Assessment of Anionic Surfactant concentration in the Najafgarh Drain: Comparative analysis

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Abstract

Anionic surfactants in the Yamuna River, particularly downstream in Delhi region, have created massive form-like conditions which may be harmful to aquatic life and humans that come in contact. The present study focused on the quantification of anionic surfactants in the Najafgarh Drain because it is discharging into Yamuna River at Wazirabad and contributes in the surfactants concentration in Yamuna. The average concentrations of anionic surfactants were observed to be an above permissible limit (WHO 1mg/l, BIS 0.2mg/l) at four out of five monitored locations, Onkar Nagar (1.076±0.093 ppm), Shakti Nagar (1.391±0.441 ppm), Mukherjee Nagar (1.279±0.282 ppm), and Signature Bridge (1.302±0.552 ppm). The Bharat Nagar (0.980±0.432 ppm) site was showing concentration below WHO permissible limit but above BIS desirable limit. The experimental work done based on the EPA standard method (5540 A, 5540 B, 5540 C) and analysis of samples done by UV-Spectroscopy at 652 nm wavelength. Also include comparative analysis of similar work between Najafgarh drain and Okhla barrage, ITO, Wazirabad barrage from the literature review on Delhi water bodies. Based on the results obtained in the study, it was inferred that the water quality of Yamuna River at Najafgarh drain was poor and thus requires regular monitoring and call for immediate effective strategies.

Keywords: Anionic surfactant, Najafgarh Drain.

Introduction

The National Capital Territory (NCT) of Delhi is one of the fast growing metropolitan cities in the world. It faces a massive problem of voluminous generation of wastewater. This wastewater is mainly contributed by numerous drains of NCT Delhi that have considerable impact on surface water and groundwater systems of the territory. Due to the increasing in urbanization and industrialization in Delhi national capital region (NCR) water bodies are highly susceptible to hazardous pollutants because of highly discharge of waste water without proper treatment directly into water bodies. The effect on surface water is visible from river Yamuna where upstream of Wazirabad, the colour of river water is bluish/greenish which changes to dark grey downstream of Wazirabad, from where the Najafgarh drain joins river Yamuna (Shekhar et al., 2013).

The Najafgarh drain is the biggest drain in NCT Delhi, discharging 287.5 million litres per day (MLD) (0.2875 million m3/day) wastewater into river Yamuna, Drain enters Delhi from Haryana from the south-west corner of Delhi, It traverses a length of 51 km before joining river Yamuna and out of the 51 km stretch nearly 31 km stretch of the drain passes through south-west district from near Dhansa to Kakraula (Shekhar et al., 2013). The Najafgarh drain contributes about 60% of the total wastewater that gets discharged from Delhi into river Yamuna (Khan et al. 2022 Kumar et al., 2006). In this study was finding the concentration of anionic surfactant in the najafgarh drain. Surfactants are among the most challenging emerging contaminants which are continuously creating pollution in Yamuna River in NCR region.

Surfactants are surface-active agents that reduce surface tension and exhibit a tendency to form micelles in solvents, surfactants possess both hydrophilic (polar charged or uncharged head group) and hydrophobic (non-polar hydrocarbon tail) and thus are regarded as amphipathic molecules (Mungray et al., 2009). According to the charge of their hydrophilic moiety, surfactants can be classified into four categories: anionic, non-ionic, cationic and amphoteric (zwitterionic). Anionic surfactant's hydrophilic part carries a negative charge, nonionic surfactant's hydrophilic part is uncharged, cationic surfactant's hydrophilic part carries a positive charge, amphoteric surfactant's hydrophilic part contains both positive and negative charges.

Due to the specific chemical structure of surfactants molecules they are applied in different areas of human activity. During formulation of households or industrial products compounds from the group of surfactants are used because their presence leads to improving efficiency of the following processes: wetting/waterproofing, de- or foaming, de- or emulsification, dispersion of flocculation of solids particles in liquid phases, solubilization of non-/sparingly soluble regents in solvents,

increase or decreases of viscosity of solution phases (Madhav et al. 2024, Olkowska et al., 2014). surfactants in aquatic systems may serve to cause deterioration of water quality and it is noted that surfactants in wetlands are capable of increasing the solubility of organic and inorganic pollutants (Cho et al., 2002; Almeida et al., 2009).
A large fraction of dissolved organic matter has surface-active properties which have the ability to influence mass and energy transfer between the air-water interfaces (Hunter et al., 1981; Leko et al., 2004). Anionic surfactants contribute approximately 65% in the production and consumption at the world level (Arora et al., 2023). The global market size of surfactants in according to 2019 about 42.1 billion US dollars, and it will be reach 52.4 billion by 2025 due to large area of applications (Badmus et al., 2021).

The area of anionic surfactants application are Household detergents and cleaners, shampoos, hand dishwashing liquids, laundry detergents, personal care products, optical brighteners, dyes, dispersant, wetting, and suspending agents, ingredient of pesticides and pharmaceutical products (Ahmed and Panwar 2015, Olkowska et al., 2014).
Due to the extensive application of surfactants, their huge concentration from mostly urban or industrial and domestic wastewater can end up in municipal wastewater treatment plants or directly discharge into the open environment or water bodies (Bautista-Toledo et al., 2014; Camacho-Muñoz et al., 2014). Hence surfactants have been found relatively high concentrations in surface waters, sediments, sludge, and soils (Lara-Martín et al., 2012; Ying, 2006; Gomez et al., 2011; Olmez-Hanci et al., 2011).

Standards prescribed by various countries and organizations (table 1) for limiting uses of surfactants, and enhance wastewater treatments narrative: In Japan, the ministry of Health, Labor, and Welfare has set permissible concentrations of 0.2 mg/L and 0.02 mg/L in drinking water for anionic and non-ionic surfactants, respectively (Borghi et al., 2011). Anionic surfactants have been reported as pollutants and their permissible limit in drinking water prescribed by the WHO is 1.0 ppm (Ramanjulu et al., 2015).

Table 1:- Permissible limit of Anionic Surfactant.

Class of surfactant	Organization	Sample type	Concentration	References
Anionic	Japan, Ministry of health, Laboure & welfare	Drinking water	0.2 mg/L	(Borghi et al., 2011)
Anionic	BIS	Surface water	0.2mg/L	(Arora et al., 2023)
Anionic	WHO	Drinking water	1.0 mg/L	(Ramanjulu et al., 2015)
Anionic	Italian legislation	Drinking water Surface water Sewage Reuse in agriculture	0.2 mg/L 2.0 mg/L 4.0 mg/L 0.5 mg/L	(Borghi et al., 2011; Ferella et al., 2013)

Many environmental and public health regulatory authorities have fixed stringent limits for anionic detergent as standard 0.5 mg/L for drinking water and up to 1.0 mg/L for other purposes (Rao et al., 1995). Concentrations of 0.2, 2.0, 4.0, and 0.5 mg/L are allowed by Italian legislation for discharge into drinking water, surface water, and sewage and for reuse in agriculture, respectively (Borghi et al., 2011; Ferella et al., 2013).

Impact on Environment

Due to their antimicrobial effects, these surfactants residues promote and enhance the development of resistant bacteria, which can induce adverse effect on human health when present in drinking water or irrigation water used for agriculture (Shao et al., 2005). Given this fact, many researches trying to determine and estimate the toxicity of surfactant on aquatic and terrestrial species, and even their estrogenic effects (Ivanković et al., 2010; Jensen, 1999; Mungray et al., 2009). Exposure of surfactants to soil makes it hostile for microorganisms and the direct exposure of anionic surfactant (liner alkylbenzene sulfonate) to the plants destroyed the root cell membrane, and changes the fine structure and the permeability when applying 1 to 1000 mg/kg of LAS (Jensen, 1999). Due to their migrant capacities, their concentration increase with the depth of the soil which may present a potential risk of aquifer contamination (Xiao et al., 2015, Ahmed et al.2010). Their bioaccumulation (through the food chain and contaminated water) in liver and human serum by bonding to existing proteins may raise long-term concerns about their metabolic effects, they also present significant effects, including mortality, in cynomolgus monkeys (oral dose of 0.75 mg/kg/day), 12 rabbits (oral dose of 3.75 mh/kg/day), and 13 rats (oral dose of 1.6 mg/kg/day) (Jardak et al., 2016). Even at low concentrations may reduce the effectiveness of resistance to environmental and competitive stress, reproduction, and growth of aquatic species (Hampel et al., 2012). Effect of anionic surfactant on human manly shows eye, skin irritation potentials and Surfactants caused membrane disruption (Ahmed and Panwar 2014, Tomenko et al 2007, Cserháti et al., 2002).

Material and methods

Regents and chemicals

Various regents and chemicals used in the study include nitrogen and ethyl acetate, phenolphthalein indicator, sodium hydroxide (NaOH) 1N, sulfuric acid (H_2SO_4) 1N and 6N, chloroform ($CHCl_3$), methylene blue reagent: (dissolved 100 mg methylene blue in 100 ml water, transfer 30 ml to a 1000 ml flask, added 500 ml water, 41 ml 6N H_2SO_4, and 50 g sodium phosphate, mono-basic, monohydrate, $NaH_2PO_4.H_2O$, shake until dissolved, dilute to 1000 ml), wash solution: (added 41 ml 6N h_2so_4 to 500 ml water in a 1000 ml flask added 50 g $NaH_2PO_4.H_2O$ and shake until dissolved, dilute to 1000 ml).

Study Area and Sample Collection

Water samples were collected from downstream flow at five different locations from Najafgarh drain in the Delhi region. Multiple samples were collected in a day from Onkar Nagar, Bharat Nagar, Shakti Nagar, Mukherjee Nagar, and Signature Bridge. Sampling points were selected considering the population load, demographical distribution of drain and sources of wastewater.

Samples were collected from the surface using the grab sampling method from a well-mixed zone near to the sore of drain in 1L High-Density Polyethylene (HDPE) bottle with air tight caps, clean pre-washed with distilled water. The HDPE bottles were rinsed several times before filling with water samples from the drain. Sampling points were purposely located at approximately 200-1000 meter downstream locations. All the samples were immediately carried to the laboratory and stored at 4° Celsius until analysis. Collection, preservation and transportation of water samples to the laboratory and analysis were executed as per the Environmental Protection agency (EPA) standard methods.

Table 2:- Sample name with sample site.

S.no	Sampling Sites	Latitude°	Longitude°
1	Onkar Nagar	28.402207	77.093898
2	Bharat Nagar	28.680582	77.184136
3	Shakti Nagar	28.682439	77.189514
4	Mukherjee Nagar	28.708992	77.219939
5	Signature Bridge	28.706548	77.230568

Table 3:- Geographic details of Najafgarh drain.

S.no	Area	Najafgarh drain
1	Location	Delhi
2	Catchment Area	374 Km^2
3	Length	51 km
4	Enter Point	Dhansa, south
5	End Point	Wazirabad, north
6	Discharge Contribution	60%
7	Major And Minor Drains	38

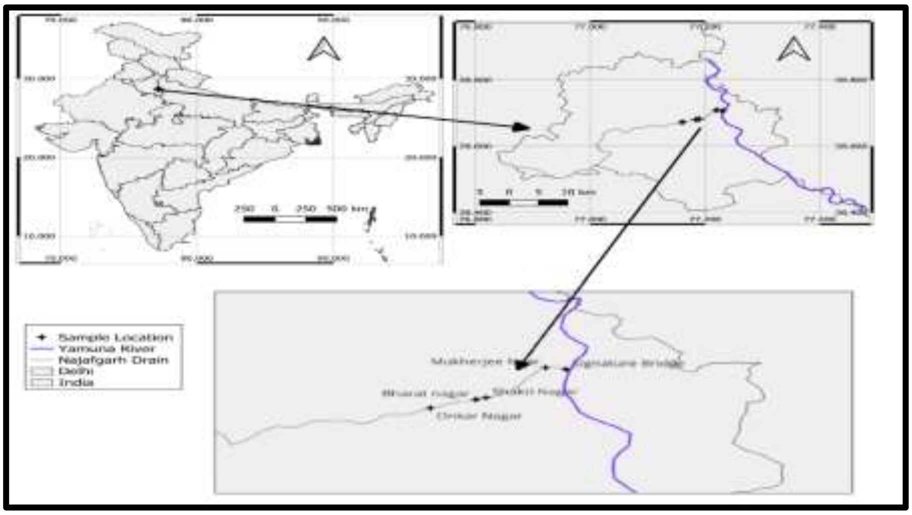

Figure 1: - Geographical representation of the study area is highlighting the sampling sites in Najafgarh drain, Delhi.

Analytical method (MBAS) for quantification of Anionic Surfactants

Sublation: Sample separation done by sublation method according to EPA standard method (5540 B). The sublation method is specific for surfactants. Before the sublation, each sample was filtered by the whatman-41 micron filter paper to removed dissolved impurities from the water samples. After the filtration filled gas washing bottle about two-third or 100ml full with ethyl acetate. Before sample fill-up, rinsed sublation column with ethyl acetate and filled with measured filtered sample in sublator about 1L total volume up to or slightly above the upper stopcock. Started the nitrogen flow, increasing the rate carefully to 1L/min initially but do not exceed a rate at which the liquid phases begin vigorous intermixing at their interface. Avoid overly vigorous intermixing, which will lead to back-extraction of the surfactant into the aqueous phase and to dissolution of ethyl acetate. Continue sublation for 5 min at 1L/min. The volume of the upper phase has decreased by more than about 20%, repeated the operation on a new samples. Sublation process isolates the surfactant from dilute aqueous solution. It is accomplished by bubbling a stream of nitrogen up through a column containing the sample and overlying layer of ethyl acetate. The surfactant was adsorbed at the water-gas interfaces of the bubbles and is carried into ethyl acetate layer. The solvent is separated, dehydrated, and evaporated, leaving, the surfactants as a residue for analysis.

MBAS method: The evaluation of anionic surfactant concentration was done by an EPA standard method (5540 C) known as methylene blue active substances (MBAS), which uses methylene blue and chloroform as solvent. Transferred a measured 500 mL volume sample of the test sample to a separatory funnel and make sample alkaline (pH=8) by drop wise addition of 1N NaOH was checked using phenolphthalein indicator, discharge pink colour by drop wise addition of 1N H_2SO_4. After that added 10 mL $CHCl_3$ and 25 mL methylene blue regent in the sample. In the Rock funnel was shake vigorously for 30 seconds and allowed the layers to separate as completely as possible and swirl the funnel to dislodge droplets from the sides of the funnel. Allow to settle for 2 min, then run of the chloroform layer into a second separating funnel. Repeat extraction two additional times, using 10 mL $CHCl_3$ each time. Added 50 mL wash solution and shake vigorously for 30 seconds. Emulsions do not formed at this stage and let settle, swirl, and draw off $CHCl_3$ layer through a funnel containing a plug of glass wool into a 100 mL volumetric flask; filtrate must be clear. Thus blue-coloured anionic pair complex is formed between anionic surfactants and methylene blue, which is extracted over chloroform and the absorbance, was measured at 652 nm using a UV-Visible spectrophotometer.

This method is recommending by EPA for measurement of concentration of anionic surfactants in water samples and also it is prescribed by CPCB and BIS, India at national level in the laboratories. That why It is easy to accessible in the laboratories and more affordable.

Result and Discussion

Quantification of anionic surfactants: The determined contents of anionic surfactant in the surface water samples from the monitoring sites were evaluated according to the regulation of the CPCB and standard method of EPA. Total twenty five samples were collected from five locations in which five samples were collected from each location. According to the WHO permissible limit of anionic surfactants for surface water is 1 mg/L and BIS desirable limit is 0.2 mg/L. The determined surfactant absorbance of samples at different sites is given in the table-4 and concentration values are shown in table-5. It is interesting that the Najafgarh drain has increased concentrations of the anionic surfactants in Shakti Nagar, Mukherjee Nagar and Signature Bridge samples as compared to others sites, where concentrations of the anionic surfactants were exceeded value of permissible limit. During the study period, the concentrations of the anionic surfactants are ranging between 0.499 to 2.026 ppm. The highest concentrations are ranging of 1.028 to 2.026 ppm as compare to the WHO permissible limit (1 mg/L)) at various sites. An average concentration ranging between 0.980-1.391 ppm was found at various sampling sites. According to the average concentration (table-7) four sampling sites were notified above the permissible limit, Onkar Nagar (1.076 ppm), Shakti Nagar (1.391 ppm), Mukherjee Nagar (1.279) and Signature Bridge (1.302 ppm) and Shakti Nagar sites was showing concentration below limit value which is 0.980 ppm but above the desirable limit of BIS (0.2 mg/L).

The increased concentrations of the anionic surfactant in this area indicate an increased presence of the septic tanks, industrial activity, and untreated wastewater from domestic use. According to the CPCB report on various drains, Najafgarh drain has long been considered a polluted drain which is discharge in the Yamuna at wazirabad. It is affected by chemical, plastic industries and household untreated wastewater. The increased concentration of the surfactant is also due to the fact that they are large cities, with an extended infrastructure and population, but not all households are drained into the sewerage and especially in municipalities that do not have a sufficiently built sewerage network.

Table 4:- Anionic surfactant Absorbance in the collected samples from surface water in the Najafgarh drain.

	Anionic Surfactant Absorbance in Samples				
Samples	**Onkar Nagar**	**Bharat Nagar**	**Shakti Nagar**	**Mukherjee Nagar**	**Signature Bridge**
S-1	0.281	0.292	0.256	0.343	0.224
S-2	0.290	0.402	0.363	0.282	0.173
S-3	0.270	0.150	0.259	0.247	0.363

S-4	0.253	0.312	0.417	0.372	0.530
S-5	0.319	0.131	0.532	0.435	0.419

Graph factor= 3.81, Concentration= Graph factor*Absorbance.

Table 5:- Anionic Surfactant Concentrations in the collected samples from surface water in the Najafgarh drain.

		Anionic surfactant concentration (ppm)				
S.no	Samples	Onkar Nagar	Bharat Nagar	Shakti Nagar	Mukherjee Nagar	Signature Bridge
1	S-1	1.07	1.112	0.975	1.306	0.853
2	S-2	1.104	1.531	1.383	1.074	0.659
3	S-3	1.028	0.571	0.986	0.941	1.383
4	S-4	0.963	1.188	1.588	1.417	2.019
5	S-5	1.215	0.499	2.026	1.657	1.596

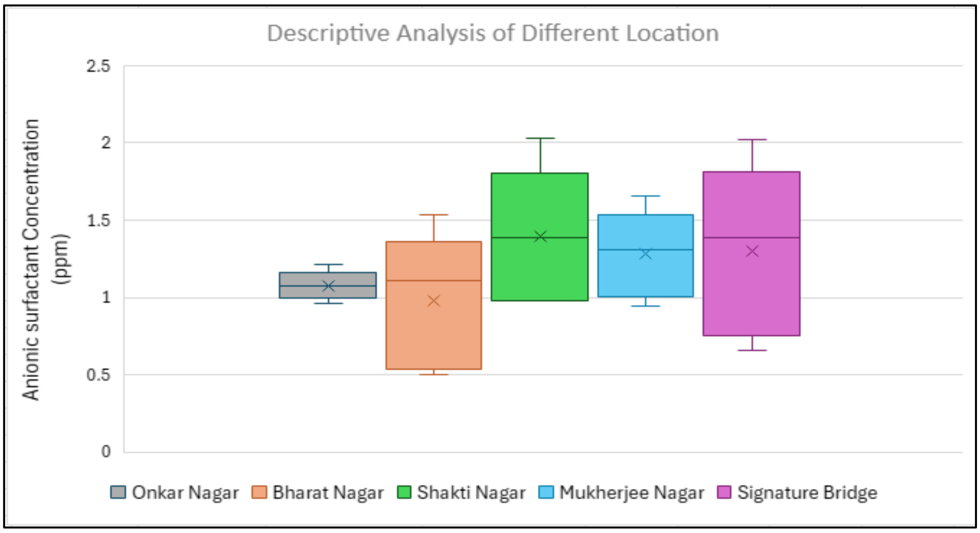

Figure 2: Representation of Descriptive Analysis of Anionic Surfactant Concentration at different locations.

Table 6:- Descriptive analytical calculation of various samples at different locations which are represented in previous graph (figure 2).

Parameter	Onkar Nagar	Bharat Nagar	Shakti Nagar	Mukherjee Nagar	Signature Bridge
Minimum	0.963	0.499	0.975	0.941	0.659
Q1	1.028	0.571	0.986	1.074	0.853
Median	1.07	1.112	1.383	1.306	1.383
Q3	1.104	1.188	1.588	1.417	1.596
Maximum	1.215	1.531	2.026	1.657	2.019

Q1= Quartile 1 values, Q2=Quartile 2 values.

Table 7:- Anionic Surfactant Average Concentrations and Standard Deviation of various sampling sites.

S.no	Sampling point	Anionic surfactants Average concentration (ppm)	Standard deviation
1	Onkar Nagar	1.076	±0.093
2	Bharat Nagar	0.980	±0.436
3	Shakti Nagar	1.391	±0.441
4	Mukherjee Nagar	1.279	±0.282
5	Signature bridge	1.302	±0.552

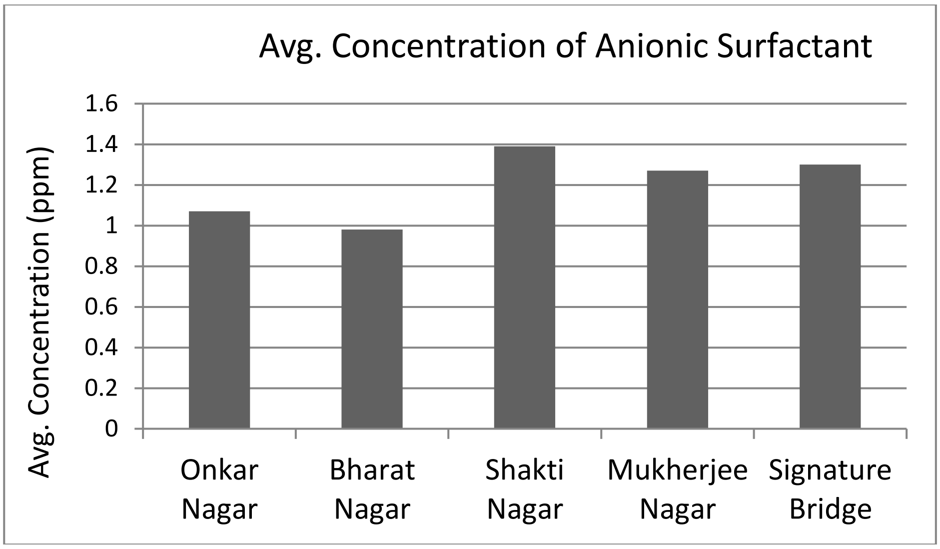

Figure 3: Graph of Average Anionic surfactant concentrations (ppm) at various sampling sites in Najafgarh drain.

Comparative Analysis of Similar Work

According to the Table-8, Okhla barrage stretch was contained higher concentration of anionic surfactant (3.89 mg/l) among all the concentrations, after that Najafgrah drain (2.026) was showing second highest concentration. Wazirabad barrage and ITO were showing lower concentration of anionic surfactants. Study of Okhla barrage stretch, Wazirabad barrage, and ITO done in the Yamuna river, and Najafgarh drain analysis was done collecting samples from Najafgarh drain, which also discharging in Yamuna river and contributing in surfactants pollution, causing foam-like conditions in Yamuna.

Table 8:- Comparative Analysis of anionic surfactants in Delhi region based on present analysis and literature review.

S.no	Study Area	Highest Anionic surfactant con. (mg/l)	Reference
1	Okhla barrage stretch	3.89	(Arora et al., 2023)
2	Wazirabad barrage	0.65	(Arora et al., 2023)
3	ITO	0.68	(Arora et al., 2023)
4	Najafgarh drain	2.026	Present study

Graph showing (figure 4) the comparative concentration of anionic surfactants, As compare to Okhla barrage Najafgarh drain contain lower value of anionic surfactant and higher than Wazirabad and ITO. Mostly due to the higher concentration of surfactants at Okhla barrage caused foaming for long period of time in Yamuna, also Okhla barrage is create higher turbulence in Yamuna river which is help in foam formation.

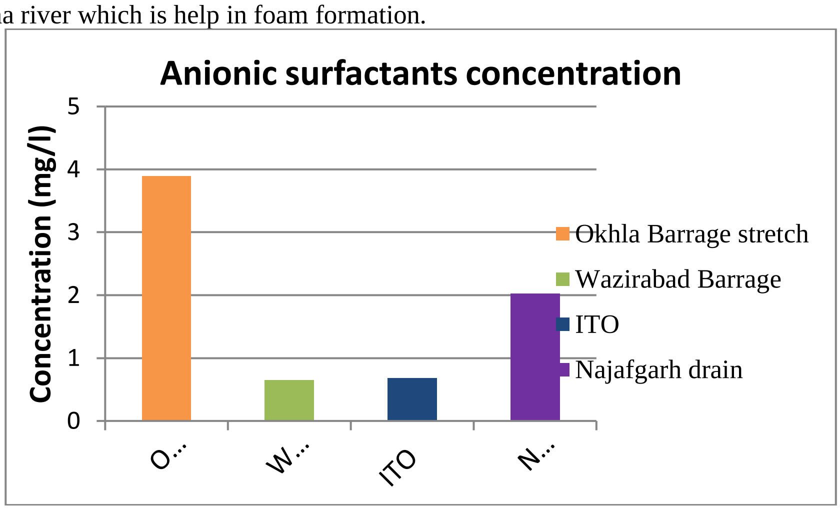

Figure 4: Comparative analysis of higher concentration of anionic surfactants at Wazirabad, ITO, Okhla Barrage and Najafgarh Drain.

Conclusion

The quantification of anionic surfactants in the Najafgarh Drain, Delhi was carried out in this study. This is discharging into the Yamuna River at wazirabad and creating pollution in it, also degrading water quality of river and causing foam like condition. In this study twenty five samples were collected from five locations (five samples from each location). Anionic surfactants in the range of 0.499-2.026 ppm were found at various sampling sites in the Najafgarh drain. The concentration of anionic surfactant was found to be higher than permissible limit at some locations and exceeded the desirable limit. Thus study establishes the presence of anionic surfactants as one of the major reasons for foaming in the water. Several studies have reported anionic surfactants to cause skin irritation, death to animals, blood toxicity. Unregulated and uncontrolled discharge of industrial and household effluents and dumping of waste must come under regulation. This approach can help mitigate the adverse effects of surfactant pollution in the water bodies and river. Effective and monitoring of waste discharge into the Najafgarh Drain by small drain to protect the Yamuna ecology and human health.

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