beginning of the research and after the third corrective actions

(m3 / h)دبی پساب	TSS(mg / l)	EDC(mg / l)	COD(mg / l)	
25	16.7	1.6	36	Reduction percentage of inflow compared to the beginning of the research
25	23	33	54	Reduction percentage of outflow compared to the beginning of the research

Table 10. Comparison of measurement results of parameters at the beginning and end of the project in the outflow of wastewater

(m^3 / hدبی پساب	TSS(mg / l)	EDC(mg / l)	COD(mg / l)	
0	10.4	90.3	43	Efficiency at the beginning of the project
25	18	93.6	59	Efficiency at the beginning of the project (percentage)
25	7.6	3.3	16	Amount of increase in the efficiency of the treatment system (percentage)

4. Discussion and conclusion

Choosing the right technology for wastewater treatment in the petrochemical industry is a complex and time-consuming issue due to the presence of various interfering factors [5]. The highest amount of increase in the efficiency of the treatment system in the outflow parameters of the treatment system is related to the flow rate of wastewater with a 25% increase and the lowest is related to the amount of EDC in the wastewater flow (3.3%). The highest efficiency of COD reduction in the inflow and outflow of wastewater to the treatment system was related to the third step of corrective actions with a reduction of 59%. The amount of COD in the outflow at the end of the project decreased by 54% compared to the beginning. The efficiency of the treatment system for this parameter was 16% compared to the beginning of the project. The highest efficiency of EDC reduction in the inflow and outflow of wastewater to the treatment system was related to the third step of corrective actions with a reduction of 93.5%. The amount of EDC in the outflow at the end of the project decreased by 33% compared to the beginning. The efficiency of the treatment system for this parameter was 3.3% compared to the beginning of the project. The highest efficiency of TSS reduction in the inflow and outflow of wastewater to the treatment system is related to the second step of corrective actions with 19.1% reduction. The amount of TSS in the outflow at the end of the project decreased by 23% compared to the beginning. The efficiency of the treatment system for this parameter was 7.6% compared to the beginning of the project. The efficiency of the treatment system for the flow rate of wastewater compared to the beginning of the project was 25%. Due to the fact that the wastewater of this plant has a small amount of OIL in the composition of the inflow to the treatment system, this parameter had no effect on the efficiency of the overall process. Since caustic soda is used to wash the product in the production process of this factory, and there is no function to control the pH in the neutral range in the treatment system, this parameter does not affect the overall process of wastewater treatment plant. In addition, due to the fact that EDC is absorbed from the outflow in the treatment process by transferring mass from the liquid phase (feed inlet to the treatment tower) to the gas phase (steam entering the treatment plant), adjusting the high and low temperature of the tower in the case of feed preheater converter is out of service is very important. Thus, adjusting the feed temperature at the moment of entering the treatment tower (about 85°C) must be done by steam injection to increase mass transfer (absorption of EDC from the liquid phase to the output gas phase of the tower). Haghighi Asl et al. (2018) examined photocatalytic degradation method as a suitable method for wastewater treatment and removal of chemical oxygen demand (COD) in one of the production units of the petrochemical industry and the effective parameters in the performance of this process. The results showed that increasing the concentration of photocatalyst at neutral pH to the optimum value of 0.84 g/l in unrestricted conditions and 2 g/l in restricted conditions increased the removal of chemically required oxygen by 93% and 77%, respectively. In fact, under the optimal conditions mentioned above, the amount of chemically required oxygen reduced from 1280 to 90 and 294, respectively. Haghighi Asl et al. (2018) emphasized on improving the quality of wastewater and corrective actions in this regard by referring to several studies on the reduction of COD in industrial wastewater of various petrochemicals around the world[6].In another study, Nikfar et al. (2012) examined the effectiveness of managing the reduction of industrial wastewater from the source on the quality of wastewater in Shahid Tondgooyan Petrochemical Company. In this research, by observing technical, process and repair issues and finally presenting management solutions, they attempted to be close to the design level in the amount of produced wastewater in the polyethylene terephthalate unit, which has a significant share in the pollution production. The results showed that the taken actions were effective, which are consistent with the results of Nikfar et al. (2012) [7]. Jalilzadeh and Asadi (2016) evaluated the effect of wastewater pH on reducing the COD of wastewater of PVC unit of Bandar Imam Petrochemical. In this study, COD reduction in the wastewater of olefin unit by UV/H2O2 photochemical reactor and the effect of pH were investigated. Based on the results, increasing the pH of the solution leads to the reduction of the degradation and COD removal of petroleum compounds. They stated that a higher rate of optical decomposition and a decrease in COD occurred at low and neutral pH values due to the formation of more active hydroxyl radicals compared to higher pH. However, the pH of the wastewater had no effect on the percentage of COD removal in Imam Petrochemical. The results of Jalilzadeh and Asadi (2016) also confirmed the obtained results from the present study [8].Table 11 presents the factors with significant impact on the overall process of the wastewater treatment system, i.e. COD reduction

Table 11. List of factors affecting the main parameters of controlling the wastewater of ethylene dichloride plant

Name	The way of affecting the performance of wastewater treatment system
EDC	As a hydrocarbon, it increases the oxygen demand of water and increases COD.
TSS	By infiltrating the suspended particles in the main stream of the wastewater, the amount of EDC absorbed by the steam injected in the inflow to the treatment tower decreases and the amount of unabsorbed EDC in the output phase increases leading to an increase in the COD and a decrease in the system efficiency. It also clogs the transmission lines and reduces the overall effectiveness by stopping the treatment.
Flow rate of wastewater	In case of excessive design increase, feed retention in the treatment tower decreases and the amount of EDC not absorbed in the output phase of the system increases, leading to an increase in COD.
High and low temperature of the treatment tower	In case of change in low and high temperature of the tower, the amount of EDC absorption from the input feed decreases The amount of unabsorbed EDC in the output phase of the system increases leading to an increase in COD since the changes in this regard have a lot to do with the EDC boiling point.
Iron in the system	In case of increased iron in the product, its washing operation faces with a problem where the amount of water and the consumption of caustic soda to absorb iron from the product increases, leading to an increase in the flow rate and TSS of system, the consequences of which are explained.

Based on the results of this study, the following suggestions should be considered to improve the process and achieve COD reduction. - Investigating the effect of using feed preheater converter on the efficiency of wastewater treatment system (not possible in this project) instead of steam entering the treatment tower. - Studying the reduction of TSS input to the treatment system by reducing this parameter by deposition in the settler and polyelectrolytes and its effect on the efficiency of the treatment system. Evaluating the reduction of flow rate of wastewater to the defined limit in the design documents by complete return of water in the third step of washing to the process cycle. Investigating an increase in the volume of wastewater treatment tower on EDC adsorption efficiency from feed flow using simulation software such as Hysis

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