The Mechanism of Linear Alkylbenzene Sulphonates Removal in Domestic Laundry Wastewater Through Constructed Rapid Infiltration Systems

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Abstract. As one of the main pollutants in domestic laundry wastewater, the direct discharge of linear alkylbenzene sulphonates (LAS) would cause great risks to the natural environment. In this paper, the constructed rapid infiltration system (CRIS) was applied to investigate its performance on removing LAS from domestic laundry wastewater. The laboratory tests indicated that the CRIS could treat the LAS-enriched wastewater efficiently and stably during the whole operation time (63 d) despite the big fluctuation of influent concentration. The LAS removal mainly occurs at the upper level of soil which was approximate 92%. The total removal efficiency could maintain approximate 99%. Mechanisms investigation found that the efficient removal of LAS by CRIS was the combination effects of soil adsorption and indigenous microbial degradation. The formation of alternative aerobic and anaerobic environments in the upper-level soil is necessary and important to the fast biodegradation of LAS. The treatment of LAS-enriched wastewater by CRIS exhibits little effects on the pH, oxidational and reductive value (Eh) and total nitrogen of soils but results in the reduction of organic matters. The results demonstrate that the CRIS is an effective and sustainable strategy to treat the LAS-enriched laundry wastewater in domestic residential community.

1. Introduction

Nowadays, the synthetic detergents are widely used in domestic life and industrial processes. Surfactants are the main functional ingredients in detergents, but they are also the priority pollutants after discharging into the environment. Linear alkylbenzene sulphonates (LAS) are currently one of the main surfactants used in the detergents due to its good properties[1, 2]. Commonly, the LAS-enriched wastewater derived from domestic and industrial processes should discharge into the municipal sewage pipe network and finally dispose in wastewater treatment plants. However, due to the inefficient supervision and management in China, large amounts of the laundry wastewater, which contained high concentration of LAS, were directly discharged into the local environments via the rainwater pipe in residential building.

Though the biodegradability of LAS was evidently improved than the traditional alkyl benzyl sulfonates, its potential environmental pollution and risks can not be avoided due to the widely application with large amounts. It has been reported that the LAS concentration in the effluents of laundry wastewater ranged from 12 to 1024 mg/L[3, 4]. The diffusive LAS in natural aquatic

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environment would exhibit evident acute toxicity to microorganisms and aquatic animals by altering and inhibiting their metabolic activities and proliferation in low concentrations (ranging from 0.3-10 mg/L)[5-7]. Also, it would affect the physic-chemical characteristics of receptors in natural environments (such as the surface water and soil) and result in the transfer of other toxic compounds, which would aggravate the environmental hazards by increasing the pollutants categories and concentrations[8]. Therefore, the direct discharge of LAS wastewater would bring severe environmental risks to the local ecosystems and the proper disposal was quite necessary.

The commonly used technologies for the LAS wastewater treatment included physical adsorption, chemical coagulation and catalytic oxidation, microbial degradation and etc[9-11]. However, due to the distributed discharge of LAS-enriched laundry wastewater in residential area, the above strategies seemed to be expensive and hard to operate according to the local conditions. The artificial constructed rapid infiltration systems (CRIS), which was considered as an environmental-friendly, effective and economic technology, has been widely applied to wastewater treatment and pollutants removal[12, 13]. It was not restricted by the land limitation and thus it was easy to build and operate in residential community. However, till now, few studies have investigated the effects of CRIS on the removal of LAS in laundry wastewater.

Thus, the aim of this study is to explore the possibility of removing LAS in the laundry wastewater by CRIS in laboratory-scale tests. The LAS removal efficiency and stability of CRIS were firstly analyzed. Then the mechanisms for the efficient LAS removal were investigated from the perspective of soil adsorption and microbial biodegradation. Finally, the influences of LAS on the soil characteristics were determined to further evaluate the feasibility and applicability of CRI S on the LAS removal.

2. Material and methods

2.1. Materials

The real LAS-enriched laundry wastewater was withdrawn from a residential community in Nanjing, China. The simulated LAS wastewater was obtained by dissolving the suitable amounts of commercial laundry powder into tap water according to the required concentration of LAS in tests. The concentration of LAS in commercial laundry powder was 140±5 g/kg.

The soil composition used in the CRIS was composed of natural soil: silica sand: zeolite at a ratio of 1:1:0.025 according to the previous study[3].

2.2. Experimental methods

2.2.1. Performance of CRIS on the LAS removal. The experiments were conducted in the CRIS reactor (as shown in Figure 1). The diameter of the CRIS was 10 cm. Three sample ports were set in CRIS at the depth of 30, 50 and 70 cm to investigate the impacts of soil depth in CRIS on the LAS removal. The operation mode of the CRIS was adopted the strategy of wet-dry alternative cycle, which was fed with LAS wastewater for 4 h and kept dry for the next 20 h. The hydraulic load of CRIS was 0.4 $m^3/m^2 \cdot d$. By determining the LAS concentrations in both influents and effluents after the CRIS treatment, the removal efficiency of LAS was obtained. Also, the typical indices of soil characteristics, including the pH, Eh, organic contents (OCs) and total nitrogen (TN), were analyzed before and after the tests to evaluate the impacts of LAS wastewater on the soil characteristics. The total operation of CRIS reactor lasted for 63 d.

2.2.2. Adsorptive effects of the CRIS on the LAS removal. The simulated LAS wastewater was prepared by dissolving the laundry power into tap water at the concentration of 60 mg/L. Then it was fed into the CRIS continuously from the inlet and was sampled in the effluents at certain intervals (2, 5, 10, 20, 40 and 60 min in the 1st day and then sampled once a day for the next 6 days) to determine the LAS concentration. Due to the shortage of required nutrients and oxygen in the influents, the aerobic bacteria responsible for LAS degradation was supposed to be inhibited and thus the microbial effects on LAS removal were neglected.

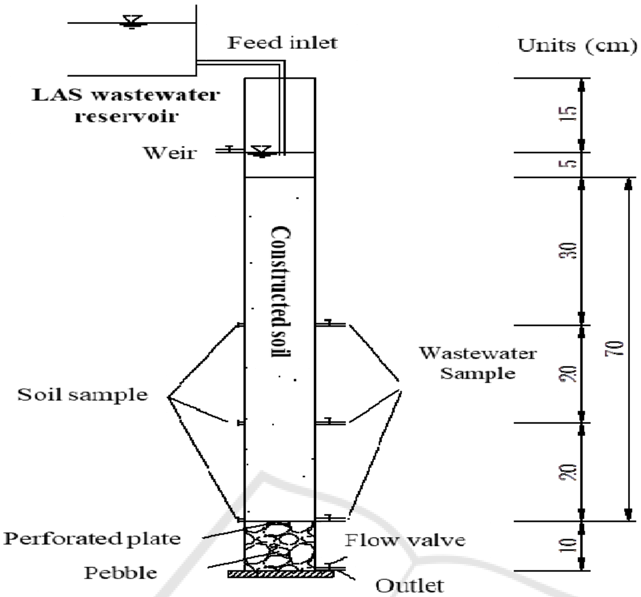


Figure 1. Structure and parameters of the CRIS reactors used in the present study.

*2.2.3. Investigations of the LAS biodegradation by the indigenous microorganisms in CRIS.*The experiments were divided into 4 groups and conducted in 16 identical serum bottles with a working volume of 250 mL. The concentration of LAS in each reactor was respectively set at 85, 150, 850 and 1000 mg/L by dissolving the commercial laundry powder into tap water. 2 g of acclimated soil were withdrawn from the long-term run CRIS reactors in three different heights (30, 50 and 70cm) and then inoculated into the reactors with proper medium. The reactors inoculated with the autoclaved soils were set as the control. The reactors were then operated at 30 ± 1 ^{o}C with a stirring speed of 130 rpm. The medium composition was as follows (g/L): peptone, 5; NH_4NO_3, 5; K_2HPO_4, 1; NaCl, 5. The mixtures were sampled in 3 d and then centrifuged to obtain supernatant for the test of LAS residue.

2.3. Analytic methods
The determinations of pH, Eh, OCs, TN, LAS were according the APHA and previous study [3,14]. All tests were conducted in triplicates, and an analysis of variance was used to test the significance of results and $p < 0.05$ was considered to be statistically significant unless otherwise stated. LAS was determined by high-performance liquid chromatography (HPLC) using a Waters chromatograph with UV detector and a C18 reversed-phase column. The mobile phase consisted of 20% of solvent A (water) and 80% of solvent B (0.15 M $NaClO_4$ in acetonitrile/water 80/20) and the flow rate was maintained at 1 mL/min. The column effluent was monitored at 223 nm.

3. Results and discussion

3.1. Effects of the CRIS systems on the removal of LAS
The effectiveness and stability of CRIS on the LAS removal was firstly investigated. As shown in Figure 2, the LAS concentration in the real laundry wastewater ranged from 26.2 to 81.0 mg/L. However, with the treatment of CRIS, the LAS were reduced remarkably. The concentration of LAS in the effluent was

merely observed to 1.85 mg/L and the removal efficiency reached to 94.9% on the day 1. The performance of CRIS on the LAS removal flocculated slightly during the initial operation due to the sudden increase of shock load that may be beyond the treating ability of CRIS. The LAS concentration in the effluents rebounded in the following several days. However, after a short acclimation, the removal efficiency was recovered and further increased to 99.5% at 8 d and maintained the high removal efficiency (up to 99%) during the whole operation time. The final concentrations of LAS in the effluents were at approximate 0.2 mg/L which could meet the strict standards for the control of surfactants in surface water (0.3 mg/L) [15].

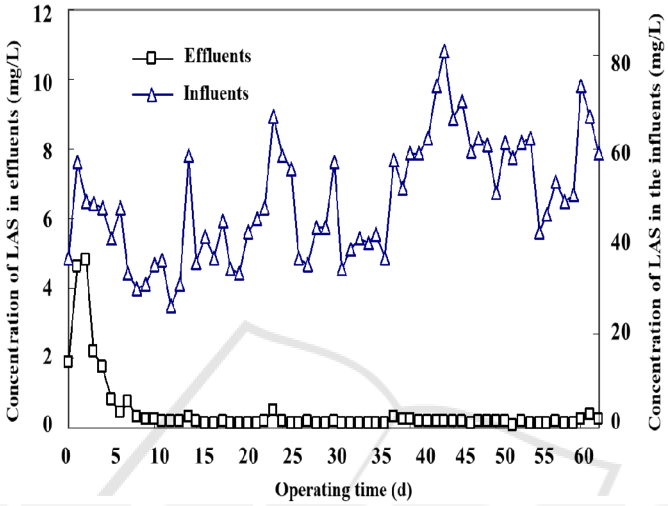


Figure 2. Performance of CRIS on the LAS removal in laundry wastewater.

Further investigation found that the LAS removal efficiency in CRIS was related to the depths of constructed soil. The average removal efficiency of LAS was respectively 92.2, 99.2 and 99.3% at the depth of 30, 50 and 70 cm in CRIS, indicating that the LAS removal was mainly accomplished in the upper-level soil (0-30 cm).

Overall, the high removal efficiency and excellent stability of CRIS indicated its effectiveness and applicability in disposing the LAS-enriched laundry wastewater.

3.2. Changes of the soil characteristics during the LAS treatment in CRIS

As a sort of wastewater, the environmental impact of LAS was also important to evaluate the feasibility of applying CRIS to treat LAS wastewater in residential areas. Thus, the typical indices of the soil characteristics, such as the pH, Eh, OCs and TN, were investigated. As shown in Table 1, the pH, Eh and TN were not significantly changed during the whole operation time in all depths of soils. The decrease of Eh in the topsoil (30 cm) could be attributed to the on-going oxidation of residual LAS which led to the consumption of oxygen. However, the organic content was evidently reduced at the depth of 50 and 70 cm in CRIS soils during the treatment. The wash-up of organics by LAS and the microbial utilization were supposed to result in the OCs decrease. But the adsorption and retainment in the upper level soil could capture most of organic substrates in influents and then compensate the loss. Thus, the OCs kept stable in topsoil.

Table 1. Changes of the soil characteristics during the LAS treatment in CRIS systems.

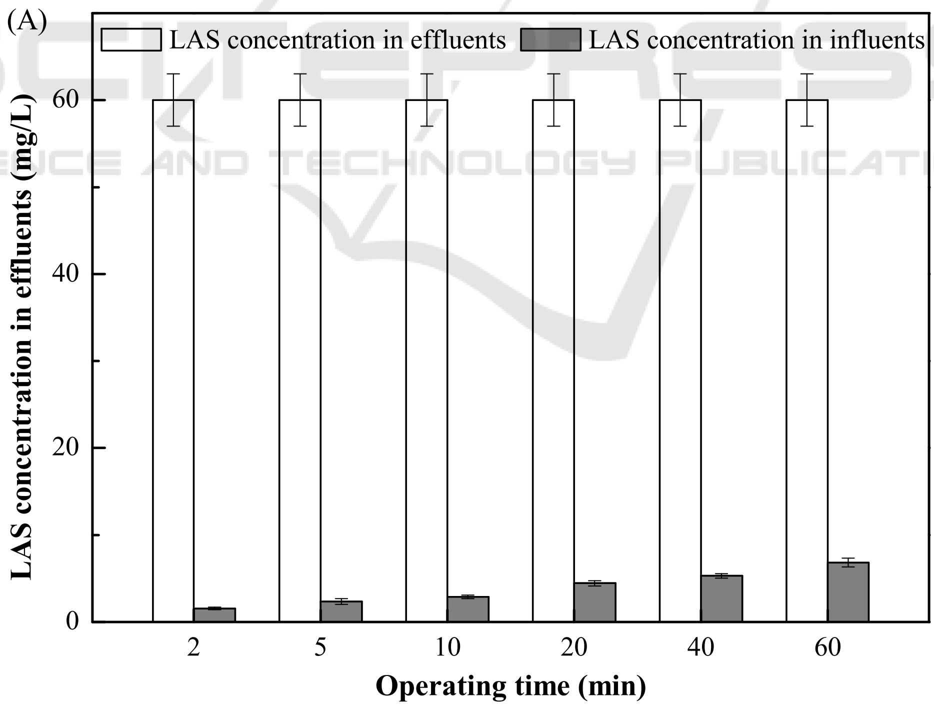
Index	pH		Eh (mV)		OCs (%)		TN (mg/kg)	
Depths	Pre-test	Post-test	Pre-test	Post-test	Pre-test	Post-test	Pre-test	Post-test
30 cm	6.22	6.39	265	187	0.79	0.77	336.5	317.2
50 cm	6.22	6.44	265	256	0.79	0.49	336.5	334.9
70 cm	6.22	6.47	265	251	0.79	0.41	336.5	328.0

3.3. Mechanisms for the efficient LAS removal in CRIS

3.3.1. LAS removal by the adsorption effects. Adsorption was one of the widely accepted mechanisms for the pollutants removal in soils [9, 16]. Therefore, the adsorptive function of soils on LAS removal was firstly investigated with synthetic LAS wastewater. As shown in Figure 3(A), in the continuous-feed CRIS, the LAS was rapidly removed after going through the CRIS as the concentration of LAS in effluents was reduced from 60 to 1.56 mg/L within 2 min. The absence of oxidants in soil and the slow microbial metabolic process excluded the possibility of chemical oxidation or microbial biodegradation of LAS in such short time. Therefore, the the rapid removal of LAS in simulated laundry wastewater was mainly attributed to the strong adsorptive ability of soils in CRIS.

However, the performance of CRIS was gradually deteriorated as the removal efficiency was reduced from the initial 97.4% to 88.6% at 60 min which could attribute to the saturation of adsorptive sites in soil particles. It was further confirmed with the extension of operating time. As shown in Figure 3(B), the adsorptive ability of soil particles in CRIS was completely lost and reached the breakthrough point as the removal efficiency was decreased to 2.33% within 7 days continuous feed of LAS wastewater. It seemed that the results were contradictory to that obtained in CRIS with wet-dry alternative operation mode. In that long-term-run test, the total feed time of CRIS was up to 252 h (*i.e.* 63 d×4 h/d), which was longer than the duration in adsorption test (168 h). However, it kept high LAS removal efficiency during the whole operation time.

The seemingly contradictory results indicated that the adsorption effect was not the mere mechanism for the efficient LAS removal.



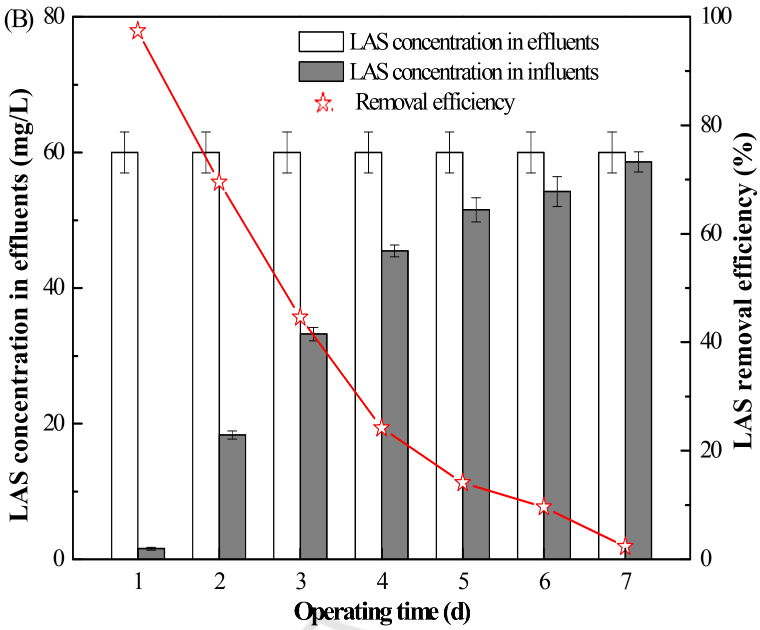


Figure 3. Removal of LAS in laundry wastewater by adsorptive effects in CRIS.

*3.3.2. Microbial degradation of LAS by the indigenous microorganisms in CRIS.*The effect of indigenous microorganisms in CRIS on the removal of LAS was also important as the biodegradability of LAS has been reported extensively, especially under aerobic condition[10, 17].

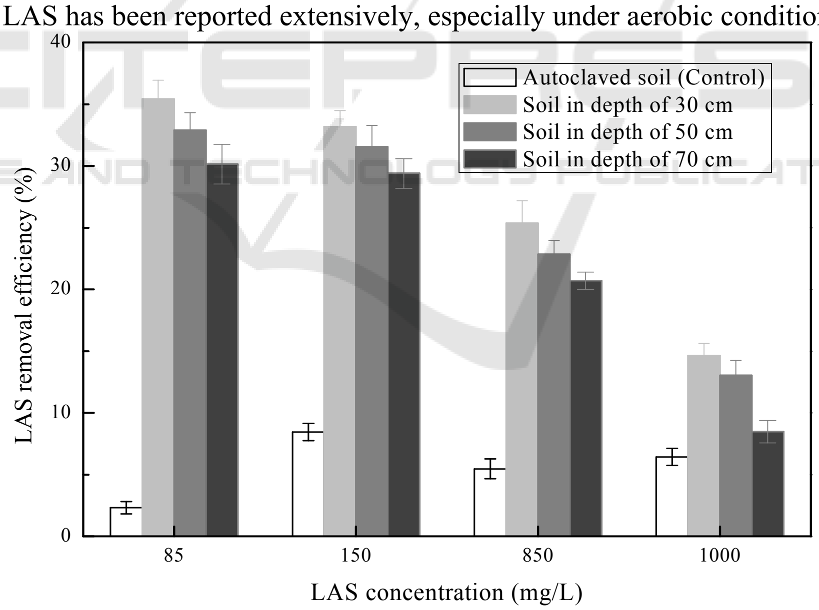


Figure 4. LAS biodegradation with the inoculation of microorganisms from acclimated soils in CRIS at different depths .

As shown in Figure 4, the removal efficiency of LAS in synthetic wastewater was obviously incremented in all batch tests with the inoculation of acclimated soils from different depths of CRIS when comparing with that in the control (inoculated with autoclaved soil). The results indicated the existence of indigenous LAS-degrading microorganisms in CRIS and their positive influences in the process of LAS biodegradation. Also, the biodegradation rate was found to be closely related with the LAS concentration. The average removal efficiency of LAS with inoculated soils from different depths was 30-35% at the low concentration of 85 and 150 mg/L. However, it was reduced to 20-25% at the concentration of 850 mg/L and further decreased to 8.5-14.6% at 1000 mg/L. The reason could be attributed to the inhibitory effects of LAS on the microbes, and the toxicities were incremented with the increase of LAS concentration[5-7]. Commonly, the concentration of LAS in domestic laundry wastewater varied from 26.2 to 81.0 mg/L. Thus, the microorganisms in CRIS could still exhibit high activities to biodegrade the LAS.

Besides, the difference of inoculation from the soils in CRIS also influenced the LAS removal and better performance was obtained with the upper level soils. It mainly attributed to the higher microbial activities and abundances in the topsoil. It has been reported that the LAS were readily biodegradable under aerobic conditions but not under anaerobic conditions[18]. The topsoil in CRIS could easily get sufficient oxygen from the air and simultaneously the retainment of organic contents by the soil particles provided the necessary substrates for microbial growth. The two advantages would ultimately benefit to the increase of microbial activities and abundances that involved in LAS biodegradation. However, the acquisition of oxygen and nutrients in subsoil was quite limited and lagged *via* the carryover in wastewater influents and thus the microbial activities were negatively affected. The reason could also explain the quick deterioration of CRIS in the adsorptive tests. In that experiment, the LAS influent was fed continuously which cut off the route of sufficient oxygen acquisition and the required time for the degradation of adsorbed LAS by indigenous microorganisms. Thus, the soil in CRIS could not recover its original capability timely for further pollutants removal.

Therefore, the processes of LAS removal by CRIS could be concluded as follows. During the wet-dry alternative cycle, the topsoil firstly accepted the LAS-enriched laundry wastewater in wet state (feed stage) and then removed most of the LAS *via* soil adsorption temporarily and rapidly, and meanwhile by the microbial degradation partially. In dry state, the microorganisms, especially in the topsoil, could efficiently degrade the adsorbed LAS in soils with the involvement of oxygen. Then the adsorptive sites in soils were released for the LAS removal in next cycle. It was the combination of soil adsorption and microbial degradation that resulted in the efficient LAS removal with good stability in the long-term run.

4. Conclusions

CRIS was an effective strategy to treat the LAS-enriched laundry wastewater. The removal efficiency was up to 99% with good stability and sustainability. The LAS was mainly removed in the upper level soils of CRIS by the combination of soil adsorption and indigenous microbial degradation. The soil characteristics in CRIS were not significantly changed in the process of LAS treatment which also indicated the feasibility and applicability of CRIS in the treating LAS laundry wastewater in the residential areas.

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