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Study On Wastewater Treatment By Advanced Oxidation Process

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Abstract: *Various dairy products are produced by dairy industries using different chemicals which generates effluent contains recalcitrant elements. Advanced oxidation process plays a efficient role in treatment of dairy wastewater using Fenton's reagents like hydrogen peroxide and ferrous sulphate. Initially pH of effluent is reduced to 4 by using sulphuric acid and to treat 1 liter of effluent we use about 2 ml of H2O2 and 1.5 mg of FeSO4. Then, pH of effluent is increased to 7 for better results floc settlement and alum is used as coagulant in coagulation process. Various tests are carried out in treated effluent like BOD; COD, pH, TDS etc. 85% of COD and 60% of BOD is removed in treated effluent in reaction time of 40 minutes in oxidation process and 1 hour in coagulation process. So, advanced oxidation process shows significant results in treatment of wastewater.*

Keywords: *Alum, Coagulation, Fenton's reagent, Floc settlement, Ferrous sulphate, Hydrogen peroxide, Oxidation process.*

I. Introduction

Wastewater treatment is a process used to convert wastewater into an effluent that can be returned to the water cycle with minimal impact on the environment or directly reused. The latter is called water reclamation because treated wastewater can then be used for other purposes. The treatment of wastewater is part of the overarching field of sanitation. Wastewater treatment process is one of the most important environmental conservation processes that should be encouraged worldwide. Most wastewater treatment plants treat wastewater from homes and business places. Industrial plant, refineries and manufacturing plants wastewater is usually treated at the onsite facilities. These facilities are designed to ensure that the wastewater is treated before it can be released to the local environment. In this process, the solids are partially removed or changed by decomposition from complex highly putrescible organic solids to mineral or relatively stable organic solids. Characteristics of wastewater are classified into physical, chemical and biological constituent. Physical properties are color, odor, temperature and turbidity. Chemical properties are classified into organic and inorganic constituents. Fats, oils, grease are organic constituents while pH, nitrogen, chlorides are inorganic constituents. A chain of operations involving receiving and storing of raw materials, processing of raw materials into finished products, packaging and storing of finished products, and a group of other ancillary operations (e.g., heat transfer and cleaning) are examples of some of the great variety of operations performed in the dairy industries. It is one of the most polluting of industries, not only in terms of the volume of effluent generated, but also in terms of its characteristics as well. It generates about 0.2–10 liters of effluent per liter of processed milk with an average generation of about 2.5 liters of wastewater per liter of the milk processed. It contains soluble organics, suspended solids, trace organics. Characteristics of a dairy effluent contain Temperature, Color, pH (6.5-8.0), DO, BOD, COD, Dissolved solids, suspended solids, chlorides, sulphate, oil & grease. It depends largely on the quantity of milk processed and type of product manufactured. The waste water of dairy contains large quantities of milk constituents such as casein, inorganic salts, besides detergents and sanitizers used for washing. All these components contribute largely towards their high biological oxygen demand (BOD) and chemical oxygen demand (COD). It is white in colour and usually slightly alkaline in nature. These effluents decompose rapidly and deplete the dissolved oxygen level of the receiving streams immediately resulting in anaerobic conditions and release of strong foul odors due to nuisance conditions. The receiving water becomes breeding place for flies and mosquitoes carrying malaria and other dangerous diseases like dengue fever, yellow fever. It is also reported that higher concentration of dairy wastes are toxic to certain varieties of fish and algae. The casein precipitation from waste which decomposes further into a highly odorous black sludge at certain dilutions the dairy waste is found to be toxic.

Although disposal or reuse occurs after treatment, it must be considered first. Since disposal or reuse is the objective of wastewater treatment, disposal or reuse options are the basis for treatment decisions. Acceptable impurity concentrations may vary with the type of use or location of disposal. Transportation costs often make acceptable impurity concentrations dependent upon location of disposal, but expensive treatment requirements may encourage selection of a disposal location on the basis of impurity concentrations. Ocean disposal is subject to international treaty requirements. International treaties may also regulate disposal into rivers crossing international borders. Water bodies entirely within the jurisdiction of a single nation may be subject to regulations of multiple local governments. Acceptable impurity concentrations may vary widely among different jurisdictions for disposal of wastewater to evaporation ponds, infiltration basins or injection wells. The principal objective of wastewater treatment is generally to allow human and industrial effluents to be disposed of without danger to human health or unacceptable damage to the natural environment. So these harmful properties of wastewater should be reduced by suitable treatment So this harmful properties of wastewater should be reduced by suitable treatment process. Treatment methods are classified into mechanical, chemical and biological treatment. Normal treatment methods like oxidation pond, trickling filter are not suitable for such effluent because various chemicals are used in industries for producing different products which contain recalcitrant element in effluent. So advanced oxidation process constitutes a promising technology for the treatment of wastewater.

II. Advance Oxidation Process

Advanced oxidation processes are a set of chemical treatment procedure designed to remove organic materials in wastewater by oxidation through reactions with hydroxyl radicals. This procedure is particularly useful for cleaning biologically toxic or non-degradable materials such as aromatics, pesticides, petroleum constituents and volatile organic compounds in wastewater. This can be used to treat effluent of secondary treated wastewater which is then called tertiary treatment. The contaminant materials are converted to a large extent into stable inorganic compounds such as water, carbon dioxide and salts. A goal of wastewater purification by means of this procedure is the reduction of the chemical contaminants and the toxicity to such an extent that the cleaned wastewater may be reintroduced into receiving streams or, at least, into a conventional sewage treatment. Six types of advanced oxidation processes, includes radiation, photolysis and photo catalysis, sonolysis, electrochemical oxidation technologies, Fenton-based reactions, and ozone-based processes. Fenton reagents are used in Fenton process and it was first proposed in 1980s for drinking water treatment and later was widely studied for treatment of industrial waste water. Fenton reagents is a solution of hydrogen peroxide with ferrous iron as a catalyst that is used to oxidize contaminants or waste water iron (II) is oxidized by hydrogen peroxide to iron (III), forming a hydroxyl radical and hydroxide ion in the process. Iron (III) is then reduced back to iron (II) by another molecule of hydrogen peroxide, forming a hydroperoxyl radical and proton. The net effect is a disproportionate of hydrogen peroxide to create two different oxygen-radical species, with water ($H^+ + OH^-$) as a byproduct:

$$Fe^{2+} + H_2O_2\ Fe^{3+} + HO\cdot + OH^- \quad (1)$$

$$Fe^{3+} + H_2O_2\ Fe^{2+} + HOO\cdot + H^+ \quad (2)$$

The free radicals generated by this process then engage in secondary reactions. For example, the hydroxyl is a powerful, non-selective oxidant. Oxidation of an organic compound by Fenton's reagent is rapid and exothermic and results in the oxidation of contaminants to primarily carbon dioxide and water. Amount of radicals produced and the activation of oxidants are crucial factors that affect the treatment efficiency. It involves 2 stages of oxidation,

- The formation of strong oxidant (example: hydroxyl radical)
- The reaction of the oxidant with organic contaminants in water.

However the term advanced oxidation process refers specifically to the process in which oxidation of organic contaminants occurs primarily through reactions. In water treatment applications, it usually refers to specific subset of process that involves O_3, H_2O_2 or UV light.

2.1 Applications Of Advanced Oxidation Process

The use of advanced oxidation processes to remove pollutants in various water treatment application has been the subject of study for around 30 years. Most of the available processes investigate in depth and a considerable body of knowledge has been built up about the reactivity of many pollutants. Various industrial applications have been developed, including ones for ground remediation, the removal of pesticides from drinking water, the removal of formaldehyde and phenol from industrial waste water and a reduction in COD from industrial waste water. The development of such advanced oxidation process applications has been stimulated by increasingly stringent regulations, the pollutions of water resources through agricultural and industrial activities and the requirement that industry meet effluent discharge standards. Recent trends are the development of new, modified advanced oxidation process that are efficient and economical. In fact, there has been some studies that offer constructive solutions. Nevertheless, it is difficult to obtain an accurate picture of the use of AOPs and its exact position in the range of water treatment processes has not been determined to date.

III. Applications Of Alum In Coagulation

Coagulation is a chemical process that involves neutralization of charge and can be used as a preliminary or intermediary step between other waste water treatment process. Iron and aluminum salts are the most widely used coagulants. In a colloidal suspension, particles will settle very slowly or not at all because the colloidal particles carry surface electrical charges that mutually repel each other. A coagulant with the opposite charge is added to the water to overcome the repulsive charge and destabilize the suspension. For example, the colloidal particles are negatively charged and alum is added as a coagulant to create positively charged ions. Once the repulsive charges have been neutralized, the Vander Waals force will cause the particles to cling together and form micro floc. Alum is used as a flocculent to remove unwanted colour and turbidity from water supplies. Alum is the coagulant of choice for many industrial and sanitary wastewater treatment applications, due to its high efficiency, effectiveness in clarification, and leaves no residual color, offers very good turbidity removal.

IV. Materials And Methodology

4.1 Materials

The chemicals and other materials used for project. Chemicals such as Hydrogen peroxide (H2O2), Ferrous sulphate (FeSO4), Alum ((Al2(SO4)3), Sulphuric acid (H2SO4), Sodium hydroxide (NaOH) are used for treatment method.

4.2 Work Methodology

Initially the effluent for treatment is collected from dairy industry and test for effluent is carried out as per IS standards. Tank is designed for volume of effluent. Then above mentioned chemicals are used for treatment followed by neutralization, oxidation, and coagulation process. After the completion of advanced oxidation process, the test will be carried out in treated water.

4.3 Material Investigation

4.3.1 Hydrogen Peroxide

It's in pure form, is a pale blue clear liquid slightly more viscous than water. It is used as an oxidizer, bleaching agent, antiseptic. Several different applications including industrial, medical, horticultural works. It is unstable and slowly decomposes in the presence of base or a catalyst. Because of its instability, it is typically stored with a stabilizer in a weakly acidic solution.

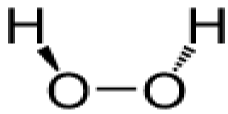

Fig.1 Hydrogen peroxide

Table 1: Properties of Hydrogen Peroxide

Sl.no	Properties	Values
1.	Chemical formula	H_2O_2
2.	Molar mass	34.0147 g/mol
3.	Density	1.450 g/cm^3
4.	Melting point	-0.43 degree Celsius
5.	Boiling point	150.2degree Celsius

4.3.2 Ferrous Sulphate

It is pale green iron salt. It is used in inks, tanning, water purification and treating anaemia. The hydrated form of ferrous sulphate is used medically to treat iron deficiency, and also for industrial applications. It is on the World Health Organization's list of essential medicines, the most important medications needed in a basic health system.

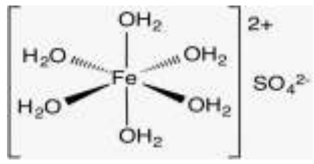

Fig.02 ferrous sulphate

Table 2: Properties Of Ferrous Sulphate

Sl.no	Properties	Values
1.	Chemical formula	$FeSo_4$
2.	Molar mass	161.91/mol
3.	Density	3.65g/cm^3
4.	Melting point	680 degree Celsius

4.3.3 ALUM

It is soluble in water and is used as a coagulating agent in the purification of drinking water and waste water treatment plants. It is a white crystalline solid hydroscopic. In water purification it causes suspended impurities to coagulate into larger particles and then settle to the bottom of the container.

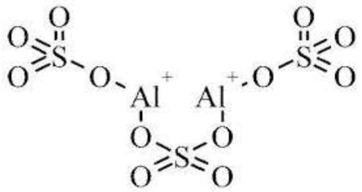

Fig.03 alum

Table 3: Properties Of Alum

Sl.no	Properties	Values
1.	Chemical formula	$Al_2(so_4)_3$
2.	Molar mass	342.15g/mol
3.	Density	2.672 g/mol
4.	Melting point	770 degree Celsius

4.3.34 Sulphuric Acid

It is a mineral acid. Its corrosiveness can be mainly ascribed to its strong acidic nature. It is a colorless, odorless liquid that is soluble in water, highly exothermic. It is a central substance in the chemical industry mainly used in manufacturing, oil refining and chemical synthesis. It is widely produced with different methods such as contact process, wet sulphuric acid. It is produced from sulfur, oxygen and water via the conventional contact process or the wet sulphuric acid process. It is used to make phosphate fertilizers, calcium and ammonium phosphates. It is used in large quantities by the iron and steel making industry to remove oxidation, rust and scaling from sheet and billets. It is also used for a variety of other purposes in the chemical industry.

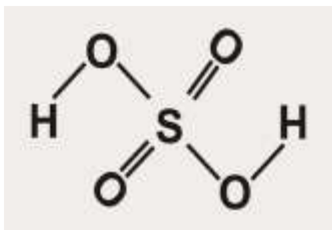

Fig.04 sulphuric acid

Table 4: Properties of Sulphuric Acid

Sl.no	Properties	Values
1.	Chemical formula	H_2So_4
2.	Molar mass	98.079 g/mol
3.	Density	1.84 g/cm^3
4.	Melting point	10 degree celsius
5.	Boiling point	337 degree celsius

4.3.5 Sodium Hydroxide

Sodium hydroxide is a highly caustic base and alkali that decompose proteins at ordinary ambient temperature and may cause severe chemical burns. It is highly soluble in water and readily absorbs moisture and carbon-di-oxide from the air. It is used in many industries in the manufacture of pulp and paper, textiles, soaps, detergents and drain cleaner.

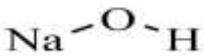

Fig.05 Sodium Hydroxide

Table 5: Properties Of Sodium Hydroxide

Sl.no	Properties	Values
1.	Chemical formula	NaOH
2.	Molar mass	39.4971 g/mol
3.	Density	2.13 g/cm^3
4.	Melting point	318 degree celsius
5.	Boiling point	1388 degree celsius

V. Results And Discussions

The experimental study results are presented and discussed in the form of tables and graphs. This chapter gives the integral information about the test results of treated and untreated effluent of dairy wastewater.

5.1 Tests For Dairy Effluent

Table 6: Test Results for Untreated Effluent

Sl.no	Characteristics	S1	S2	S3	S4	S5
1.	TURBIDITY(NTU)	608.4	592.8	588.2	625.5	642.3
2.	COD (mg/l)	380	387	405	414	396
3.	BOD (mg/l)	186.54	178.21	161.94	172.03	189.08
4.	CHLORINE (mg/l)	0	0	0	0	0
5.	pH	7.8	7.6	7.4	8	7.8
6.	TDS (mg/l)	1000	2000	1000	1500	2000

Table 7: Test Results for Treated Effluent

Sl.no	Characteristics	S1	S2	S3	S4	S5
1.	TURBIDITY(NTU)	7	7.8	7.5	8	7.9
2.	COD (mg/l)	45	54	63	72	76.5
3.	BOD (mg/l)	22.17	32.81	25.71	38.13	36.25
4.	CHLORINE (mg/l)	0	0	0	0	0
5.	pH	7	7.2	7.1	7	6.9
6.	TDS (mg/l)	600	650	690	660	720

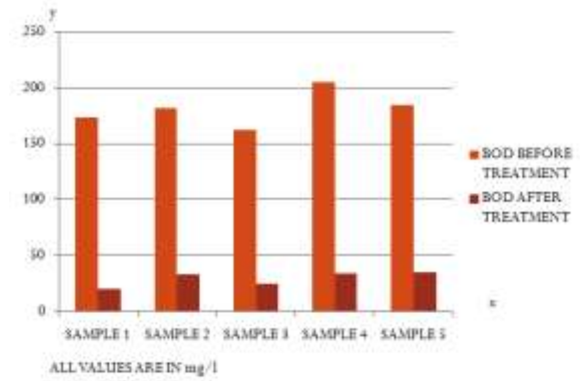

Fig 06. BOD before and after

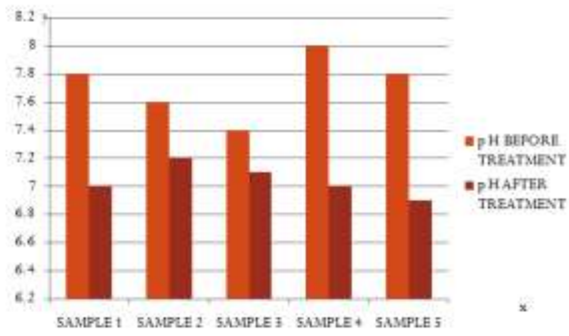

Fig 07. pH before and after

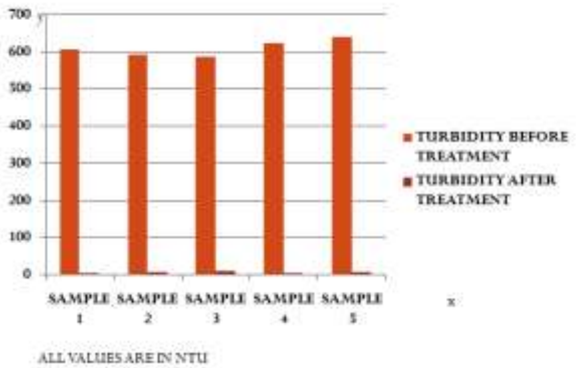

Fig 08. Turbidity before and after

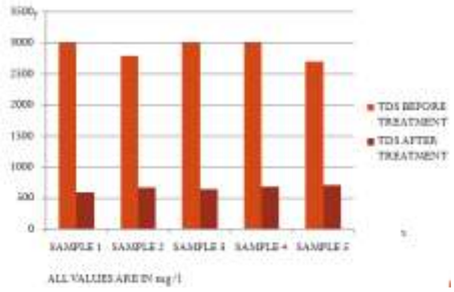

Fig 09. TDS before and after0

5.2 Discussions

Maximum COD value before the treatment was 414 mg/l and it was reduced to the minimum value after the treatment process to about 45 mg/l. The comparison resulted in the reduction percentage level to about 89.13% and it is being satisfactory in Fenton process. Maximum BOD value before the treatment was 189.08 mg/l and it was reduced to the minimum value after the treatment process to about 22.17 mg/l. The comparison resulted in the reduction percentage level to about 88.27%. Maximum pH value before the treatment was 8 and it was reduced to the minimum value after the treatment process to about 6.9. Maximum turbidity value before the treatment was 642.3 NTU and it was reduced to the minimum value after the treatment process to about 7 NTU. The comparison resulted in the reduction percentage level to about 98.9% and it is considered to be more relevant in the overall treatment process. Maximum TDS value before the treatment was 2000 mg/l and it was reduced to the minimum value after the treatment process to about 600 mg/l.

VI. Conclusion

AOPs can be utilized in wastewater treatment for overall organic content such as COD reduction, specific pollutant destruction, sludge treatment, increase of bioavailability of recalcitrant organics, and color and odor reduction. The overall results of this study indicated that the application of Fenton's reagent was a feasible method to partially treat wastewaters, allowing achieved a satisfactory decrease of dissolved oxygen content. An important parameter of wastewater treatment by the Fenton method is the pH of the solution. The process should proceed in a mildly acidic environment. The most advantageous value of pH appeared in the narrow range of pH = 3.5. Both lower and higher values of pH definitely diminish the reduction in COD. In this study, satisfactory diminution of various parameters, mainly of Turbidity, COD, BOD, EC and TDS were observed. Overall reduction in the value of COD was 89.13% which meant to be more satisfactory in the advanced oxidation process. Reduction in the Turbidity and color was achieved to be more efficiency as they were 98.9% and 99% respectively. The consumption of time played a vital part during the treatment process which was efficient at the most. The more the duration of the process decreases, the better will be the results and it can be suitable for the construction of treatment plants in the densely populated region of the world. The Fenton process exhibited economical and satisfactory COD and toxicity removal performance. The main advantage of the Fenton process is the complete destruction of contaminants to stable compounds. The costs associated with the applied processes were analyzed and evaluated to determine the most suitable process. The Fenton treatment could help in reducing the effluent treatment plant (ETP) construction cost as the COD load to ETP reduced with the application of Fenton process. Therefore, the combination of a biological treatment with a chemical oxidation by Fenton's reagent for wastewater will give an effluent that in terms of organic matter content that can be directly discharged into water bodies.

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