

Aquatic environmental monitoring and removal efficiency of detergents

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Abstract

In this study, the detergent's concentrations in aquatic environment principally drinking and surface water along River Nile and near rural village were determined to report the influence of different physicochemical characteristics on the distribution of linear alkylbenzene sulfonate (LAS) that lead to toxicity in human beings. The removal efficiency of LAS using zeolite and granular activated carbon technique was assessed.

The results showed wide variations observed between surface (0.07–0.38 mg LAS/l) and bottom water (0.05–0.17 mg LAS/l) due to increase in population density and human activities that recorded highest concentration along rural area (surface: 1.24–2.45 and bottom: 0.93–1.083 mg LAS/l). Low concentration of surfactants was found in drinking water (0.005–0.007 mg LAS/l) compared to the concentration of the corresponding water samples along the River Nile. In conclusion, the study indicated that the treatment processes for drinking water production were insufficient for the complete removal of surfactants and adsorption process by using zeolite as low cost, most beneficial, economically feasible method as well as easy to operate for producing high quality of water.

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1. Introduction

Environmental studies reported that the problem of detergents is growing rapidly in developing countries and rural communities (Feisthauer et al., 2004). It is noted that inappropriate and less efficient water purification process led to presence of surfactants in the finished water due to their physicochemical properties (high water solubility and often poor degradability) which allow them to penetrate through all natural filtration steps and man-made treatments, thus presenting a potential risk in drinking water supply (Norfazzrin et al., 2012).

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Detergents are compounds derived from synthetic organic chemicals (mainly surfactant) that have cleaning power. These compounds generally xenobiotic compounds contain a polar head group (soluble in water – hydrophilic) and non-polar hydrocarbon tail (insoluble in water – hydrophobic) properties in one molecule (Ying, 2006). Surfactants are classified as anionic, cationic and non-anionic and amphoteric by their ionic activity (special nature) in water (Dehghani et al., 2007). LAS (linear alkylbenzene) is mainly a group of anionic surfactant (Shafqat et al., 2012) that is found in drinking water (Makwana et al., 2012), as well as in domestic and industrial wastewaters in extended volume than any other groups because of their ease and low cost of manufacture (Salvato et al., 2003).

Pattusamy et al. (2013) have recently reported that detergents must be prevented from entering in channels to avoid eutrophication of aquatic environments, because detergents prevent the growth of microorganisms that are pathogenic species in nature with higher loads in river. The surfactants are also responsible not only for causing foam in rivers and creating procedural problem during wastewater treatment and but also for reduction of water quality (Vinod et al., 2012). Environmental studies reported that it must be elucidated and assessed the potential health hazards of detergents on aquatic life form which hampers water quality (Adewoye, 2010; Udiba et al., 2013). This phenomenon will eventually promote negative impacts toward human health that leads to blood toxicity, as well as eye and skin irritation (Fujii et al., 2007). LAS has toxic impact on aquatic faunas, floras in soil, preventing soil from re-depositing and as a result, causing environmental problems for cultivated vegetables (Ghoochani et al., 2011). It can also induce severe damage to vital organs, even hematological, hormonal and enzyme disturbances (Ogundiran et al., 2009), growth and development of the plankton constituents (Mukherjee et al., 2010), as well as toxic to aquatic life at ≤ 0.025 LAS/l. LAS has adverse effects on aquatic species at 0.005 LAS/l (Misra et al., 1987) and may cause histological degradation in fish species (Fujii et al., 2007).

Detergents play an important role toward increasing pollution originated from wastewater that comes from residential areas in the form of household detergent, agriculture runoff in the form of herbicides and insecticides and from certain industries (Vinod et al., 2012). About 90–97% of the detergents can be biodegraded by bacteria and can get decomposed in small quantities in anaerobic conditions (Yangxin et al., 2008). Biotechnology techniques recently have described an important group of bio-surfactants using lipases or enzymes that can reduce environmental load of detergent products as the chemicals used in conventional methods; they are biodegradable and non-toxic, and also leave no harmful residues (Fariha et al., 2010).

Water for human consumption must be free of microorganisms and chemical substances in concentrations large enough to cause environmental imbalance and disease (Aremu et al., 2011; Shivaraju, 2012).

Thus, determination of surfactants, in river water as raw water supply, drinking and treated water, is important since surfactants have become a threat to our water supply network. Many researchers have shown that activated carbon is an effective adsorbent for treating water with high concentrations of organic compounds (Syafalni et al., 2012b). Its usefulness is derived mainly from its large micropore and mesopore volumes and the resulting high surface area (Fu and Wang, 2011). Low cost adsorbent such as zeolite nowadays has been explored for its ability in many fields especially in water treatment. Natural zeolite has negative surface charge which gives advantages in absorbing unwanted positive ions in water such as heavy metals; these ions can move within the large cavities allowing ionic exchange and reversible re-hydration (Jamil et al., 2010), and adsorbent surfaces are particularly useful for altering the surface charge from negative to positive with surfactant in order to achieve higher performance in removing organic matter (Chao and Chen, 2012).

This study aimed to analyze the concentration of detergent in surface and bottom water of River Nile used for drinking water. The influence of physical–chemical measurements on the distribution of detergent load was also being investigated because its bioaccumulation can lead to toxicity in the human beings. In addition, the current ability of water treatment processes toward the removal of detergent was examined and the performance of removal of LAS from aquatic environment by means of zeolite and granular activated carbon was assessed.

2. Materials and methods

The present work investigated water characterization for four sites along River Nile ecosystem during summer 2013. In situ measurements, chemical (inorganic and organic) pollutants and bacteriology measurements were analyzed for 16 environmental samples according to (Eaton et al., 2005) methods. The data were compared with water quality standards (Egyptian Environmental Law 48 – Decision 92/2013, WHO, 2006 and European Community, 1989).

Table 1
Sampling locations.

No.	Site	Classification	Code
1	Delta Barrage	Surface water of River Nile – reference point	RP
2	Bahada Baradah Shlqan	Distribution water network – tank water	T1 T2 T3
3	El-Qanater City	Surface water of River Nile at drinking water plant Drinking water plant – inlet Drinking water plant – outlet Drinking water plant– inlet – bottom Drinking water plant– outlet – bottom	S1 S2 SB1 SB2
4	El-Rahway drain	Beginning drainage water Beginning drain – drainage water – bottom River Nile – outfall drain – drainage water River Nile – outfall drain – drainage water – bottom River Nile – upstream outfall drain River Nile – upstream outfall drain – bottom River Nile – downstream outfall drain River Nile – downstream outfall drain – bottom	SR1 SRB1 ER2 ERB2 UR3 URB3 DR4 DRB4

2.1. Environmental sampling program

2.1.1. Study area

The study investigated four sites that were Delta Barrage, distribution water network, drinking water plant and El-Rahway drain along River Nile. Eight samples were collected from Delta Barrage-El-Kanater El-Khayria (used as a reference point); drinking water plant is called El-Qanater El-Khayria, which serves as main fresh water supply for drinking water production (four samples: surface and bottom water from inlet and outlet) and for three drinking water tanks from Bahada, Baradah, and Shlqan (distribution water network) as shown in Table 1. River Nile at Rosetta branch was subdivided into five reaches based on locations of known waste inputs (Ezzat et al., 2014) as illustrated in Fig. 1. El-Rahawy drain is one of the main drains; it receives considerable amount of wastewater from the vicinity of Rahway drain with residential area in rural community along Rosetta Branch (El-Sheikh et al., 2010). It starts at 30 km – Mansouria Rayah, North to Cairo at El-Kanater El-Khayria area, Egypt. El-Rahawy drain lies between latitudes 30° 10' N to 30° 12' N and longitudes 31° 2' E to 31° 3' E. It is about 12.41 km and passes through El-Rahway village, receives agricultural and domestic wastes from many villages distributed along it, without purification in addition to sewage of El-Giza governorate and discharges these wastes directly without treatment into Roetta branch of the River Nile (El-Sheikh et al., 2010). The drain is surrounded by dense population and wide agricultural lands, while it discharges about 2.8 m/day including 1.9 m/day sewage effluents (Gaber et al., 2013).

Totally eight samples were collected from El-Rahway drain area (surface and bottom) beginning from El-Rahway drain, El-Rahway drain outfall, and two sites in Rosetta branch (upstream and downstream those drain outfall).

2.1.2. Water samples collection

Water samples were collected from investigated sites at depth of 60 cm (16 samples), using plastic bottles (1 l capacity) for physicochemical, total organic carbon (TOC), and surfactant parameters and were stored in refrigerator at 4 °C prior to analysis (Eaton et al., 2005). Measurements were always carried out during the sampling day in order to keep a minimum fluctuation of the physical and chemical parameters caused by temperature differences.

2.2. Water analysis

2.2.1. Field measurements

In situ, field measurements including temperature, dissolved oxygen (DO), TDS, pH and electrical conductivity (EC) were measured using multi-probe system, model Hydralab-Surveyor.

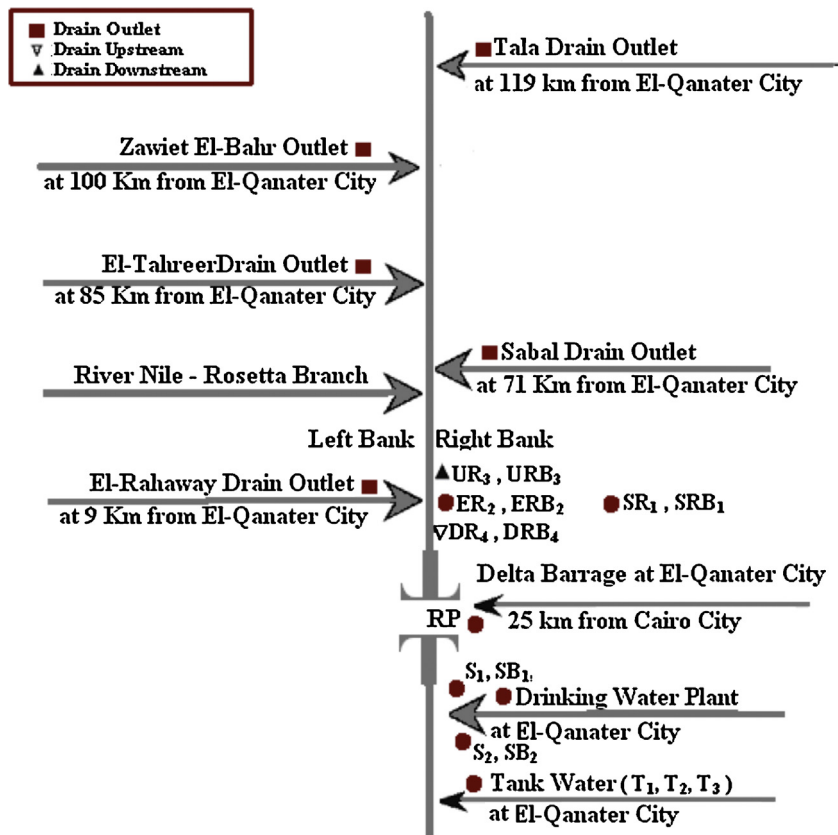


Fig. 1. Schematic diagram of sampling locations.

2.2.2. Laboratory analysis

The water quality parameters were determined using standard techniques (Eaton et al., 2005), and important parameters which are playing main role in the human health were considered. In laboratory, total dissolved solids (TDS) were determined by the gravimetric method (Method 2540B) while carbonate and bicarbonate were detected by titration method using 0.02 N H_2SO_4 (Methods 2310B and 2320B).

Organic measurements are selected to represent gross fraction of organic matter including biological oxygen demand (BOD) using BOD fast respirometry system model TS 606/2 at 20 °C incubation in a thermostatic incubator chamber model WTW (Methods 5210B and 5210D), chemical oxygen demand (COD) using Huch DR – 2010 (Method 5220D), and total organic carbon (TOC) using a Multi N/C-3100 (Method 5310C). In addition, the measurements of LAS were performed using a Huch DR – 2010 (Method 5540C).

On other hand, total coliforms (TC) and fecal coliforms (FC) were determined using membrane filter technique by a filtration system completed with stainless steel autoclavable manifold and oil-free “MILLIPORE” vacuum/pressure pump. Water samples were filtered through sterile, surface girded “SARTORIOUS” membrane of pore size 0.45 μm and diameter 47 mm, according to standard methods no. 9222B and 9222D on M-Endo Agar LES, M-FC agar, and M-Enterococcus agar medium, respectively. All media used were obtained in a dehydrated form, from Difco, USA. Results were recorded as Colony Forming Unit (CFU/100 ml).

2.3. Treatment

Adsorption technique was used to remove organic matter concentrations using natural zeolite and activated carbon. Serial batch studies were conducted at room temperature to examine the influence of time and dosage effects to eliminate organic matter (LAS, COD) and TDS from environmental samples. These functions were carried using a plastic column with dimensions: 7 cm diameter and 50 cm length. Total volume of 100 ml water sample (influent) was

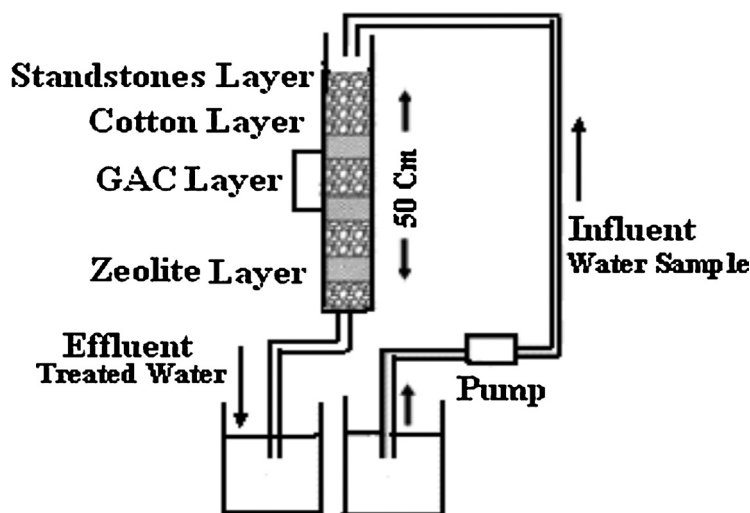


Fig. 2. Schematic diagrams of lab-scale post column water quality.

pumped in the up flow mode from the vessel into the column using a master flex peristaltic pump at a minimum flow rate of 50 ml/min. Effluent samples were collected at various time intervals, while maintaining room temperature and analyzed to check treatment performance.

2.3.1. Batch studies

A working volume 100 ml water sample in 500 ml conical flasks with adsorbent dosage (zeolite – Z or active carbon – GAC) was shaken at a speed of 400 rpm and fixed time (10 min) to determine optimum dosage of adsorbent. Then, another working volume 100 ml water sample in 500 ml conical flasks, optimum adsorbent dosage (zeolite – Z or active carbon – GAC) was shaken at a speed of 400 rpm and changeable times to determine optimum time. The percentage of treatment removal was finally determined, plotted, and compared for two adsorbents.

2.3.2. Post column studies

Post column water quality was prepared using both adsorbents (active carbon-bed layer 1 and zeolite-bed layer 2) at optimum dosage that were filled inside the column at a specific depth with the supporting layers of sandstones, cotton wool, and perforated net as filtration system for dosage effect and as shown in Fig. 2.

3. Results and discussion

3.1. Water characterization

With El-Qanater El-Khayria City as reference point (RP), the analysis reported that organic and inorganic measurements in River Nile are still on the average, at a fairly clean level (Environmental Law 48 – Decision 92/2013; WHO, 2006) under strong dilution conditions as shown in Tables 2 and 3. Surfactant concentration (0.001 LAS/l) was within limits according European Community (1989) (0.2 LAS/l) and its level is safe (0.025 LAS/l) for aquatic organisms (Misra et al., 1987).

3.1.1. Physicochemical characteristics

The sites represent a good model for the environmental exposure to different types of pollutants. The exact percentage of linear alkylbenzene sulfonates (LAS) that have negative environmental impact released into the environment mainly depends on the physicochemical and biological properties as well as the way those are used in detergents and cleaners and disposed of linear alkylbenzene sulfonates (LAS) as anionic surfactants. Table 2 represents water characteristics in the reference point, water tank, River Nile for water supply and River Nile along rural area. The obtained results were compared to water quality standards (Egyptian Environmental Law 92/2013; WHO, 2006).

Table 2
Characteristics of field measurement in water sample.

Code	Temp. (°C)	pH	Total alkalinity (mg/l)	TDS (mg/l)	Total hardness (mg/l)
RP	28	7.39	130	255	63.68
Tank water					
T1	29.1	8.01	165	183	70.13
T2	29.4	7.94	170	183	69.91
T3	29.5	8.00	155	183	67.51
Drinking water plant					
S1	30.2	7.62	302	271	89.99
SB1	30.5	7.47	200	486	142.59
S2	30.9	8.1	317	258	166.3
SB2	31.6	7.90	174	440	764.16
El-Rahway drain					
SR1	32.4	8.35	546	1870	926.38
SRB1	32.7	7.69	596	9390	2315.95
ER2	32.2	8.14	342	1270	771.93
ERB2	32.9	7.71	511	5630	1929.95
UR3	32.1	7.80	154	571	179.78
URB3	31.5	7.40	209	1713	224.53
DR4	32.2	7.86	325	662	578.94
DRB4	32.7	7.55	419	3.310	1072.18
Permissible limits (mg/l)					
WHO	N.A.	6.5–8.5	N.A.	1000	N.A.
Egyptian law 92/2013	N.A.	7–8.5	150	500	N.A.

N.A.: Not available.

3.1.1.1. Temperature. The distribution of water temperature showed surface water temperatures ranging from 29.1 °C to 32.2 °C and was higher than those at the bottom with a difference of 1–3 °C as a result of air temperature variations as shown in [Table 1](#).

3.1.1.2. pH value. pH values play an important role in many life processes and reflect the productivity and pollution levels of the aquatic environments. pH values varied between 7.47 and 8.1 along investigated sites (pH of natural water is around 6.5–8.5). This explains the effects of different effluents in the surface water of the River Nile. The lower pH values were observed at drinking water station of El-Qanater El-Khayria City (inlet-surface water) and River Nile (upstream Rahway drain outfall). Moreover, the pH values in the sites showed relatively high levels in the surface waters, compared with those recorded in the bottom waters. Thus, an increase in the phytoplankton population produces increasing in photosynthetic activity by algae led to reduce the amount of CO₂ in surface water, increase oxygen super saturation due to high photosynthetic activity and increase in the pH value ([Sawidis and Bellos, 2005](#); [Abdel-Gawad and Hammad, 2011](#); [Amer and Abd El-Gawad, 2012](#)). The spatial variation of pH values in the sites was limited within the study; it ranged between 7.62 and 7.86 for surface layers and 7.47 and 7.90 for bottom layers. The study showed slight gradient temperature and pH in investigated sites and these parameters did not affect the relationship between detergent concentration and physiochemical parameters ([Minareci et al., 2009](#)).

3.1.1.3. Total dissolved solids. In the present study, TDS are used as an indicator to reflect salinity changes resulting from the mixing of fresh water (River Nile) and wastewaters as the result of the amount of drainage water and the rate of treatment process. TDS of surface and bottom samples were mostly affected by the corresponding water types as represented in [Table 1](#). TDS values showed a big variation according to the water type and distance of the different sites from the effluents ([Okbah et al., 2013](#)). The minimum surface TDS (271 mg/l) value was observed at drinking water station of El-Qanater El-Khayria City (inlet-surface water) while maximum salinity (662 mg/l) was observed at River Nile (downstream Rahway drain outfall). TDS distribution in the investigated sites showed a noticeable increase

Table 3
Characteristics of environmental measurements in water sample.

Code	DO (mg/l)	Surfactant (LAS/l)	Oxidizable organic matter			TC (CFU/100 ml)	FC (CFU/100 ml)
			COD (mg/l)	BOD (mg/l)	TOC (mg/l)		
RP	7.85	0.001	3	2	0.253	133	40
Tank water							
T1	7.55	0.007	1	0.0	0.217	0.0	0.0
T2	7.50	0.005	1	0.0	0.234	0.0	0.0
T3	7.53	0.006	1	0.0	0.241	0.0	0.0
Drinking water plant							
S1	7.01	0.09	15	12	0.935	232×10^3	2×10^3
SB1	5.64	0.07	21	17	0.785	115×10^4	1×10^4
S2	7.34	0.07	3	1	0.065	0.0	0.0
SB2	5.01	0.05	11	8	0	156×10^2	5×10^2
El-Rahway drain							
SR1	2.1	2.45	220	160	12.654	565×10^6	5×10^5
SRB1	0.9	1.83	510	320	30.872	851×10^8	123×10^7
ER2	3.5	1.24	130	100	11.056	622×10^5	315×10^4
ERB2	1.6	0.93	270	210	23.681	258×10^7	497×10^6
UR3	6.01	0.13	22	16	1.325	694×10^3	1×10^3
URB3	4.18	0.09	34	26	2.068	125×10^5	21×10^4
DR4	4.5	0.38	53	40	4.952	724×10^4	13×10^4
DRB4	2.9	0.17	105	91	9.657	111×10^6	876×10^5
Permissible limits (mg/l)							
WHO	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.A.
Egyptian law 92/2013	≤ 5	0.05	10	6	N.A.	≤ 5000	N.A.

LAS is allowed in surface water at 0.2 LAS/l for abstracting drinking water (European Communities, 1989) and LAS has adverse effects at 0.005 LAS/l (Misra et al., 1987). N.A.: Not Available; N.D.: Not Detected.

in the bottom layer (1713–9390 mg/l) compared to those in the surface water (271–662 mg/l) at El-Rahway drain of the investigated area, as a result of drainage discharge without treatment.

3.1.1.4. Total alkalinity. Carbonate and bicarbonate ions are the main components contributing to the alkalinity in most natural waters. Total alkalinity values showed high levels in surface water (302–317 mg/l) compared to those in bottom water (174–200 mg/l) at drinking water plant. Higher total alkalinity measurements in summer season reflect the important role of temperature in increasing photosynthetic activity in summer and consequently causing an increase in total alkalinity (Okbah et al., 2013). Total alkalinity of surface water at drinking water plant (inlet and outlet) was (174–200 mg/l) less than that at beginning El-Rahway drain and outfall El-Rahway drain (511–546 mg/l) that clarified the effect of human activities, agriculture process and the standard rules for drinking plant building capacity. While total alkalinity of surface water was (154–546 mg/l) less than that of bottom water (209–596 mg/l) along Rahway drain. The improvement of alkalinity values at upstream drain outfall and downstream drain outfall might result from self-purification process along El-Rahway drain outfall.

3.1.1.5. Total hardness (TH). Total hardness gives information about the concentration of Ca and Mg ions. Many human activities and waste disposal in water systems result in the leaching of chemicals which cause an increase of total hardness values. As shown in Table 2, low hardness values were recorded at raw tank (distribution water network), outlet drinking water station and in the vicinity of River Nile upstream Rhaway drain outfall. The low total hardness of the surface water might result with the large amounts of fresh water and supported by the strong relation between total hardness and salinity (Okbah et al., 2013). Generally, hardness values showed lower levels in surface water than bottom layer (ranged 89.99–179.78 and 142.59–1072.18 mg/l as CaCO_3) during the investigation.

3.1.2. Chemical and bacteriology measurements

The study was essentially conducted to analyze detergents concentration as LAS, dissolved oxygen, and bacteriology measurements to investigate the distribution of LAS concentrations along sites (Fig. 1). Table 3 represents water characteristics in chemical and bacteriology concentrations in comparison to water quality standards (Environmental Law 92/2013; WHO, 2006) that reflected possible environmental risk associated with drainage water at (SR1–DR4) sites and drinking water station site. While the chemical and bacteriology characterizations of tank water (T1–T3) were within acceptable limits of national watercourses standards.

3.1.2.1. Dissolved oxygen. Dissolved oxygen (DO) is considered a useful parameter for the identification of different water masses and its distribution reflects to great extent the local processes of oxygen production balance and consumption in water courses. In the investigated sites, the absolute surface and bottom DO values fluctuated between 0.9 and 7.34 mg O₂/l as shown in Table 3. The lower DO levels were found in surface (2.1–3.5 mg O₂/l) and bottom (0.9–1.06 mg O₂/l) at Rhaway drain. The high values in surface water may be due to the dissolution of O₂ from the air to the surface water, while the low values in the bottom water may be attributed to respiration of organisms and biochemical transformations of organic matter.

The most important factors, controlling the DO budget, are the quantity and quality of the discharged sewage wastes, the exchange of water with the adjoining open Rhaway drain outfall, and the high rate of photosynthetic activity of phytoplankton production that produce large amounts of oxygen. Also, in the summer season, the lowest DO coincided with the lowest TDS at surface layers. The effect of temperature on DO concentrations was indicated by the strong inverse correlations found between the two variables. Water temperature decrease leads to an increase in oxygen solubility and a decrease in the rate of bacterial decomposition (Abdel-Gawad and Hammad, 2011; Amer and Abd El-Gawad, 2012).

3.1.2.2. Oxidizable organic matter. High values of oxidizable organic matter (OOM) pollution are an indicator of water, which was linked to sewage effluents discharged into Rhaway area (160 mg/l) that showed spatial and temporal variations. Vertically, the pattern of organic matter distribution showed an increase with depth at most sites (Table 3). The variability of OOM content increased in surface water of River Nile from 1.5 to 2.7 times than those recorded in the bottom water. The regional distribution of OOM values was higher at the sites located at Rhaway drain (SR1, 2.1 mg O₂/l) and in the vicinity of the drain (DR4, 4.5 mg O₂/l) and decreased further away of it at sites S1, S2, and UR3. The concentrations of organic matter in the surface and bottom waters of the investigated sites were noticeably high due to an increase in human population and activities during summer season.

3.1.2.3. Distribution of LAS. The concentrations of surfactant were interrupted with water quality standards for water samples in investigated area. LAS concentrations in raw water supply complied with (European Communities, 1989) standard limits (S1 – 0.09 LAS/l, S2 – 0.05 LAS/l) as shown in Table 3. While LAS concentrations in rural communities were (ER2 – 1.24 LAS/l, UR3 – 0.13 LAS/l, DR4 – 0.38 LAS/l) that exceeded (European Communities, 1989) limits. These high concentrations may be attributed to the increase in population density, human activities, unawareness environment behaviors and increased domestic loading in comparison with LAS concentrations in raw water supply. LAS concentrations along River Nile at El-Rahway drain were (SR1 – 2.45 LAS/l) that receives a variety of organic wastes. This waste generated from highly residential area and street dusts that contain large amount of surfactants can dissolved and enter water column (Hanif et al., 2009).

The high amount of surfactants observed in sites (S1 – 0.09 LAS/l, S2 – 0.07 LAS/l, UR3 – 0.13 LAS/l, ER2 – 1.24 LAS/l and DR4 – 0.18 LAS/l) during summer season along River Nile suggested that the intensity of sunlight probably enhances the production of surfactants. The oxidation process triggered by sunlight might lead to an increase of those more hydrophilic compounds and increase the surface-active properties of organic compounds (Norfazzrin et al., 2012). The highest concentrations of LAS at both surface and bottom layers are due to increasing water temperature in the summer season because temperature was found to have a decisive effect on the degradation rate (Okbah et al., 2013).

Treatment of raw water with alum and regulation of pH followed is able to eliminate the presence of surfactants. But surfactants detected in treated water (tank water T1 – 0.007 LAS/l, T2 – 0.005 LAS/l and T3 – 0.006 LAS/l). They provided other factors play their role in the elimination process of surfactants which polymers exhibit surfactants

properties and act as a coagulant/flocculating aids (charged polyelectrolyte in water). Thus, these surfactants are not completely removed and were found to be capable of bypass all purification steps (Norfazrin et al., 2012).

Generally, LAS concentrations in most of the surface water sample were lower than in the bottom water at all stations (Table 3) which may be attributed to the fact that the natural tendency of surfactants LAS is to accumulate first on the surface of the aqueous medium (air–surface water interface) while the degradation improves in bottom layer attributed to the great budget of bacteria as well as the physical–chemical characteristics of surfactants. In addition, the oxidizing conditions and high amounts of dissolved oxygen encouraged bacterial action on a large number of organic compounds easily biodegradable and LAS concentrations will be diminished due to the rate of biodegradation that was remarkably accelerated in the presence of sediment (Okbah et al., 2013).

3.2. Treatment

The characterization of environmental samples in investigated area showed high concentration of LAS (0.05–2.45 mg/l), BOD (8–210 mg/l), TOC (0.217–12.654 mg/l), OOM (11–510 mg/l) and other environmental measurements in some sites exceeded (European Communities, 1989; Environmental Law 92/2013; WHO, 2006) standard limits as shown in (Tables 2 and 3). The study clarified that the removal of emerging polar contaminants during drinking water treatment is incomplete such as LAS (0.005–0.007 LAS mg/l) for tank water and unsatisfactory – (0.05–0.09 LAS mg/l) along drinking water plant (inlet and outlet) (Bolong et al., 2009; Norfazrin et al., 2012) and bioaccumulation of LAS led to potential health hazards (Udiba et al., 2013). This phenomenon is due to their physicochemical properties (high water solubility and often poor degradability) which allow them to penetrate through all natural filtration steps and man-made treatments, thus presenting a potential risk in drinking water supply (Shivaraju, 2012). Then, selective treatments of GAC or Z in batch studies were conducted that included two functions: effect of adsorbent dosage and time.

3.2.1. Batch studies

Checking removal efficiency of LAS from aquatic environment using a series of adsorbents by means of zeolite and granular activated carbon for investigated sites was done. There were two factors influencing the adsorption capacity: adsorbent dosages and time that were observed in the batch study. These factors eliminated LAS mg/l (0.001–0.09) successfully from reference point, tank water, drinking water plant (inlet, outlet) at 1 h and using 3 g-GAC and 6 g-Z. While these factors eliminated LAS mg/l (0.13–0.38) effectively along El-Rahway drain (upstream drain outfall and down stream drain outfall) at 4 h and using 3 g-GAC and 6 g-Z. The optimum conditions removed LAS concentrations (1.24–2.45 LAS mg/l) to 0.5, 0.1 for beginning El-Rahway drain and El-Rahway outfall at 10 h and 10 g of Z or GAC, respectively.

3.2.1.1. Effect of adsorbent dosage. The effect of adsorbent dosage was studied for all adsorbents employed on COD and TDS, with removal by varying the dosage of adsorbent and keeping all other experimental conditions constant (pH, time). The pH was set to normal conditions which were most favorable in obtaining the highest removal efficiency. To find the optimal adsorbent dosage of zeolite (Z) and granular activated carbon (GAC), the appropriate experiments were carried out at adsorbent dosages varied in the range from 0.5 g to 10.0 g. The experimental results for all the adsorbents are illustrated in Figs. 3–7.

Figs. 3 and 4 display the relationship between the amount of adsorbent mass (dosage) and adsorption efficiency for Z and GAC in terms of removing TDS. The TDS (183–1870 mg/l) removal of Z increased from about 45% to 82% with increasing adsorbent dosage of Z from 0.5 g (101–1025 mg/l) to 10 g (20–370 mg/l) whereas for GAC, removal percentage increased from 25% to 51% with increasing adsorbent dosage from 0.5 g (137–1403 mg/l) to 10 g (80–1120 mg/l).

Adsorbent dosage (0.5–7 g) led to TDS removal of about 85% and 55% for Z and GAC respectively. Slight degradation of TDS with increasing GAC adsorbent dosage was related to unsaturated adsorption of active sites during the adsorption process as shown in Fig. 4. Zeolite had proven to have better TDS removal for tank water (183–20 mg/l), surface water of River Nile at drinking water plant (inlet and outlet) (271, 258 – 33, 30 mg/l), upstream drain outfall and downstream drain outfall (271, 662 – 60, 188 mg/l) as shown in Fig. 3. TDS removal for Rahway drain wastewater (beginning El-Rahway drain and El-Rahway drain outfall) reached the maximum permission limits of Egyptian Environmental law (Decision 92/2013) with 10 g/l Z dosage (1870, 1270 – 500, 388 mg/l).

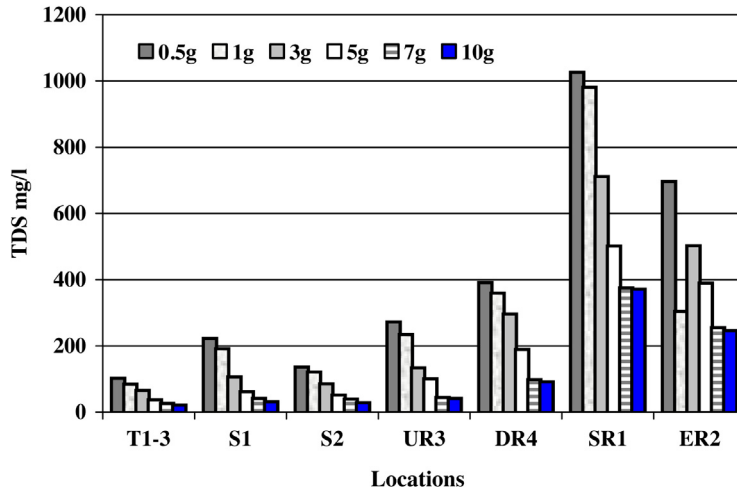


Fig. 3. TDS removal of environmental samples against dosage for zeolite.

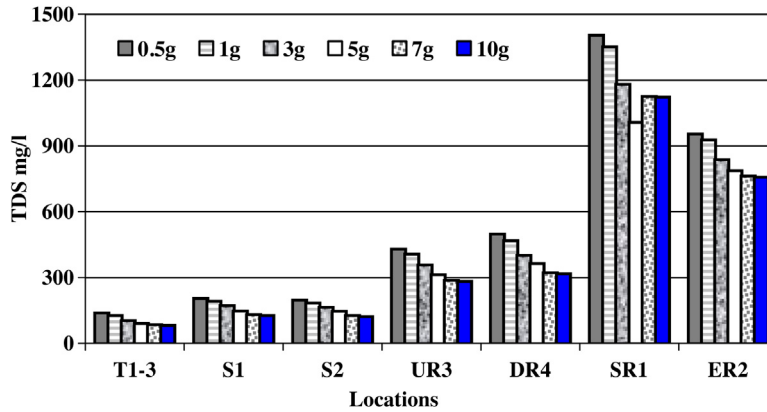


Fig. 4. TDS removal of environmental samples against dosage for GAC.

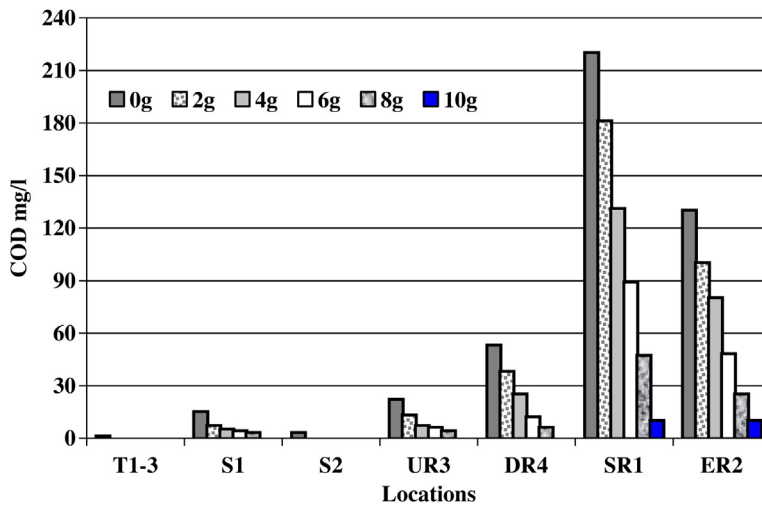


Fig. 5. COD removal of environmental samples against dosage for zeolite.

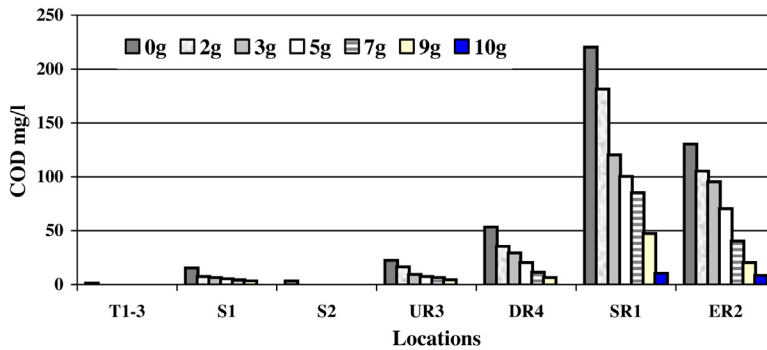


Fig. 6. COD removal of environmental samples against dosage for GAC.

Adsorbent dosage 6 g/100 ml-Z eliminated efficiently COD concentrations from 11 mg/l to 0 mg/l and from 510 mg/l to 6 mg/l in investigated water samples for the drinking water plant and El-Rahway drain, respectively to reach 75% removal efficiency. While for tank water, COD concentrations were removed from 1 to 0 mg/l, surface water from 3 and 15 mg/l to 0 mg/l at drinking water plant (inlet and outlet) and from 22, 53 mg/l to 6 mg/l at El-Rahway drain (upstream drain outfall and downstream drain outfall). Adsorbent dosage 10 g/100 ml Z eliminated efficiently organic matter concentrations from (SR1 – 220 mg/l and ER2 – 130 mg/l) to 10 mg/l as shown in Fig. 5.

The highest improvement for COD using 3 g/100 ml of GAC dosage was 60% that achieved COD values from 3–22 mg/l to 0–9 mg/l for River Nile water at drinking water plant (inlet and outlet) and upper El-Rahway drain outfall. GAC dosage 5 g/100 ml reduced organic matter concentrations from 53 mg/l to 0 mg/l-COD that complied with Environmental Law 92/2013 permission limits at downstream El-Rahway drain outfall. While COD concentrations at beginning El-Rahway drain and El-Rahway drain outfall reduced from 220, 130 mg/l to 10, 8 mg/l, respectively as shown in Fig. 6.

The results illustrated in Fig. 7 showed that the maximum removal percentage of LAS for tank water and surface water of River Nile at drinking water station (inlet and outlet) at 0.5 GAC g and zeolite dosage was 100%. Moderate increase in LAS removal was identified along El-Rahway drain (upstream drain outfall and El-Rahway drain outfall) with the addition dosage 3.5 g/100 ml of GAC and zeolite while abatement of removal efficiency began subsequently at adsorbent dosage of 4 zeolite g/100 ml to 5 GAC g/100 ml, respectively for El-Rahway drain wastewater (beginning El-Rahway drain and downstream drain outfall) as shown in Fig. 7.

3.2.1.2. *Effect of time.* Removal efficiency for TDS and COD was recognized to be increased by increasing contact time. At the time interval 1–3 h was a slow removal process for both adsorbents dosage addition. The removal efficiency at 1 h treatment was slight (20–60% for TDS) for all environmental samples. Significant removal for COD was (66–100%) in tank water, surface drinking water station (inlet) but slightly rapid for Rahway drain wastewater (beginning El-Rahway drain, El-Rahway drain outfall and downstream drain outfall) (7–60%) as shown in Fig. 8. Poor removal efficiency at 1-h treatment indicated that the required time to remove all parameters was insufficient.

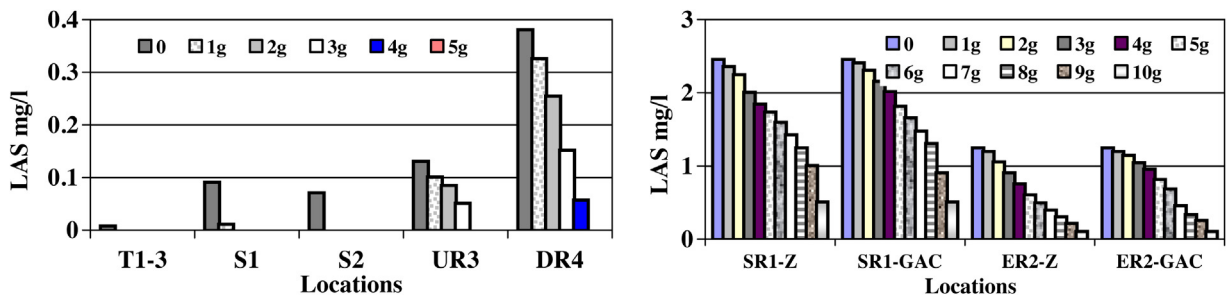


Fig. 7. LAS/l removal of environmental samples against dosage for adsorbents (Z or GAC).

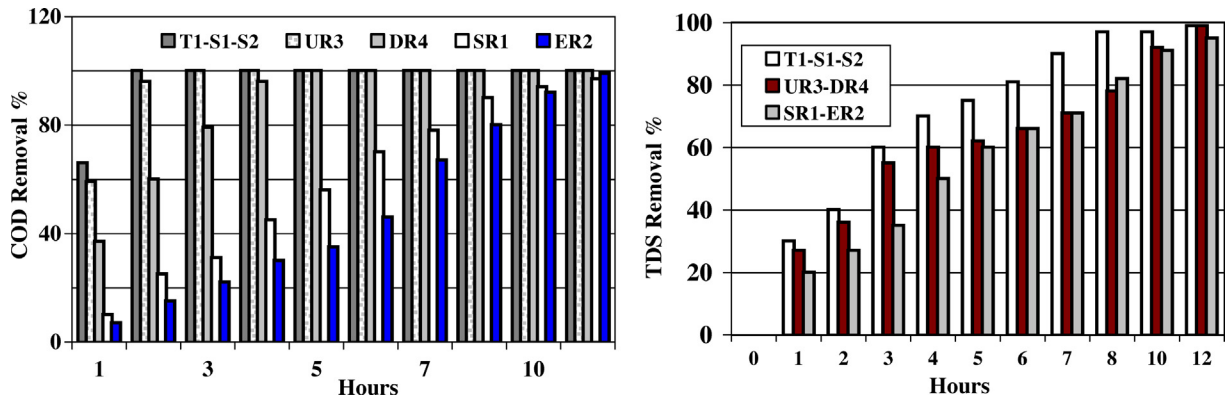


Fig. 8. Percentage removal of TDS and COD at flow rate 50 ml/min.

While at 5 h treatment, TDS removal was (60–75%), COD removal recorded 100% for all environmental samples except Rahway drain wastewater (beginning El-Rahway drain and El-Rahway drain outfall) 39% and 56% as shown in Fig. 8. The obtained results showed that the time of contact between adsorbate and adsorbent is proven to play an important role during the uptake of pollutants from water samples by adsorption process. In addition, the improvement of adsorbent surface was managed by contact time and dosage in order to enhance the removal efficiency. Then, the use of adsorbent in water pollution control can be predicted by the time taken to attain its equilibrium (Okbah et al., 2013).

It is evident that adsorption process showed notable removal at run for 10 h was 78–97% and 91–97% for TDS and COD, respectively. Furthermore, the highest removal for TDS and COD was obtained at 12 h of contact time with 95–99% and 99–100% removal efficiency that complied with Egyptian Environmental law (92/2013) as shown in Fig. 8.

3.2.2. Post column

Post column treatment (Fig. 2) showed the highest removal for COD, TDS, and LAS and improvement of DO level (100%, 60%, 99%, and 100%) at 3 h, respectively for all samples except Rahway drain wastewater. Rahway drain wastewater recorded highest improvement at 12 h (95%, 92%, 93%, 97%, and 99%) for TDS, COD, DO, and LAS, respectively. The arrangement of sandstone, Z and GAC had the highest removal efficiency (adsorption capacity) for all parameters.

These results indicated that Z and GAC had successfully treated water in which the environmental measurements concentration reached the level of compliance with the standard drinking water quality limits (European Communities, 1989; Environmental Law 92/2013; WHO, 2006) and safe for aquatic organisms.

Recently, many methods have been designed and proven their effectiveness in treating raw water such as coagulation, flocculation, absorption, filtration and combining (Liu et al., 2011; Syafalni et al., 2012a). Careful consideration of the most suitable method is important to ensure that the adsorption process is the most beneficial, economically feasible method as well as easy to operate for producing high quality of water in a particular location. Therefore, the obtained results showed that activated carbon is an effective adsorbent for treating water with high concentrations of organic compounds (Syafalni et al., 2012b). Its usefulness derives mainly from its large micro-pore and meso-pore volumes causing high surface area (Fu and Wang, 2011) but its high initial cost makes it less economically viable as an adsorbent.

Besides, zeolite as low cost adsorbent nowadays has been explored for its ability in many fields especially in water treatment. Natural zeolite has negative surface charge which gives advantages in absorbing unwanted positive ions in water such as heavy metals that their solubility increased in the presence of detergents. These ions and water molecules can move within the large cavities allowing ionic exchange and reversible rehydration (Jamil et al., 2010). So, using natural zeolite is a successful method for protecting the aquatic environment in investigated sites from the negative impact of LAS and others. Moreover, the effectiveness of zeolite has been improvised by modified zeolite in order to achieve higher performance in removing organic matter.

4. Conclusion

The study focused on LAS determination using cationic dyes by spectrophotometric measurement of the intensity extracted colored complex. The study investigated the influence of anthropogenic activities at nearby areas (vicinity of village, town or residential area) and the impact of environmental measurements toward surfactants load in the river was also being investigated. The suggested treatment removed LAS using a series of adsorbents by means of zeolite and granular activated carbon that have high ability.

The results indicated that surfactants are at present not successfully removed by water treatment process for sewage wastewater in environmental samples. Consequently, such surfactants might promote harmful effects toward the environment, aquatic environment and human health. Zeolite as low cost adsorbent can be considered a successful mineral for protecting the aquatic environment from the negative impact of LAS and achieved higher performance in removing organic matter.

5. Recommendations

The findings of this research clearly hint that the use of surfactant in detergents should be banned and disposal of all types of waste material should be scientifically planned.

1. Fish play a major ecological role in aquatic food-webs because of their function as carrier of energy from lower to higher trophic levels. The effect of surfactant on fish must be studied as a “warning system” in natural water.
2. Health and sanitary authorities have to regularly monitor and control drinking water contamination.
3. Disinfection process of drinking water must be totally complete for water supply system.
4. Periodic drinking water quality monitoring is necessary in drinking water supply and storage system. Old and corroded pipes are not able to carry good quality of drinking water and an alternative technique for this problem is suggested here employing microbial growth resistant material coated metal or ceramic pipes for the safe drinking water supply system.

Conflict of interest

There is no conflict of interest.

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