Radiation Treatment of Skim Serum Wastewater from Natural Rubber Latex Centrifuging Units

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The skim serum wastewater generated during the centrifuging of natural rubber latex is highly polluting in nature. The raw wastewater and its anaerobically treated form were subjected to the gamma irradiation treatment. Different combinations of Fenton's reagent and different doses of gamma radiations were also applied. The effectiveness of treatment was assessed in terms of pH, turbidity, chemical oxygen demand, biochemical oxygen demand, total Kjeldahl nitrogen, ammoniacal nitrogen, total solids, dissolved solids and sulphide. Changes in the concentrations of biochemical constituents and enumeration of total bacterial population were also used to assess the treatment efficiency. Anaerobically treated effluent can be more effectively treated using gamma radiation and Fenton's reagent. Most of the biochemical constituents and bacterial populations were completely removed from the anaerobically treated effluent by this method of treatment.

Keywords: gamma ray, irradiation, rubber latex centrifuging, skim serum wastewater, Fenton's reagent.

Introduction

Natural rubber (NR) latex is obtained from the bark of the rubber tree (*Hevea brasiliensis*) by tapping. Structurally, NR is a cis-1, 4-polyisoprene (C_5H_8). NR latex is a colloidal system comprised of rubber globules dispersed in an aqueous serum. Processing of fresh latex is essential to maintain its quality. Field latex (preserved by adding ammonia, which inhibits bacterial growth) is unsuitable for most latex applications as its rubber content is low. For most product manufacture, latex of minimum 60% dry rubber content is essential. One of the important methods for the concentration of preserved field latex (contains 30% to 33% of rubber) is centrifuging using high speed centrifuges to obtain 60% rubber and skim latex containing 4–6% of rubber. Skim latex, which contains about 0.8% of ammonia, is coagulated with 98% sulphuric acid to recover rubber. The skim serum produced after coagulation of rubber contains a significant amount of non-rubbers, which include proteins, sugars, lipids, carotenoids and organic and inorganic salts originating from latex and a very small amount of uncoagulated latex (Kumaran, 1987). These constituents are excellent substrates for the proliferation of micro-organisms generating high biochemical oxygen demand (BOD) and objectionable odour and needs proper treatment.

Radiation treatment is emerging as an environment friendly technology for recycling wastewater. Gamma rays are used for treating industrial effluents that are very hard to be treated by conventional methods. Advantages of the method mainly are that it does not create by-products, elimination of the hazard of overdosing of oxidising agents and a high process rate and efficiency. Through primary and secondary products of water radiolysis, the ionising radiation causes the decomposition of organic compounds contained in water. In pilot plant and industrial installations, the advanced oxidation process has been used in the treatment of drinking water and industrial wastewater (Kos & Perkowski, 2003, Rice, 1997). Much interest is evinced on the potential of using gamma radiation in the treatment of municipal and industrial wastewater and drinking water (Waite et al., 1992). Radiation

combined with biological processes has been used in the treatment of wastewater originating from production of antibiotics and metallurgy where large quantities of detergents and fats are used in the production process (White, 1978). Investigations on the effect of gamma radiation on poliovirus infectivity seeded in sludge samples, elimination of the endocrine-disrupting activity of 17 beta-estradiol, reduction in the population of coliphage, total coliforms and total flora present in raw sewage and secondary effluent, comparison of the toxicity responses of irradiated wastewater effluent samples to chlorinated municipal wastewater effluent samples, and treatment of several animal viruses found in effluent from an animal disease laboratory have been reported (Kimura et al., 2004, Farooq et al., 1993, Getoff, 1996, John & Blatchley, 1999, Thomas et al., 1982). Gamma rays are used for the treatment of sewage (Jung et al., 2002, 2004, Meeroff et al., 2004), pulp mill bleach effluents (Wang et al., 1994), surfactant and petroleum product wastewater, dyeing complex wastewater and paper mill effluents (Pikaey, 2001) and for the disinfection of wastewater (Basfar & Rehim, 2002). The main advantage of the gamma radiation treatment is its ability to inactivate pathogens with a high degree of reliability associated with the process in a clean and efficient manner ensuring easy operation and maintenance of the plant.

Since there is a growing interest in advanced oxidation processes like radiation technology to treat wastewater, a study was initiated to apply this method in combination with chemical oxidants like Fenton's reagent to treat the skim serum wastewater from a centrifuging rubber latex factory. The objective of the present study was to investigate the impact of gamma irradiation on the treatment of raw and anaerobically treated skim serum effluent. The combined effect of gamma radiation and Fenton's reagent on these effluents was also studied. The impact of radiation treatment on the chemical oxygen demand (COD), biochemical oxygen demand (BOD), total Kjeldahl nitrogen (TKN), ammoniacal nitrogen (AN), turbidity, sulphides

and phosphates and biochemical constituents like soluble protein, free amino acids, phenol, total sugar, reducing and non-reducing sugars and population of total bacteria were also part of the study.

Material and methods

Natural rubber skim serum effluent samples were collected from a centrifuge latex concentration unit in Kottayam district of Central Kerala, India. To obtain an anaerobically treated sample for the study, the effluent was subjected to anaerobic treatment in a bench-scale upflow anaerobic sludge blanket (UASB) reactor. Raw and treated samples were analysed for various parameters as per standard methods (APHA et al., 1992) and the results of analysis are given in Table 1.

Table 1

Characteristics of raw and anaerobically treated effluent

Parameter	Raw effluent	Anaerobically treated effluent
1	2	3
pH	3.6	8.5
Turbidity (NTU)	350	107
COD	36,400	4,508
BOD	27,300	815
TKN	7,000	4,480
AN	5,000	3,500
Total solids (TS)	60,000	32,418
Dissolved solids (DS)	58,000	30,554
Sulphide	14.00	235
Phosphate	2,600	1,525

All units except pH and turbidity are expressed in mg/L

Gamma irradiation of effluent samples was done at the Radiation Vulcanization of Natural Rubber Latex (RVNRL) Plant of Rubber Research Institute of India (RRII), Kerala, India using a laboratory scale Co-60 gamma source.

The effects of the following factors were investigated: the dose of radiation viz. 0.5 kGy to 100 kGy, pH of the effluent, addition of various chemicals like ferrous sulphate, Fenton's reagent and pollutant concentration of the effluent. After irradiation, the samples were analysed for various parameters to evaluate the extent of treatment. Biochemical analysis of the wastewater for concentration of total sugars (Scott Jr. & Melvin, 1953), reducing sugars (Nelson, 1944), total and soluble proteins (Lowry et al., 1951), phenols (Swain & Hills, 1959), and free amino acids (Moore & Stein, 1948) were carried out as per standard analytical techniques using a UV-visible recording spectrophotometer UV-240. The standard serial dilution plate technique of Pramer and Schmidt (1965) was employed for the enumeration of microbiological population.

Results and discussion

Effect of irradiation dose on pollutant removal

Effect on COD and BOD removal

The effect of the exposure rate on the treatment of the raw effluent was investigated within the range of 0.5 kGy (0.05 Mrad) to 100 kGy (10 Mrad). The COD removal efficiency was found to increase as the dose of gamma radiation increased from 0.5 to 2.5 kGy. The maximum COD removal efficiency of 24% was achieved at 2.5 kGy; thereafter, it showed fluctuations as shown in Figure 1.

A further increase of the dose up to 100 kGy had practically little effect on COD removal. For BOD removal, the same trend was noticed. A maximum BOD removal efficiency of 60–65% was obtained for the radiation dose of 2.5 to 3 kGy.
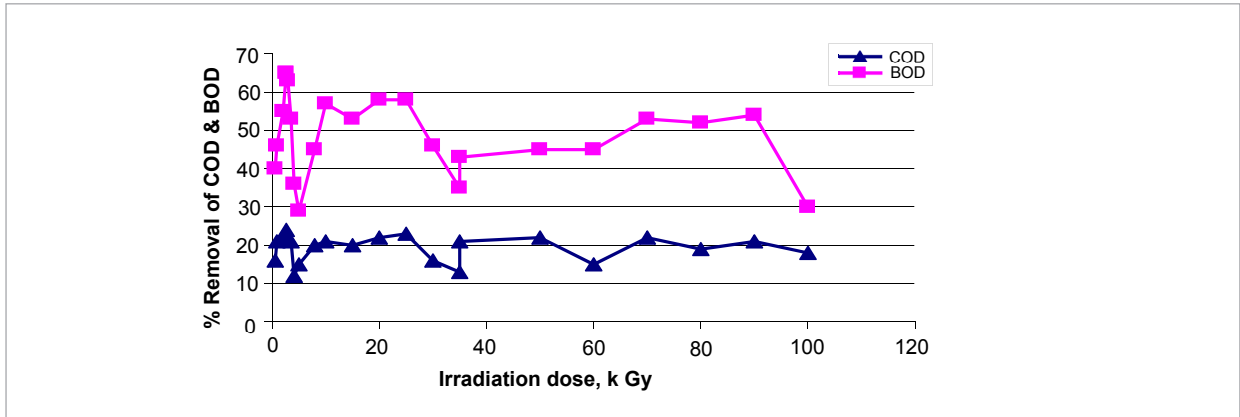
Effect on pH

There was no significant change in pH after irradiating with gamma rays as is evident from Figure 2. A very slight increase in pH was observed for almost all irradiation doses, and this may be due to the reactions of hydroxyl radicals generated during radiolysis.

Effect on TKN, AN, TS, DS and turbidity removal

Gamma radiation showed only 23% and 28% removal of TKN and AN, respectively, in the range of 1 to 2.75 kGy (Figure 3).
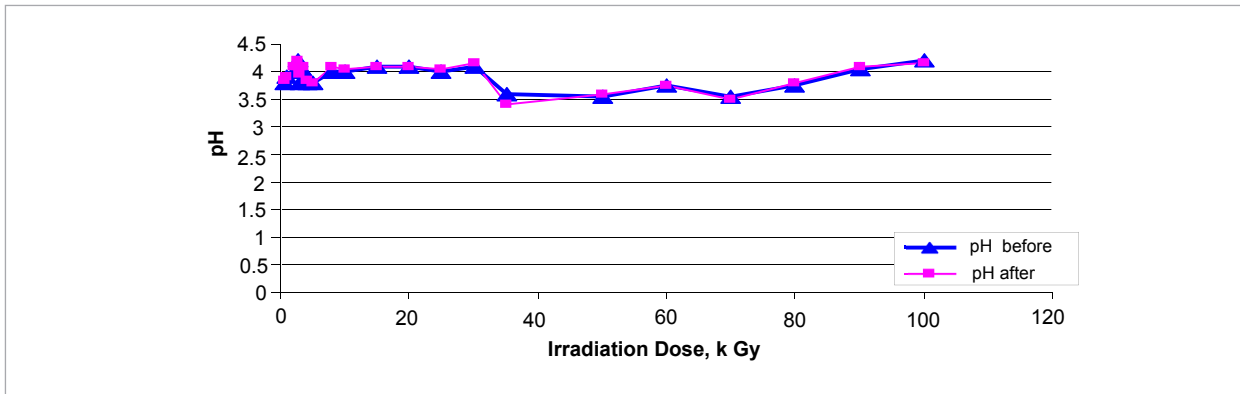
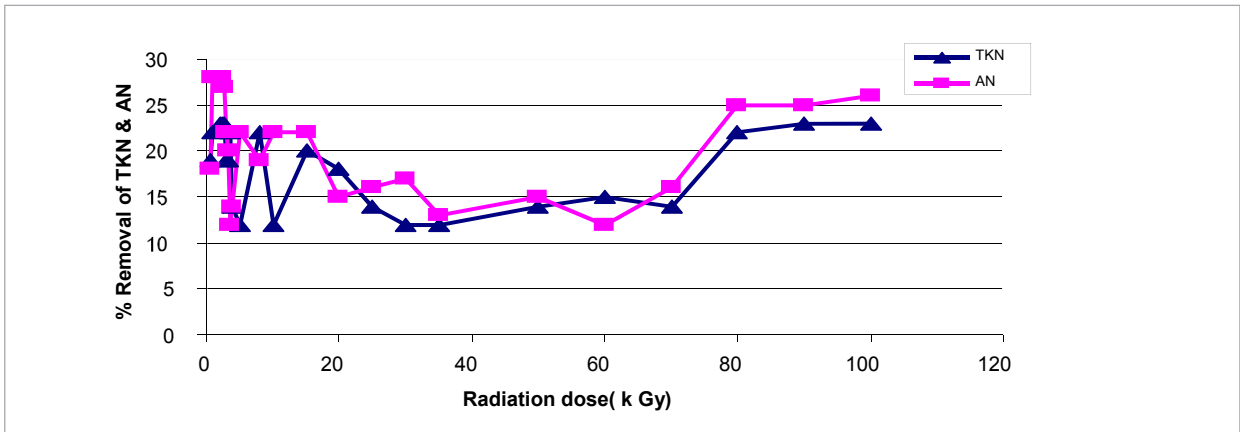## Fig. 1

Percentage removal of COD and BOD vs radiation dose
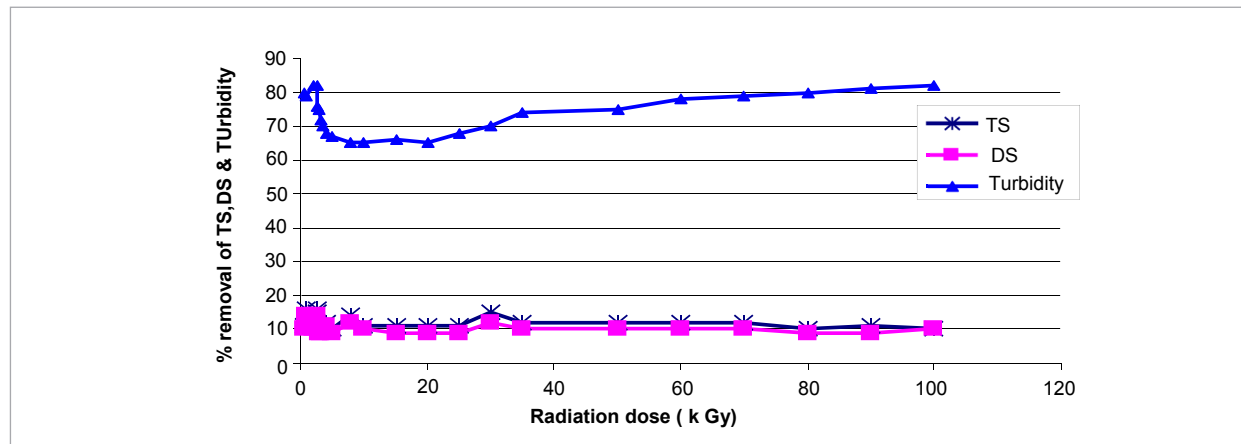

Fig. 2

Effect of irradiation on pH

Fig. 3

Effect of the radiation dose on TKN and AN removal

Fig. 4

Effect of the radiation dose on TS, DS and turbidity removal

Maximum removal of TS and DS were 16% and 14%, respectively, for the doses in the range 1–2.75 kGy. However, the turbidity removal was in the range of 80 to 82%. Maximum turbidity removal was obtained for an irradiation dose of 0.5 to 2.5 kGy and 70 to 100 kGy (Figure 4).

It was observed that after gamma irradiation the effluent became very clear and good settling was observed even at a radiation dose as low as 0.5 kGy.

From the percentage removal of pollutants obtained, a dose of 2.5 kGy was taken as the optimum dose of irradiation to treat skim serum effluent. This may be attributed to the fact that a radiation dose of 2–3 kGy can effectively decompose the contaminants in the wastewater (Gautam et al., 2005).

Factors influencing the efficiency of radiation treatment

Influence of pH and gamma radiation on COD and BOD removal

To study the effect of pH and gamma radiation on the removal of pollutants, the pH of the effluent was adjusted to 3, 4, 5, 6, 7, 8 and 9 before subjecting to gamma radiation at a dose of 2.5 kGy. The effect of pH on percentage reduction of COD and BOD is illustrated in Figure 5. A reduction in the percentage removal of

Fig. 5

Effect of pH on COD and BOD removal efficiency
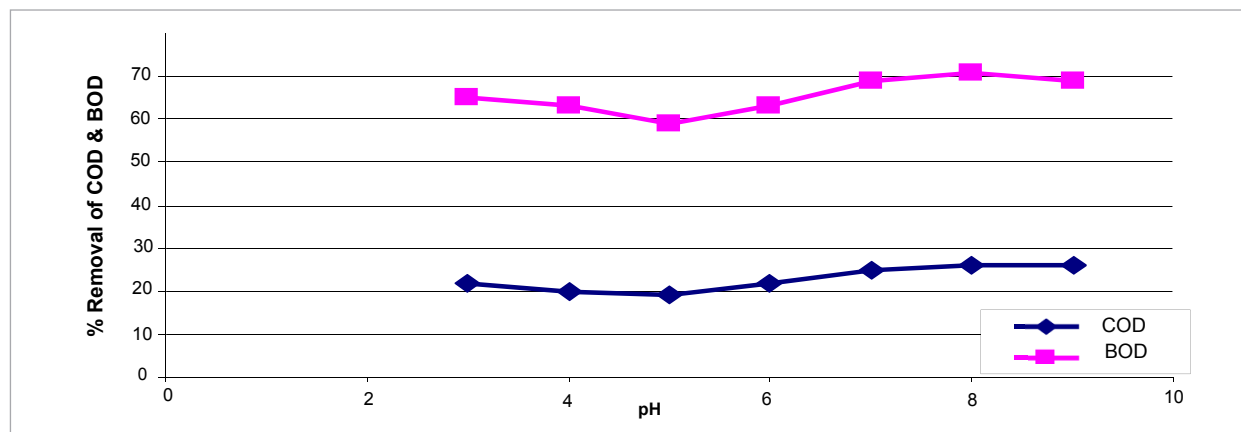
COD and BOD was observed as the pH of the effluent increased from 3 to 5 and then showed a steady increase as pH changed from 5 to 7. The values remained almost constant after pH 7. Therefore, pH between 7 and 8 could be taken as the optimum.

In the advanced oxidation process, OH has got a predominant role in the decomposition of organic molecules. Perkowski and Kos (2003) observed the same trend of maximum decomposition of organic contaminants at neutral or slightly alkaline pH in the decolouration of model dye house wastewater using the advanced oxidation process.

Influence of various reagents

The objective of this study was to ascertain the individual and combined effect of various reagents added to the wastewater before subjecting it to gamma irradiation. The following reagents were added to the raw effluent: (a) 200 mg/L of iron, (b) 5 mL/L H_2O_2, (c) 200 mg/L of iron and 5 mL/L H_2O_2 along with a control without any reagent, subjected to gamma radiation having a dose of 2.5 kGy and analysed for various parameters. The results are given in Table 2.

A slight increase in pH occurred when the effluent was irradiated alone and a decrease in pH occurred when the effluent was irradiated either in the presence of iron or iron and hydrogen peroxide. When hydrogen peroxide alone was added, there was no change in pH after irradiation.

Maximum reduction of COD and BOD was obtained when the raw effluent was irradiated in the presence of 200 mg/L of iron + 5 mL/L of H_2O_2 compared with individual applications of the reagents. Radiation in the presence of H_2O_2 alone showed negative values in the removal of turbidity, and the COD and BOD reduction were also comparatively low. In the absence of iron, formation of hydroxyl radical was negligible, and this should have negatively affected the treatment efficiency.

Effect of gamma radiation at various concentration of iron in Fenton's reagent ($FeSO_4$ + H_2O_2)

The effect of gamma irradiation in the presence of Fenton's reagent to remove pollutants was studied. Oxidation by Fenton's reagent is catalysed by Fe^{+2}. Experiments were conducted to ascertain the effect of Fe^{+2} and to find out the optimum dosage of Fe^{+2} for the degradation of pollutants in the wastewater. The effluent sample was subjected to gamma radiation having a dose of 2.5 kGy in the presence of Fenton's reagent having different concentrations of iron viz., 20 mg/L, 80 mg/L, 140 mg/L, 200 mg/L, 300 mg/L, 400 mg/L along with a fixed dose of H_2O_2 (5 mL/L of 30% H_2O_2).

The addition of ferrous sulphate and hydrogen peroxide resulted in the reduction of pH since the ferrous sulphate catalyst typically contains residual H_2SO_4. When the effluent was subjected to gamma radiation in the presence of Fenton's reagent, pH was found to decrease in all the cases as evident from Table 3.

This drop in pH could be attributed to the fragmentation of the organic molecules present in wastewater

Table 2

Influence of gamma radiation in presence of various reagents to remove pollutants

RE and the following reagents	pH		Percentage removal		
	Before	After	Turbidity (NTU)	COD	BOD
1	2	3	4	5	6
γ	4.15	4.20	45	23	64
γ + 200 mg/L of Fe	3.15	3.10	55	29	69
γ + 5 mL/L H_2O_2	4.15	4.15	–53	25	63
γ + 200 mg/L iron + 5 mL/L H_2O_2	2.9	2.80	82	36	73

Table 3

Effect of gamma radiation at various concentration of iron in Fenton's reagent

RE + H_2O_2 (5 mL/L + Fe (conc. given below)	pH		Percent removal			
	Before γ	After γ	Turbidity (NTU)	COD	BOD	Phosphate
1	2	3	4	5	6	7
RE + γ (without any reagents)	4.00	4.05	45	23	63	12
20 mg/L iron	3.90	3.80	87	29	70	17
80 mg/L iron	3.50	3.40	90	30	72	29
140 mg/L iron	3.25	3.15	92	31	74	35
200 mg/L iron	2.90	2.80	95	33	75	44
300 mg/L iron	2.75	2.70	95	33	74	46
400 mg/L iron	2.25	2.20	95	31	73	54

into organic acids as the reaction progresses. The effect of iron concentration in Fenton's reagent on the removal of turbidity showed that maximum turbidity removed was 95% when the concentration of iron was 200 mg/L to 400 mg/L. There was a steady increase in the removal of turbidity as the concentration of iron increased from 80 mg/L to 200 mg/L. Good sedimentation of coagulated particles was observed after irradiation and the wastewater became very clear.

The optimum dose of iron concentration in Fenton's reagent was assessed in terms of its efficiency to remove COD and BOD. It was observed that on incremental increase of Fe^{+2} dosages, an increase in the reduction of COD and BOD values was observed as is evident from Table 3 and maximum percentage removal of COD and BOD was obtained at a concentration of 200 mg/L of iron. At this concentration of iron in Fenton's reagent, 33% of COD and 75% of BOD were removed. A further increase in the concentration of iron (200 mg/L to 400 mg/L) had only a marginal impact. A higher concentration of iron catalyst results in an increased rate of generation of OH radical, which in turn limits the reaction rates with Fenton's reagent. A constant ratio of Fe to substrate above the minimal threshold level produced the desired end products. The ratio of iron to substrate ay affect the distribution of reaction products; and a supplemental aliquot of Fe, which saturates the chelating properties in the wastewater, makes available unsequestered iron to catalyse the formation of hydroxyl radicals (Walling, 1975). Since the pollution load is very high in skim serum wastewater, a concentration of 200 mg/L of iron could be taken as the optimum concentration in Fenton's reagent to treat this effluent.

In the case of phosphate, the removal efficiency increased as the concentration of iron increased from 20 mg/L to 400 mg/L. Without Fenton's reagent, phosphate removal efficiency was only 12% and it increased from 17% to 54% when iron concentration in Fenton's reagent increased from 20 mg/L to 400 mg/L. As the concentration of iron increased, it combined with the phosphate and was removed as iron phosphate.

Effect of gamma radiation at various concentration of H_2O_2 in Fenton's reagent

The effect of different concentrations of hydrogen peroxide on raw effluent in the presence of 200 mg/L of iron and gamma ray was investigated by adding 5 mL/L to 30 mL/L of 30% H_2O_2 to the effluent and irradiating it with a dose of 2.5 kGy. The optimum dose of H_2O_2 was 10 mL/L in the presence of 200 mg/L of iron since the highest removal of turbidity, COD, BOD and phosphate took place at this dose (Table 4).

A high ratio of Fe^{+2} and H_2O_2 was needed for chain initiation as shown in Eq. 1 (Rivas et al., 2001).

Table 4

Effect of gamma radiation at different concentrations of H_2O_2 in Fenton's reagent

| RE + 200 mg/L of Fe + γ + H_2O_2 (Conc. given below)	pH		Percentage removal			
	Before γ	After γ	Turbidity (NTU)	COD	BOD	Phosphate
1	2	3	4	5	6	7
5 mL/L	2.75	2.8	75	33	71	43
10 mL/L	2.70	2.8	82	35	77	46
20 mL/L	2.70	2.8	66	35	75	5
30 mL/L	2.25	2.3	40	30	75	2

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^* + OH$$
$$K_1 = 70 \ m^{-1}s^{-1} \ (\text{chain initiation}) \qquad (1)$$
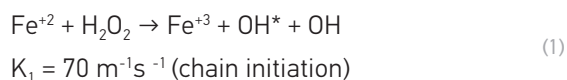
At low concentrations of H_2O_2, the radical chain reactions are quickly terminated since OH radicals produced mainly react with the ferrous iron and not with hydrogen peroxide (Buxton et al., 1988).

$$OH^* + Fe^{+2} \rightarrow OH^. + Fe^{+3}$$
$$K_2 = 3.2 \times 10^y \ m^{-1}s^{-1} \ (\text{chain termination}) \qquad (2)$$
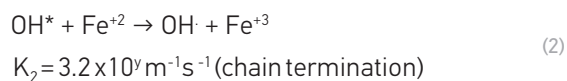
Excess of H_2O_2 reacts with OH^*, thus scavenging hydroxyl radicals by H_2O_2 and consequently reducing the efficiency of treatment as shown in Eq. 3. The oxidation rate seems to be negatively affected by the increase of H_2O_2 concentration.

$$OH^* + H_2O_2 \rightarrow H_2O + HO_2 \qquad (3)$$

The higher percentage degradation efficiency is that hydroxyl radicals can oxidise organic pollutants by abstraction of hydrogen producing organic radicals which are highly reactive and can be further oxidised (Walling and Kato, 1971).

$$RH + {}^*OH \rightarrow H_2O + R^* \qquad (4)$$

A higher concentration of H_2O_2 reacts with the highly potent OH^* radicals to produce perhydroxyl radical OH_2, which has low oxidation potential than OH^* radical.

As the concentration of H_2O_2 increased, a sudden fall of phosphate removal took place (from 46 to 5 and 2 % for 10 mL/L to 20 mL/L and 30 mL/L, respectively). This might be due to the interference caused by the excess perhydroxyl radical OH_2 produced by the addition of a high amount of H_2O_2 during the formation of iron phosphate. Formation of a large amount of froth was observed when the concentration of hydrogen peroxide increased from 10 mL/L to 30 mL/L due to the evolution of gases like CO_2, H_2 and O_2.

From these studies, it was concluded that the optimum doses of iron and hydrogen peroxide needed in Fenton's reagent to treat skim serum effluent were 200 mg/L and 10 mL/L, respectively.

Effect of gamma radiation on pollutant removal at different concentration levels of wastewater

Raw effluent of different concentrations like 100%, 75%, 50% and 25% was prepared by diluting raw effluent with distilled water, and pH was adjusted to 4 and placed in a gamma chamber for gamma radiation having a dose of 2.5 kGy. The effect of gamma radiation on different concentrations of effluent was then analysed in terms of COD, BOD and phosphate removal.

The highest COD, BOD and phosphate removal were obtained for undiluted effluent. When the concentration of effluent decreased from 100% to 25%, COD removal

Fig. 6

Percentage removal of COD, BOD and PO$_4$
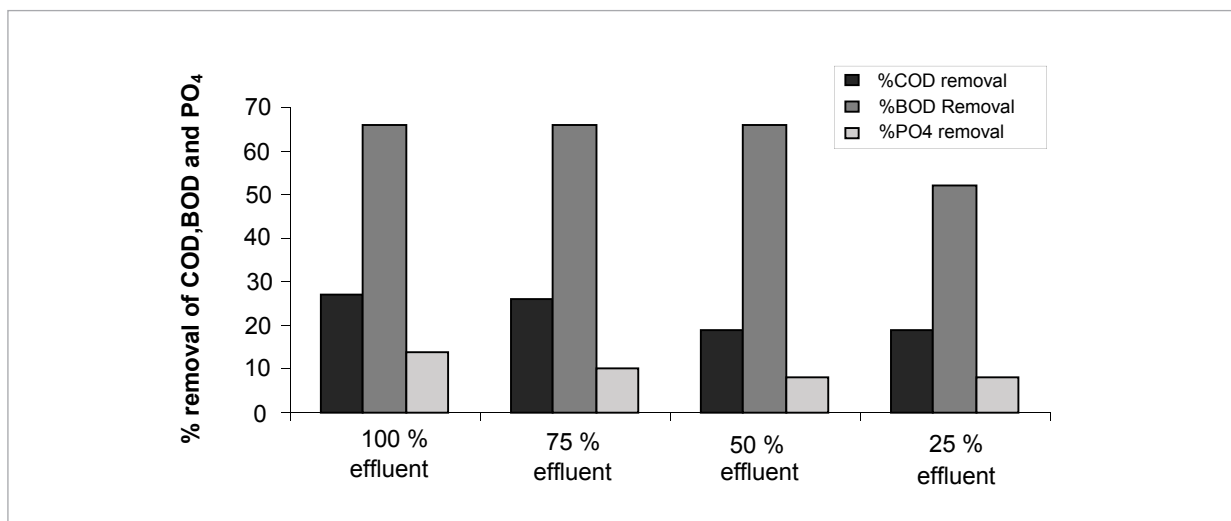
decreased from 27% to 19%. However, BOD removal was 66% for dilution up to 50% effluent concentration, which declined to 52% for the 25% effluent concentration (Figure 6). In the case of phosphate, there was a steady decrease from 14% to 8% removal for the concentration change from 100% to 25%. As dilution increases, the effective number of ions per mL that can be degraded by gamma radiation also decreases.

Effect of gamma radiation and Fenton's reagent on anaerobically treated effluent (ATE)

Effect of gamma radiation and various reagents on ATE

When ATE effluent was subjected to gamma irradiation of 2.5 kGy without Fenton's reagent, 55% of turbidity, 29% of COD, 45% of BOD and 27% of sulphide were removed. However, when treated with Fenton's reagent alone (without gamma irradiation), 100% of turbidity, 35% of COD, 59% of BOD and 89% of sulphide were removed. This shows that Fenton's reagent has good capability to remove sulphide and turbidity. Compared with raw wastewater, anaerobically treated effluent showed higher removal efficiency of pollutants while subjected to gamma radiation in the presence of Fenton's reagent (Table 5). In the anaerobic reaction, organic molecules are degraded by hydrolysis,

fermentation and methanogenesis into simple monomers, acetate, hydrogen, methane and carbon dioxide (Metcalf & Eddy, Inc., 2003), and this enhances the removal of COD and BOD compared with raw effluent.

As the concentration of iron in Fenton's reagent increased from 20 mg/L to 200 mg/L, percentage removal efficiencies of COD increased from 41 to 77, BOD from 57 to 96, sulphide from 52 to 95 and TKN from 16 to 19. The values remained almost constant for further increase in the concentration of iron to 400 mg/L. However, its effect on AN was not so prominent. In all treatments where Fenton's reagent was used, 100% removal of sulphide could be achieved.

Effect of pH and Fenton's reagent on radiation treatment of anaerobically treated effluent

To study the effect of pH and gamma radiation in the presence of Fenton's reagent on ATE, pH of the ATE was adjusted to 2.5, 3, 5, 7 and 8. To each of these sets, 5 mL/L of H$_2$O$_2$ and 200 mg/L of iron were added and irradiated with 2.5 kGy. From Table 6, it is evident that 97% of turbidity, 72% of COD, 88% of BOD and 100% of sulphides were removed at pH 3. This was the maximum reduction of pollutants obtained when anaerobically treated effluent was subjected to gamma irradiation in the presence of Fenton's reagent at various pH.

Table 5

Effect of gamma radiation and various reagents on ATE

Reagent type ATE	pH		Percentage removal					
	Before γ	After γ	Turbidity (NTU)	COD	BOD	Sulphide	TKN	AN
1	2	3	4	5	6	7	8	9
ATE + γ (Without reagent)	7.8	8	55	29	45	27	8	6
ATE + 200 mg/L Fe + 5 mL/L H_2O_2 (without γ)	3.25	3	100	35	59	81	12	8
ATE + 20 mg/L Fe + 5 mL/L H_2O_2 + γ	3.75	3.5	100	41	57	52	16	8
ATE + 80 mg/LFe + 5 mL/L H_2O_2 + γ	3	2.9	100	54	80	64	18	9
ATE + 140 mg/L Fe + 5 mL/L H_2O_2 + γ	3	2.9	100	66	81	83	19	9
ATE + 200 mg/L Fe + 5 mL/L H_2O_2 + γ	2.7	2.6	100	77	96	95	19	10
ATE + 300 mg/L Fe + 5 mL/L H_2O_2 + γ	2.6	2.5	100	76	95	94	19	10
ATE + 400 mg/L Fe + 5 mL/L H_2O_2 + γ	2.6	2.5	100	77	96	92	19	10

Table 6

Effect of pH and Fenton's reagent on radiation treatment of ATE

pH before	pH after	Percentage removal			
		Turbidity (NTU)	COD	BOD	Sulphide
1	2	3	4	5	6
2.5	2	97	70	86	100
3	2.3	97	72	88	100
5	4.5	63	68	76	99
7	7.4	98	33	74	95
8	8	98	23	75	77

Previous studies using Fenton's reagent showed that pH near 3 was optimum for Fenton oxidation (Rivas et al., 2001). At higher pH, the ferric ions form Fe(OH)$_3$, which has a low activity and does not react with hydrogen peroxide[31]

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^* + OH \qquad (5)$$
$$2\,Fe^{+2} + H_2O_2 + 2\,H^+ \rightarrow 2\,Fe^{+3} + 2\,H_2O \qquad (6)$$

The pH value influenced the generation of *OH radicals and, thus, increased the oxidation efficiency. The precipitation of iron occurs as its hydroxide reduces the availability of Fe^{+2} and, hence, oxidation transmission (Faust & Hoigne, 1990, Walling, 1975). The need of H$^+$ ion to decompose H$_2$O$_2$ is evident from Eq. 6 indicating the necessity for an acidic environment to produce the maximum amount of hydroxyl radicals.

Biochemical analysis of the radiated effluent

Biochemical analysis of raw and irradiated wastewater was done by estimating the change in the concentrations of soluble protein, phenols, total and reducing sugars and free amino acids. The soluble protein concentration of raw effluent (RE) was 865 mg/L. Removal efficiency for soluble protein increased from 38.8% to 47% as the dose of radiation increased from 2.5 kGy to 50 kGy (Table 7).

Addition of Fenton's reagent alone removed 36.3% of soluble protein. However, gamma radiation of 2.5 kGy in the presence of Fenton's reagent removed 87% of soluble protein. In the case of phenol, the maximum removal efficiency for a radiation dose of 2.5 kGy was 25%. As the dose of radiation increased from 2.5 kGy to 50 kGy, an unusual increase in the concentration of phenol than the original one was observed. It is reported that the first step in the phenol decomposition by radiolysis and photo catalysis is oxidation of phenol forming various aromatic intermediates, such as hydroquinone, catechol, pyrogallol and hydroxyhydroquinone (Hashimoto et al., 1979). The hydroxyl radicals produced during radiolysis might have combined with some of the organic molecules producing phenols. However, in the presence of Fenton's reagent alone and a combination of Fenton's reagent and gamma radiation, phenol removal efficiency was 43% and 48%, respectively.

Gamma radiation could remove 36.5% to 67.6% of total sugar when the dose of radiation increased from 2.5 kGy to 50 kGy. Nevertheless, the presence of Fenton's reagent and gamma radiation increased the concentration of total sugar from 1,250 mg/L to 1,567 mg/L. Estimation of reducing sugar and non-reducing sugar also showed unusual values by the simultaneous effect of Fenton's reagent and gamma radiation. This may be due to the decomposition of big organic molecules to small sugar molecules in the presence of Fenton's reagent and gamma radiation.

Table 7

Results of biochemical analysis

No	Sample details (γ in kGy)	Soluble protein	Phenol	Total sugar	Reducing sugar	Non-reducing sugar	Free amino acid
1	2	3	4	5	6	7	8
1	RE	865	586	1,250	1,095	155	15,952
2	RE + 2.5 γ	529	440	793	666	127	11,633
3	RE + 50 γ	458	710	405	317	88	14,929
4	RE + FR	551	335	456	267	189	20,082
5	RE + FR + 2.5 γ	110	307	1,567	2,912	203	17,556
6	ATE	289	45	56	36	20	5,779
7	ATE + 2.5 γ	nil	52	nil	nil	nil	7,726
8	ATE + 3.5 γ	nil	60	nil	nil	nil	5,145
9	ATE + FR	nil	22	nil	nil	nil	5,650
10	ATE + FR + 2.5 γ	nil	27	nil	nil	nil	6,442
11	ATE + FR + 5 γ	nil	27	nil	nil	nil	6,123

Abbreviations used: RE – raw effluent; ATE – anaerobically treated effluent; γ – gamma radiation; FR – Fenton's reagent. All values are expressed in mg/L

The initial concentration of free amino acids was 15,952 mg/L. For a radiation dose of 2.5 kGy, 27% removal was possible. As the radiation dose increased further from 2.5 kGy to 50 kGy, free amino acid removal decreased to 6.4%. However, the addition of Fenton's reagent alone and with gamma radiation resulted in an increase in the concentration of free amino acids to 20,082 mg/L and 17,556 mg/L, respectively. An increase in free amino acids concentration may be due to the decomposition of proteins into individual amino acids in the presence of Fenton's reagent and gamma radiation.

Soluble protein was completely removed when anaerobically treated effluent was subjected to radiation at a dose of 2.5 kGy in the presence of Fenton's reagent. Phenol concentration was found to increase from 45 mg/L to 52 mg/L and 60 mg/L for the gamma radiation dose of 2.5 kGy and 3.5 kGy. However, when treated with Fenton's reagent, phenol concentration decreased by 51% and the combined effect of Fenton's reagent and gamma radiation removed only 40% of phenol. Almost complete removal of total sugar as well as reducing and non-reducing sugars was possible when anaerobically treated effluent was subjected to irradiation. Estimation of free amino acid showed an increase from 5,779 mg/L to 7,726 mg/L when anaerobically treated effluent was subjected to a radiation dose of 2.5 kGy. This may be due to the complete decomposition of proteins leading to the formation of amino acids. When the dose was increased to 3.5 kGy, amino acid content decreased from 5,779 to 5,145. Again, its concentration increased to 6,442 mg/L and 6,123 mg/L, respectively, when treated with Fenton's reagent and a combination of Fenton's reagent with gamma radiation. These changes may be due to the formation of radicals and the cleavage of carbon-carbon, carbon-hydrogen, carbon-oxygen and carbon-nitrogen bonds under high-energy radiation.

Microbiological analysis of gamma irradiated effluent

The total bacterial count of raw as well as irradiated effluent was found out by culturing the samples. The results are given in Table 8. Gamma irradiation having

Table 8

Results of bacteriological analysis

No	Sample (γ in kGy)	Total bacteria (cfu/mL)
1	2	3
1	RE	27×10^4
2	RE + FR	2×10^3
3	RE + FR + 2.5 γ	nil
4	RE + 2.5 γ	nil
5	ATE	19×10^5
6	ATE + 0.5 γ	13×10^4
7	ATE + 1 γ	6×10^4
8	ATE + 1.5 γ	23×10^3
9	ATE + 2 γ	60×10^2
10	ATE + 2.5 γ	46×10^2
11	ATE + 3 γ	30×10^2
12	ATE + 3.5 γ	18×10^2
13	ATE + FR	4×10^4
14	ATE + FR + 2.5 γ	2×10^2
15	ATE + FR + 5 γ	1×10
16	ATE + FR + 10 γ	nil

Abbreviations used: RE – raw effluent; ATE – anaerobically treated effluent; γ – gamma radiation; FR – Fenton's reagent. All values are expressed in mg/L

a dose of 2.5 kGy in the presence or absence of Fenton's reagent completely removed total bacterial population of raw effluent.

Anaerobically treated effluent when subjected to gamma irradiation having a dose of 2.5 kGy in the presence or absence of Fenton's reagent did not remove total bacteria completely. The radiation dose of 5 kGy to 10 kGy in the presence of Fenton's reagent was needed to remove bacteria completely from the anaerobically treated effluent.

Conclusion

1 The gamma radiation dose of 2.5 kGy could be taken as the optimum dose of radiation to treat raw skim serum wastewater.

2 For effective pollutant removal along with the optimum gamma radiation dose, 200 mg/L of iron and 10 mL/L of H_2O_2 could be taken as the optimum concentration of iron and H_2O_2 in Fenton's reagent. Phosphate removal efficiency was found to increase as the iron concentration in Fenton's reagent increased to 400 mg/L.

3 The effect of irradiation was more prominent in the presence of Fenton's reagent. pH around 7 could be taken as the optimum pH to treat raw effluent using gamma radiation, but pH around 3 was most effective for gamma irradiation along with Fenton's reagent.

4 Anaerobically treated effluent could be more effectively treated using gamma radiation and Fenton's reagent. Sulphides present in the anaerobically treated effluent could be completely removed when irradiated in the presence of Fenton's reagent.

5 Biochemical analysis of the radiated effluent (raw) showed that 87% of soluble protein could be removed for a dose of 2.5 kGy in the presence of Fenton's reagent. In the presence of Fenton's reagent and gamma radiation, 48% of phenol was removed. For anaerobically treated effluent subjected to the gamma radiation dose of 2.5 kGy, soluble protein was completely removed. With Fenton's reagent, phenol concentration could be reduced by 51%, and almost complete removal of total sugar as well as reducing and non-reducing sugars was achieved.

6 The gamma radiation dose of 2.5 kGy, irrespective of the presence of Fenton's reagent, could completely remove total bacterial population of raw effluent. In the case of anaerobically treated effluent, the addition of Fenton's reagent in combination with a radiation dose of 5 kGy to 10 kGy was needed to remove bacteria completely.

Acknowledgement

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Natūralaus kaučiuko latekso centrifugavimo metu susidariusių nuotekų apdorojimas spinduliuote

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Natūralaus kaučiuko latekso centrifugavimo proceso metu susidariusios serumo nuotekos yra labai teršiamos. Anaerobiniu būdu išvalytos nuotekos taip pat buvo apdorotos ir gama spinduliuote. Tokiam nuotekų apdorojimui buvo taikomi skirtingi Fenton reagento ir skirtingų dozių gama spinduliuotės deriniai. Nuotekų išvalymo veiksmingumas buvo įvertintas pagal pH, drumstumą, cheminį deguonies poreikį, biocheminį deguonies poreikį, bendrą Kjeldahlio azotą, amoniakinį azotą, bendras kietas medžiagas, ištirpusias kietas medžiagas ir sulfidą. Biocheminių sudedamųjų dalių koncentracijos pokyčiai ir bendro bakterijų populiacijos skaičiavimai buvo naudojami nuotekų išvalymo efektyvumui įvertinti. Anaerobiniu būdu valomos nuotekos gali būti veiksmingiau apdorojamos gama spinduliuote su Fentono reagentu. Rezultatai parodė, kad daugelis biocheminių sudedamųjų dalių ir bakterijų populiacijų buvo visiškai pašalintos iš anaerobiniu būdu apdorotų nuotekų šiuo metodu.

Raktiniai žodžiai: gama spinduliuotė, apšvitinimas, gumos latekso centrifugavimas, nuotekų valymas, Fentono reagentas.