

RADIATION TREATMENT FOR RECYCLING OF INDUSTRIAL WASTEWATER FOR INDUSTRIAL USAGE - BIOLOGICAL AND IRRADIATION TREATMENT OF MIX INDUSTRIAL WASTEWATER IN FLOOD MITIGATION POND AT PRAI INDUSTRIAL ZONES

Khomsaton Abu Bakar ,Jamaliah Sharif , Sarala Selambakkanu, Ting Teo Ming , Natsha Isnin, Hasnul Nizam Osman, Khasmidatul Akma M.K Azmi, Khairul Zaman Hj Mohd Dahlan , Nasehir khan Em Yahya.

Malaysian Nuclear Agency (Nuclear Malaysia), Bangi, 43000 Kajang, Selangor, MALAYSIA.

Abstract

In this researched, activated sludge system and E-Beam was used to treat mixed industrial waste water from mitigation pond A. The objectives are to study the effect of hydraulic retention time (HRT) in activated sludge and effect of absorbed dose, current and energy to the characteristic of mix industrial wastewater and Di(2-ethylhexyl) phthalate(DEHP) added in the wastewater . DEHP is a type of plasticizer and quantified by GC-MS. Microbe identification in activated sludge was also carried out in this study. At 48hrs HRT, percentage reduction for COD, color, suspended solid were 62.3%, 36.7% and 67.1% respectively. While at 24hrs HRT, COD, color and suspended solid were reduce by 26.0%, 14.9% and 61.3% respectively. Microbial analysis showed six bacteria present in the activated sludge based on 16SrRNA gene sequences. Mixed industrial wastewater was irradiated using electron beam at 1Mev, 5mA and 10mA in a batch system with 3, 6, 8,10 and 12kGy doses. COD, color and suspended solid reduced with the increasing of absorbed dose. Mixed industrial wastewater added with DEHP in the second batch was irradiated with dose up to 300kGy. Concentration of DEHP also reduced with increasing of dose and more effectively decreased in acidic and aerated condition.

1. Introduction

Mixed industrial wastewater in holding pond pumping station A in Seberang Perai was derived from the treated effluent from various industries in the vicinity. The main industries that release their treated effluent into the holding pond are textiles, plastic, chemical/fertilizer and oleochemical. It can contain up to 1,500 m³ per day. The holding pond A is a flood mitigation step in the industrial area and as an immediate receiving water body prior to the release of the effluent into the sea. Effluent in the pond A was not treated with any treatment and the characteristic of wastewater differs from every time. In this study, sample was collected in September and December 2011 and also in January and April 2012. Another sample collected in July 2012 was treated with activated sludge only.

A lot of research activities on radiation application for wastewater treatment has been done especially in textiles industrial wastewater (B.Han et al.,2002; Kim et al., 2007). Gamma radiation for sewage treatment was also studied by (J.G.Graino, 2001;M.R.Shah et al.,2001). In this study, electron beam radiation was applied for treatment of mixed effluent industrial wastewater. Wastewater was irradiated with the same irradiation conditions(3,6,8and 12kGy) in previous study conducted in 2011. By doing this, effect of radiation on the characteristic of wastewater for the rest of the year can be identified. Additionally, wastewater was spiked with DEHP in different batch and irradiated with the same irradiation conditions. The purpose is to study the effect of e-beam irradiation on DEHP concentration. Di(2-ethylhexyl)

phthalate(DEPH) is widely used as a plasticizer in flexible vinyl products. Plastics may contain from 1 to 40% DEPH by weight and are used in consumer products such as rainwear, footwear, flooring wire and cable food packaging material and children's toys. DEHP was expected to have leached into Pond A because there are companies producing the above mentioned products nearby.

Mixed industrial wastewater was also treated using activated sludge system. This system consists of three basic components which are;

1. reactor in which the microorganisms responsible for treatment are kept suspended and aerated;
2. solid liquid separation, clarifier tank; and
3. a recycle system for returning sludge from clarifier back to the reactor.

Flow rate of the influent into the reactor was varied to obtain different hydraulic retention time. Identification of microbe present in the reactor was done by private laboratory.

2. Materials and Method

2.1. Sample preparation

Mixed industrial wastewater was collected from the centre pump house A, as shown in fig.1. Mixed industrial wastewater was screened to segregate solid material such as sand, rubbish and grass prior to the treatment. Samples pH was adjusted to pH 6.5 to pH 8.5 prior to biological treatment. The pH for samples treated with radiation will not be changed.

2.2. Radiation Treatment

In order to irradiate, the samples were filled in a tray and placed on a trolley and transported into the irradiation chamber. Irradiation of samples was conducted using EPS3000 EB machine in a batch system. The first batch consists of mixed industrial wastewater only and second batch consists DEPH in mixed industrial wastewater. Speed of conveyor and beam current (mA) were adjusted according to irradiation dose required. The irradiation doses selected for this study were 3kGy, 6kGy, 8kGy and 12kGy for the first batch while doses were increased to 50kGy, 100kGy, 150kGy, 200kGy and 300kGy for the second batch. The current used for dose 3kGy was 5mA and current used for 6-12kGy was 10mA whereas 30mA current was used for dose 50-300kGy. The variations in current were to ensure compatibility of the conveyor speed with irradiation dose acquired.

2.2.1. Extraction of DEPH

The procedure in this method involves the use of separating funnel (1000ml). n-Hexane (purity 97%) purchased from Merck Chemicals was used for extracting DEHP from water samples. 1:4 ratio was used for water sample and hexane for extraction. After mixing, the funnel was gently turned from vertical to a horizontal position and shaken vigorously. The stopcock was opened and closed quickly to release the pressure built up from solvent vapor. This process was repeated until no further vapor is released when the stopcock is opened. The funnel was placed in the holder (ring on ring stand) and left overnight to allow the liquids to stand until the layers were completely separated. The lower layer was drawn out followed by upper layer into two beakers. The upper layer which consists of hexane and DEHP was filtered to remove the dirt from the water samples. A small amount of sodium sulphite, anhydrous (Na_2SO_3) was placed on the filter paper to absorb any element of water that might

be present in the extracted solvent. Water is capable of destroying the GC-MS column. The filtered solvent was dried in a fume chamber to obtain DEHP.

2.2.2. GC-MS Analysis

DEHP was analyzed using Finnigan Trace GC Ultra with flame ionization detector (GC/FID) equipped with auto-sampler, an on-column, splitless capillary injection system with Finnigan Trace GC Ultra capillary column (30m x 0.25mm x 0.25 μ m film thickness). The operating condition is as follows:

- the column was maintained at a temperature of 50⁰C for 1.5 min
- the temperature was increased to 270⁰C with an incremental rate of 20⁰C /min.
- the temperatures of the injector and detector were maintained at 260⁰C and 280⁰C respectively.
- Helium was used as a carrier gas at a flow rate of 1.0 mL/min
- and the injection of sample was 2.0 μ L.

2.2.3. MS Condition

1. Ion Source Temperature: 200⁰C
2. Interface Temperature: 300⁰C
3. Start m/z: 5.00
4. End m/z: 30.00

2.3. Biological Treatment

The Lab scale activated sludge system was made with acryl. It consisted of equalization tank(10L), aeration tank(4L) and clarifier(4L). Wastewater was fed into aeration tank and transferred into clarifier with a peristaltic pump. The water was aerated with diffusers that were connected to small aquarium pump to maintain dissolved oxygen (DO) concentration above 4mg/l in the aeration tank. The dissolved oxygen was monitored daily by a DO meter in the aeration tank. Parameters such as pH, and mix liquor suspended solid were controlled in this system to ensure that the system worked. The process run continuously in order to determine steady state condition.

2.3.1. Microbe identification

One ml sample was taken from reactor tank and diluted with sterile distilled water. Tryptonesoyar agar (TSA) acts as medium for the growth of the microbes. Then, a loop was used to transfer small amount of sample onto the petri dish containing TSA medium. The petri dishes were placed in the incubator at temperature of 30⁰C. The plates were incubated about half a day. Isolation of single colony was done using the same technique and repeated until single colony appeared. Petri dishes containing single colony were sent to other lab for microbial analysis and identification using 16S rRNA Gene Sequences.

2.4. Analysis

Samples were analysed before and after irradiation. COD is equivalent to the amount of oxygen required to chemically oxidize the organic matter contained in wastewater. To determine the COD, sample was first digested using dichromate (HR range plus) in Hach reactor and COD value was determined by Hach-2400 spectrophotometer. pH of the sample

was analyzed using pH meter (WTW Multi 340i). Hach DR 5000 spectrophotometer was used for color measurement. Turbidity was measured by turbidity meter and suspended solid was analyzed according to APHA method.



Fig 1. Inlet of a Pump A house.

4. Result and discussion

4.1. Mixed-industrial Wastewater Characteristics in the Holding Pond Pumping Station A

The results indicated that the nature of the water changed every month as expected. These changes depended on the activities surrounding the plant and climatic factors such as rain and sunshine. Table 1 shows the compliance or non compliance to Malaysia Standard Environment Quality Act (Industrial Effluent) Regulation 2009. The pH for all the samples complied to the Act (pH5.5-pH9.0). Whereas only samples taken in September 2011 complied to the COD standard value of 100mg/l. Table.1, also shows significant difference between the values of COD and BOD₅. It seemed that the wastewater may contain substances that are quite difficult to treat such as chemicals. Properties of wastewater in Dec. were higher as compared to other months and this is normal scenario during rainy season, where industries discharged untreated effluent into drain and flow into the Pond A. From the overall result, it shows that there is a need to lower the COD value to comply with the set standard.

TABLE 1: WASTEWATER CHARACTERISTICS IN THE HOLDING POND PUMPING STATION A.

Parameters	Sept.11	Dec.11	Jan.12	Apr.12
pH	6.48	8.05	7.22	6.98
COD(mg/l)	45	135	124	106
BOD(mg/l)	-	6	12	11
Suspended solid(mg/l)	37	237	55	46
Color (ADMI)	14	74	19	77
Turbidity (NTU)	7.8	25.3	4.8	26.2

4.2. Effect of radiation on characteristics of effluent (holding pond pumping station A)

4.2.1 Effect of irradiation on COD

Figure 1,2 and 3, show the COD, suspended solid and color were higher in sample collected in December as compared to other months. December is rainy reason, and this result showed similar trend to the study conducted by (Norli 2003) due to the wash out from all over factories flowing into the holding pond. Other reason was that all substance raised from the bottom of the pond caused turbulence during rain and illegal discharged of untreated wastewater from premises.

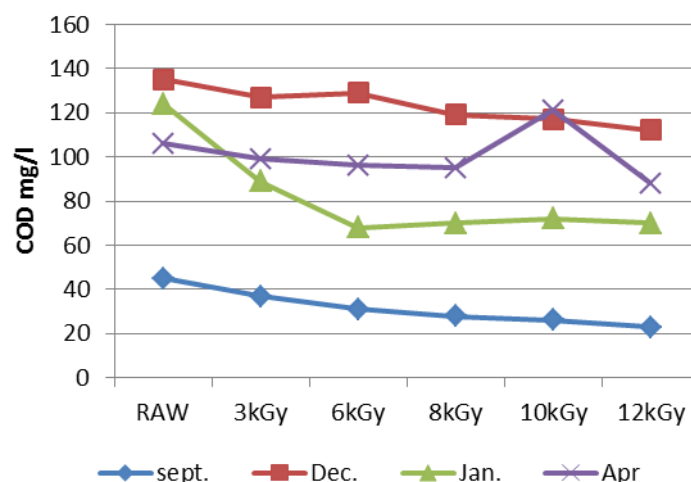


Fig.2. Effect of radiation on COD sample in specific months.

In general, the value of COD decreased when dose is increased for samples collected at different months (Fig.1). This is due to the degradation of organic pollutant with active radical produced in the water during irradiation. The average reduction in COD is 35.6% for sample in September, 10.5% for December, 40.5% in January and 43.4% for sample in April, as the samples were exposed to the doses between 3kGy to 12kGy. Sample in December with highest COD value showed less percentage reduction. This indicated that COD removal efficiency was dependent on the initial concentration of COD.(Teo Ming 2008).

4.2.2 Effect of Beam current on COD

Effect of beam current on characteristic of wastewater can be seen by comparing the properties of wastewater at dose 3kGy and 6kGy. This was because 5mA beam current was used to irradiate sample at 3kGy dose while 10mA beam current was applied to obtain 6kGy dose. The average reduction in COD is 14.6% for all samples irradiated with 5mA beam current at 3kGy. The COD value reduced by 22.5% for sample irradiated with 10mA beam current at dose 6kGy. More electrons were produce at higher beam current that will react with the wastewater to form more reactive species such as OH., H.and e_{aq}^- through radiolysis of water. More reactive species at higher beam current had improved the efficiency of COD removal compare to lower beam current.

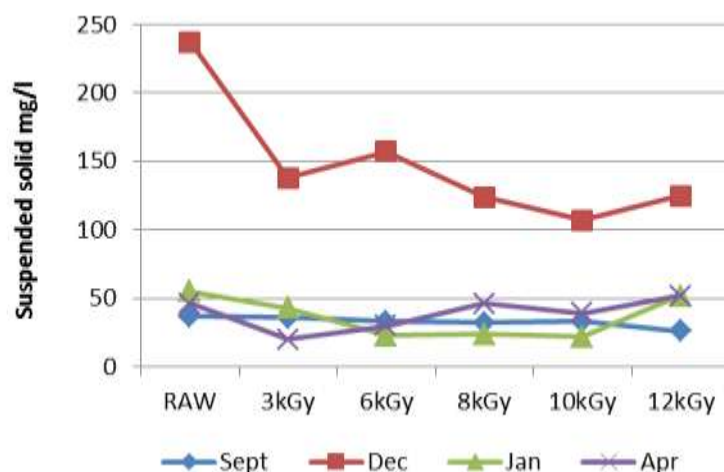


Fig.3. Effect of radiation on suspended solid sample in specific months.

4.2.3. Effect of radiation on suspended solid

Suspended solid in mixed industrial wastewater shows inconsistency trend when it is subjected to e-beam radiation as shown in figure 2. Significant reduction of suspended solid is shown by sample collected in December 2011. The average reduction for this sample is 45.1%. Inconsistent trend of suspended solid as the dose increased may be due to transformation of pollutant degradation. Many organic pollutants can be transformed into insoluble or sparingly soluble compounds upon irradiation, to form higher weight product [Ponomarev et.al1999; Pikaev et.al. 1977]. Normally, organic compounds having a molecular weight of more than 200 amu have low solubility. Statement above may explain the inconsistent trend of suspended solid for sample in September, January and April.

4.2.4. Effect of radiation on Color removal

Significant reduction of color occurred for the December 2011 and April 2012 samples [Fig.3]. The average reductions are 56.8% and 59.5% for December 2011 and April 2012 respectively. Destruction of chromophore bond and benzene ring contribute to decoloration (Cs.M.2009). No changes of color occurred after irradiation at dose between 3kGy and 12kGy for samples in January 2011 and September 2012. This was possibly because the color causing-compound does not present in the mixed industrial wastewater. Generally, the molecule of organic compound in the wastewater was in the simple form, without chromophore bond or benzene ring in the molecules. This explains the process of mineralization that occurs directly without the process of degradation and resulting in COD reduction in Fig.1.

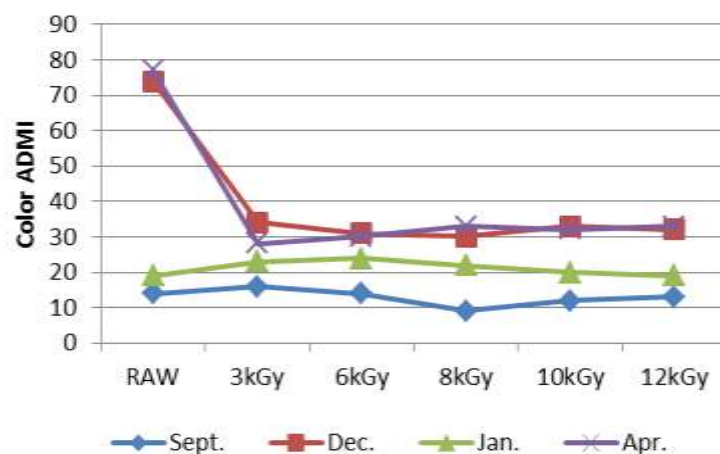


Fig.4 . Effect of radiation on suspended solid sample in specific months.

4.2.5. Effect of irradiation on DEHP concentration.

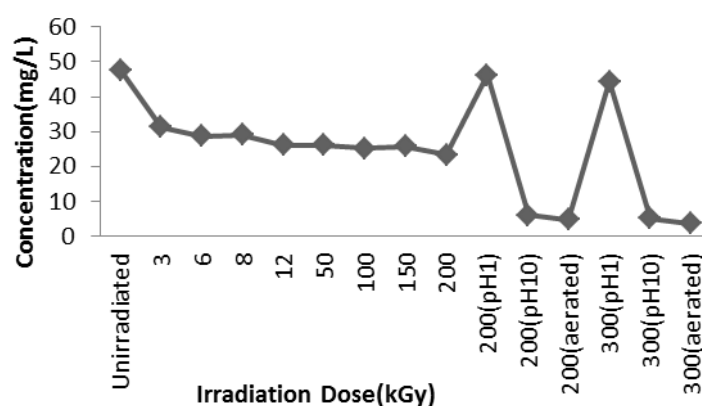


Fig.5. DEHP concentration at various dose and conditions.

The initial DEHP found in industrial wastewater was 47.62mg/L. After irradiation the concentration of DEHP depletes gradually especially when irradiation doses increases. The highest percentage of reduction was found in the sample aerated overnight before irradiation at 300kGy. The reduction percentage was 84%. Hydroxyl radical (reactive species) formed through radiolysis of water is responsible for decomposition of pollutants. Hydroxyl radical produced will attack the aromatic molecules and produce intermediates (Getoff, N., 2002). The higher the dose, more OH radicals are produced and hence there is an increase in the reduction of DEHP concentration. Aeration will provide more oxygen to the water samples. The oxygen molecules make the radiolysis process more effective during irradiation. Significant reduction was observed in the peak area as dose of irradiation increases.

4.3. Characteristic of mixed industrial wastewater after treatment in activated sludge

4.3.1. Effect of 48 hours hydraulic retention time on water properties for 14 days in the biological treatment.

Hydraulic retention time in the reactor was 48 hours and the process was continued for 14 days to determine the steady state condition which means the effluent showed constant value

of COD, suspended solid and color. Within 48 hours retention, there were reduction of 62.3%, 67.1% and 36.7% for COD, suspended solid and color respectively. These values more or less become constant on the eighth day. This means, the microbes that used, was able to mineralize some of the organic material within 48 hours. The COD and suspended solid removal further increased to 65.8% and 89.0% on day ten to fourteen. This may be due to the destruction of complicated molecule structure of organic compound at the beginning (2,4,6 and 8 day) to form simple molecule on the day ten. Destruction of complicated molecule structure may be described as high color removal rate occurred on the second day to day eight as compared to day ten to fourteen.

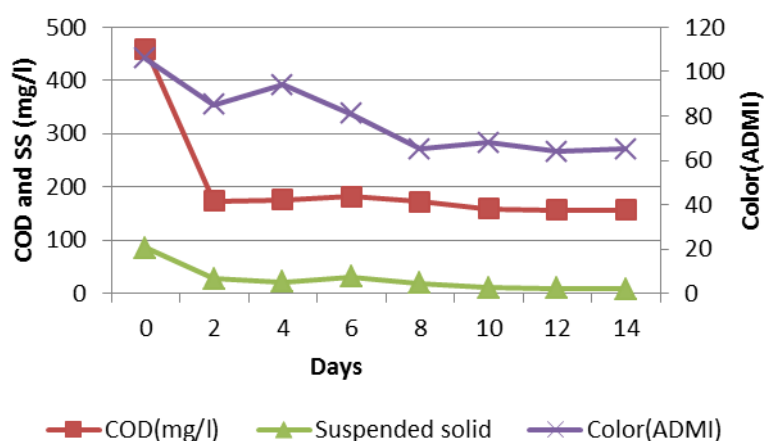


Fig.6. Water characteristics of sample after 14 days treatment in biological treatment.

4.3.2. Effect of 24 hours hydraulic retention time on water properties for 14 days in the biological treatment

Fig.7 (a), (b) and (c) show the COD, suspended solid and color of the effluents after the activated sludge process. There are little significant reduction for COD(a) and color((c) except for suspended solid. The average reduction of COD, suspended solid and color were 26.3%, 62.3% and 17.0% respectively. Although the results show a small reduction of COD, suspended solid and color, it was observed that a steady stage for parameter tested was obtained on day twelve onwards.

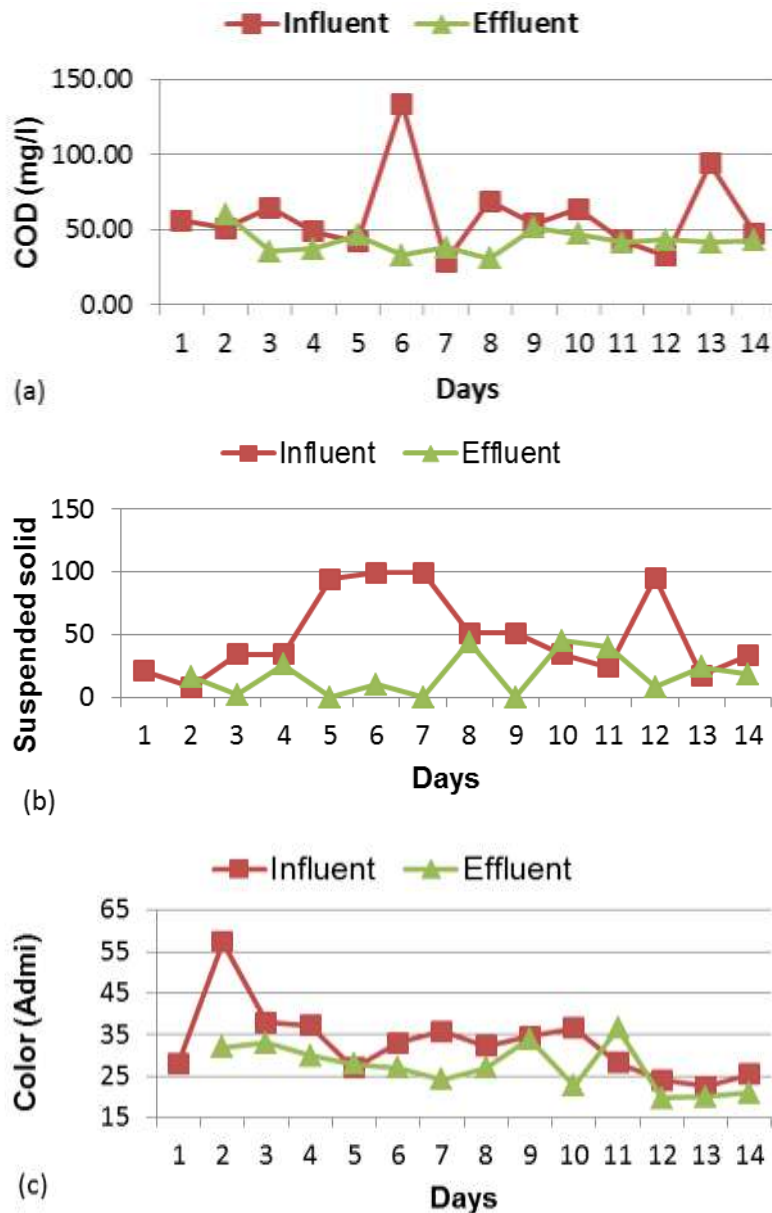


Fig.7. Effect of HRT on COD, suspended solid and color of mix industrial wastewater during 14 day treatment in activated sludge system.

4.3.3. Effect of HRT on characteristic of effluent in activated sludge process.

From Table.2, it is shown that the removal efficiency was lower for tested conditions when the HRT is at 24 hours. As the HRT decrease from 48 hours to 24 hours, the COD removal efficiency decreased from 62.3% to 26.3%. A decrease of HRT for the activated sludge process means an increase in substrate loading for the microbes. At the HRT 48h, the substrate loading is low and the retention time is enough to treat the substrate in the wastewater.

TABLE 2 SHOWS THAT REMOVAL EFFICIENCY OF COD, SUSPENDED SOLID AND COLOR FOR TWO DIFFERENT HRT

Hydraulic Retention Time (HRT) Hour	COD %	Suspended Solid %	Color %
48	62.3	67.1	36.7
24	26.3	62.3	17.0

4.4. Microbe Identification.

Bacteria identification was carried out once during the 15-days activated sludge operation where the sample was taken on day 8th. There are six bacteria presented in the reaction tank. However this research did not identify which bacteria that is responsible for pollutant degradation in activated sludge process.

TABLE 3. TYPES OF BACTERIA PRESENT IN THE REACTOR TANK DURING THE ACTIVATED SLUDGE PROCESS.

No.	Bacteria Name
1.	<i>Microbacterium ginsengisoli</i>
2.	<i>Rhizobium</i> sp
3.	<i>Azotobacter vinelandii</i>
4.	<i>Agromyces</i> sp.
5.	<i>Aeromonas caviae</i>
6.	<i>Shinella granuli</i>

5. Conclusion

E-beam radiation is capable of reducing COD in mixed industrial wastewater at lower dose, however the removal efficiency is dependent on the initial concentration of COD. Irradiation is also able to reduce DEHP concentration in wastewater and the reduction is better when aeration was introduced into wastewater prior to irradiation. In activated sludge treatment, the removal efficiency was lower for COD, suspended solid and color at HRT of 24 hours as compared to the HRT of 48 hours. Steady state was obtained earlier (day 8) for the 48 hours HRT, compared to day 12 for 24 hours HRT.

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