Effectiveness of Waste Stabilization Ponds in Removal of Linear Alkyl Benzene Salfonate (LAS).

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**Abstract**

Detergents contain synthetic or organic surface active agents called surfactants, which are derived from petroleum product precursors. They have the common property of lowering the surface tensions of water thus allowing dirt or grease adhered to various articles to be washed off. Linear alkyl benzene sulfonate (LAS) is an anionic surfactant most commonly used. Discharge of raw or treated wastewater containing this chemical into the environment causes major public health and enviromental problems. In this study, samples were taken from the raw wastewater and effluents of treatment ponds of Elzaraby waste stabilization ponds over a period of one year. The treated effluent is either discharged into surface waters or reused for agricultural irrigation. The samples were analyzed according to the standard methods. The results obtained from the samples taken in different seasons showed that the highest overall removal efficiency of LAS was achieved in the summer season (77%), and the least efficiency observed in the Winter season (55%), while the maximum overall efficiency of BOD5 was in summer (88%) and minimum efficiency was (73%) in winter season. The Dissolved oxygen concentrations along the pond series (DO) ranged between 0.18 to 4.8 mg/l.

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**1- Introduction**

Waste stabilization ponds (WSP) are large shallow basins enclosed by earth embankments in which raw wastewater is treated by entirely natural processes involving both algae and bacteria (Mara. 2004), WSPs are usually the most appropriate method for domestic and municipal wastewater treatment in developing countries, where the climate is most favorable for their operation. WSPs are low-cost, low-maintenance, highly efficient. The only energy they use is direct solar energy, so they do not need any electromechanical equipment, saving expenditure on electricity and more skilled operation. WSPs can be classified with respect to the types of biological activity occurring in a pond. Three types are distinguished; anaerobic, facultative and maturation ponds. Usually WSPs system comprises a single series of the aforementioned three ponds types or several such series in parallel (H. Ramadan and Victor 2011).

 Environment can be affected by waste water pollutants, such as surfactants (surface-active agents), which enter domestic wastewater treatment plants (WWTPs) through discharge into municipal sewage systems, and cause major public health problems. Surfactants in sewage are found as a result of the use of consumer products like detergents, cleaning and dish washing agents, and personal care products. Surfactants consisted mainly of four types; anionic (negatively charged group), nonionic (uncharged group), cationic (positively charged group) and amphoteric (positive and negative charged group) (Tsz. K. K, 2011). According to the data reported by Comite´Europe´en des Agents de Surface et de leurs Intermediaries Organiques (CESIO) (2004) that 998000 tons of anionics surfactants and 1231000 tons of non-ionics were manufactured during the year 2000 in the EU, these together account for about 90% of the total production of synthetic surfactants.

Linear Alkylbenzene Sulfonate (LAS) (Fig .1) is the most frequently employed synthetic anionics surfactants, whose production amounts to 1,040,000 t/year in the U.S.A., Jaban and, Western Europe (Matthew and Malcolm, 2000). After use, LAS are discharged via WWTPs into aquatic environments, sewage sludges after treatment are incorporation into soil as soil fertilizers. Venhuis and Mehrvar (2004) have reported that 0.02–1.0 mg/l of LAS in aquatic environment can damage fish gills, cause excess mucus secretion, decrease respiration in the common goby, and damage swimming patterns in blue mussel larva and LAS concentration of 40~60 mg/kg dry wt. of sludge interfere with the reproduction and growth of soil invertebrates and earthworms. Surfactants are also responsible for causing foam in rivers and effluents of treatment plants and reduction of water quality.



Fig. 1. General chemical structure of LAS, where x and y corresponds with the number of CH2 on each side of the benzene sulphonate group (7x+10y) (Liwarska-Bizukojc, Drews & Kraume, 2008)

 LAS mainly show eye and skin irritation potentials and damage human skin (Eagel et al., 1992). Under field conditions, LAS had acute effect on freshwater plankton and organisms including bacteria to crustaceans (Venhuis and Mehrvar, 2004). Range of LAS concentration in sewage of 3~21 mg/L has been reported (Hol t and Bernstein, 1992), while McAvoy et al. (1993), in USA, monitoring at 50 wastewater treatment facilities in eleven states showed average LAS levels in raw sewage ranging from 4.0 to 5.7 mg /l. LAS levels in raw sewage from five European countries ranged from 4.0 to15.1 mg /1 (DiCorcia et al., 1994; Feijtel et al., (1995)).

Physical and biological methods of sewage treatment partially remove LAS and prevent them from reaching the natural environments. The removal efficiency of LAS depends on the method of treatment. Mungray and Kumar (2007) found that removal efficiency of LAS in two WSPs in India were 88% and 47%. A removal efficiency of LAS more than 99% has been reported by several researchers for activated sludge process ASP. In case of up-flow anaerobic sludge blanket (UASB), the removal efficiency of LAS was found to be 30%, while In trickling filter based STPs, total removals were found to be lower and more variable than ASP It was found in USA, average removals of 83% (Trehy et al., 1996) and 77% (McAvoy et al., 1993).

The main objectives of this study is to evaluate the removal efficiency of LAS in an existing system of waste stabilization ponds (WSPs) in Elzaraby village, Abutig, Assiut governorate Egypt. Also some physical and biological characteristics of the waste water through the treatment plant are investigated.

**2-Material and Methods**

**2.1. Description of wastewater treatment plant**

A recent full-scale system of WSPs was constructed in 2009 in Elzaraby village in Upper Egypt. Elzaraby WSPs are designed to treat domestic waste water from Abutig city, with mean daily design flow rate of 16500 m3 /day. The physical characteristics of the ponds are given in Table 1. The wastewater after screening is used to feed two parallel anaerobic ponds (A1~A2). Each anaerobic pond has a square with shape 10790 m2 top water surface area and 4.4 m working depth. The two effluent of the anaerobic ponds is used to feed two facultative ponds (F1~F2) with top length of 292m, 166 m top width at the water level and 2.5 m working depth. The effluent from the facultative ponds passes through two parallel lines of maturation ponds. Each line comprising a first, second and third maturation pond, (M1~M6). Each of the maturation ponds has 164 m length and 115 m width at the top water level of ponds and working depth 1.5 m.The treated effluent is either discharged into surface water or reused for agriculture irrigation.

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| Ponds |  Dimensions (m)of the water body |  Design basis |
|  Bottom/top Length (m) |  Bottom/top Width (m) |  Water Depth (m) |  Water Volume (m3) | Flow rate (m3/day) |  HRT (day) |
| A1-A2 |  146/163.6 |  45.4/63 |  4.4 |  37257 |  8250 |  4.5 |
| F1-F2 |  277.8/288.8 |  154/164 |  2.5 |  112680 |  8250 |  14 |
| M1-M2 |  158/164 |  104/110 |  1.5 |  25854 |  8250 |  3.0  |
| M3-M4 |  158/164 |  104/110 |  1.5 |  25854 |  8250 |  3.0 |
| M5-M6 |  158/164 |  104/110 |  1.5 |  25854 |  8250 |  3.0 |

Table 1. Design basis for physical and operational characteristic of Elzaraby WSPs.

**2.2 Wastewater sampling**

Wastewater samples were collected monthly from the plant through a period of one years, from Spt. 2011 to Aug. 2012 to study the seasonal removal efficiency of LAS in natural WSPs, Monthly-samples of raw wastewater after screening and effluents from each type ponds were collected (S1to S5) as shown in ( Fig. 2) of the sampling points. The samples were collected in plastic containers of 2 litre capacity.



 Fig. 2. The layout of Elzaraby WSPs

The following parameter were studied; water temperature (T), pH value, dissolved oxygen (DO), biochemical oxygen demand (BOD5) and liner alkyl benzene salfonate (LAS). All analysis have been carried out according to standard methods for examination of water and waste water (APHA, 2005). LAS measurement in sampies of sewage as methylene blue active substance (MBAS) using the Spectrophotometer as prescribed in standard methods (APHA, 2005). pH value were measured using; multi meter with pH sensor. Determination of biochemical oxygen demand (BOD5) by; electronic pressure sensor (Oxidirect) apparatus, determination of dissolved oxygen (DO); multi meter with DO sensor.

3. RESULTS AND DISCUSSIONS

In this study, a complete one year monthly samples of wastewater were taken from WSPs of Elzaraby plant from locations S1~S5 totally 60 samples. The average seasonal values of T, pH, DO, BOD5 and LAS through the ponds were calculated.

3.1 Wastewater temperatures in the ponds

The wastewater temperature for the four season of the year from (Spt. 2011 to Aug. 2012) through the water pass in WSPs are illustrated in (Fig. 3). Measured temperatures of wastewater through the ponds were ranged between 18 0C and 35 0C. The maximum wastewater temperature in anaerobic ponds was 31.8 0Cin summer season while the minimum was 22.1 0Cinwinter season. In facultative ponds, the temperature were ranged between 20.1 0C to 30.6 0C in winter and summer, respectively. In the last maturation ponds the minimum and maximum temperature were 18 0C in winter and 27 0Cinsummer season.

Fig. 3. Wastewater temperature for different season through the wastewater

 pass in Elzaraby WSPs.

As shown in (Fig. 3), it is clear that the wastewater temperature decreases along the pass of the ponds and maximum temperature occurs in summer season . The decreasing rate is find to be much higher in the summer season (80C) than that in the winter season (4.40C), this due to the higher evaporation rate from the surface of the ponds which accomplished with higher latent heat in summer compared with that in winter season.

3.2 pH variations along the pond series

The average seasonal variation of the measured pH value for the raw sewage and effluent from each type of ponds in the period from Spt. 2011 to Aug. 2012 are presented in (Fig. 4). The average pH value of raw wastewater ranged between 6.63~7.4, while increased in anaerobic ponds to be 6.75 and 7.8 as minimum and maximum values in winter and summer seasons, respectively. In maturation ponds the measured pH recorded a maximum value in summer 8.8 and a minimum value in winter was 7.7.

As shown in (Fig. 4), the pH values of the ponds’ wastewater has it’s higher values in the summer season, and it increases along the wastewater pass with the highest values in the last maturation ponds. The increased of pH value in maturation ponds is due to rapid photosynthesis by the pond algae, which consumes Carbon dioxide (CO2 )faster than it can be replaced by bacterial respiration; as a result carbonate and bicarbonate ions dissociate. Algae fix the resulting CO2 from the dissociation while hydroxyl ions (OH-) accumulate so raising the pH value. Similar results were found by Mahmod et al .(2010).

 Fig. 4. Seasonal variation of pH value measured along Elzaraby WSPs.

3.3 DO concentration along the ponds series

 The seasonal concentrations of DO in raw wastewater were found to be between 0.11 to 0.25 mg/l as a minimum and a maximum values in spring and summer seasons, respectively, while seasonal values of DO increased in facultative ponds and recorded a range 1.36~2.5 mg/l in winter and summer season, and the average values of DO in the effluent of maturation ponds recorded 3.8, 3.6, 4.93 and 5.8 mg/l in autumn, winter, spring and summer seasons, respectively, as shown in (Fig. 5). It is clear that the value of DO in the summer season increases relative to the winter season, because the rate of algae photosynthesis and the cellular metabolism of microorganisms in the ponds are enhanced by high temperatures and retarded by low temperatures. Algal oxygen production is directly related to photosynthesis, which depends on temperature variations.

 Fig. 5. Seasonal concentration value of DO measured along Elzaraby WSPs.

From the figure, it is clear that the average concentrations of DO along the ponds series ranged from 0.11 mg/l in anaerobic ponds to 5.7 mg/l in the last maturation ponds. Similar results were reported by Nasr et al. (2007).

**3.3 BOD average seasonal concentration value**

For comparison the mean values of the measured unfiltreted BOD5 in different four seasons of the year are plotted as shown in (Fig. 5). The average concentration of BOD5 values in raw wastewater were ranged between 426.3 mg /l to 305 mg/l in summer and winter seasons respectively, while they recorded in anaerobic ponds 314~167.5 mg/l as a maximum and a minimum values. In facultative ponds BOD5 concentrations were found to be ranged between 275~111 mg/l, while the effluent of the last maturation ponds has BOD5 concentrations of 43.5, 51.5, 55 and 73.3 mg/l in autumn, winter, spring and summer seasons, respectively.

 Fig. 6. Seasonal concentration value of BOD measured along Elzaraby WSPs.

From (Fig. 6). It is clear that the maximum BOD5 values occur in the summer season, while the minimum BOD5 values are in the winter season. The reason of this phenomenon is that high air and water temperature and sun light intensity occurs in summer season relative to other seasons, which increased algal grow (Ali et al., 2005).

**3.4 LAS average seasonal concentration value**

Linear Alkyl Benzene Salfonate (LAS) concentrations at the sampling points were monthly measured in the period from Spt. 2011 to Aug. 2012for Elzaraby WSPs.

The average seasonal concentrations of LAS at the sampling locations are plotted as shown in (Fig. 7). LAS concentrations in raw wastewater recorded an average seasonal values as 6.2, 6.7, 11.9 and 14.8 mg/l in autumn, spring, summer and winter season, respectively. Sewers contain microbial populations capable of initiating LAS biodegradation and concentration of LAS in wastewater treatment plant WWTP influents depends on the length of the sewer, travel time and the degree of the microbial activity present in sewers (Matthijs et al., 1999). So the increased the LAS concentration in the winter season influent of the plant compared with other seasons is due to low water temperature which causing a low microbial activity in sewers. In Contrast, LAS concentration in the summer season is higher than those in autumn and spring seasons which can be attributed to higher concentrations drained from source houses. From the figure, it is clear that LAS concentration values in the anaerobic ponds to recorded 7, 7.6, 13.9 and 16.4 mg/l in autumn, winter, spring and summer seasons, respectively. These values are higher than those of the concentration values of LAS in raw wastewater, similar increase of LAS concentrations values in anaerobic ponds was reported in Yazd WSPs in Iran (Asghr et al,. 2010). The reasons for this increase in LAS concentration can be attributed to the bad degradation of LAS in anaerobic condition (Guang Ying, 2004, John Jensen, 1999). the additional reason is that actual average daily flow rate of Elzaraby WSPs at measurement time was around 10000 m3/ day, which leads to an actual HRT in the anaerobic ponds of 7.5 days causing high water losses by evaporation from the pond surface, therefore the water volume decreased and consequently the concentration of LAS increased.

 Fig. 7. LAS avareage seasonal concentration value in Elzaraby WSPs

The LAS concentration in maturation ponds (M1) recorded 6.1 mg/l as a maximum value in winter season, and recorded 3.2 mg/l as a minimum value in summer season. In effluent of maturation ponds (M6) LAS recorded 6.4 and 2.1 mg/l in winter and summer seasons, respectively. Similar result were reported by Asghr et al,. (2010).

As present in (fig. 8), it is clear that the concentration values of LAS, DO and pH along Elzaraby WSPs series were ranged between 10.18~3.15 mg/l, 0.18~4.8 mg/l and 6.9~8.2, respectively. From figure, it is clear that LAS concentrations in WSPs are multi-factorial, dependent on a synergistic interaction between pH, DO and sun Light. Because of good algal growth The high level of algal photosynthetic activity not only raises the pH of the ponds but also increases its DO content and biodegraded LAS. (Mungray and Kumar, 2008, Martin and Johannes, 1996) .

 Fig.8.The average annual variations of LAS, DO and pH for Elzaraby WSPs.

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As shown in (Fig. 9), the overall removal efficiency of LAS in comparison with removal efficiency of BOD5 in Oct. 2011 were 63%, 78%, and decreased in Jan.2012 to be 55%, 73%, and increase in Jul. 2012 to be 77% , 88%, respectively. From the figure, it is clear that the overall removal efficiency of LAS and BOD in Elzaraby WSPs in hot months is higher than in cold months because of high air temperature and sun light intensity occurs in summer season relative to other seasons, which increased algal grow and increased biodegradation of LAS, similar result were reported by Asghr et al,. (2010).

Fig. 9. The monthly overall removal efficiency of LAS and BOD5 for Elzaraby WSPs from Spt. 2011 to Aug. 2012.

**4. CONCLUSION**

1-Surfactants play a major role in our society. Ultimately, their usage in such large quantities means that their ultimate fate is highly important, LAS is the most frequently employed synthetic anionic surfactants.

2- There is a variable Change in LAS concentration values in raw wastewater along the four season.

3- The maximum over all removal efficiency of LAS occurs in summer season, while minimum removal in winter.

4- There is a inverse relationship between LAS concentration values and DO.

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