Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2020.25106

181 (2020) 123–130
March

Performance evaluation of anaerobic moving bed bioreactor (An-MBBR) for pretreatment of desizing wastewater

Hafiz Muhammad Aamir Shahzad[a], Charel Baumann[b], Sher Jamal Khan[a,*], Harald Schönberger[c], Frank-Andreas Weber[b], Zeshan[a]

[a]*Institute of Environmental Sciences and Engineering (IESE), School of Civil and Environmental Engineering (SCEE), National University of Sciences and Technology (NUST), Sector H-12, Islamabad, Pakistan, Tel. +92 3449167770; email: s.jamal@iese.nust.edu.pk/sherjamal77@gmail.com (S.J. Khan), Tel. +92 3327329292; email: ashahzad.phdiese@student.nust.edu.pk (H.M.A. Shahzad), Tel. +92 3327424488; email: zeshansheikh@iese.nust.edu.pk (Zeshan)*
[b]*Forschungsinstitut für Wasser-und Abfallwirtschaft an der RWTH Aachen (FiW) e.V., Aachen, Germany, Tel. +49 17699018210; email: charel.baumann@rwth-aachen.de (C. Baumann), Tel. +49 1737848918; email: weber@fiw.rwth-aachen.de (F.-A. Weber)*
[c]*Institut für Siedlungswasserbau, Wassergüte und Abfallwirtschaft Universität Stuttgart, Stuttgart, Germany, Tel. +49 71168563723; email: harald.schoenberger@iswa.uni-stuttgart.de*

Received 3 June 2019; Accepted 28 October 2019

ABSTRACT

Only a few textile mills in Pakistan have installed wastewater treatment plants, and even if installed, aerobic treatment processes are hardly operational due to high energy requirements. The performance of a pilot-scale anaerobic moving bed bioreactor was thus investigated in terms of organic removal and biogas production as a potentially energy-efficient pretreatment of real textile desizing wastewater. The pilot plant was operated under on-site conditions for 122 d at Kohinoor Mills Limited Kasur, Pakistan. The temperature of the bioreactor was in the mesophilic range of 22°C–36°C, while pH and oxidation-reduction potential were in the range of 7.7–8.0, and –580–630 mV, respectively. The volumetric organic loading rate of the bioreactor varied 0.2–2.0 kgCOD/m^3/d. Almost 50% of chemical oxygen demand (COD) removal was achieved and COD conversion into biogas was 0.35 m^3_{biogas}/kgCOD$_{removed}$. The produced biogas had a high methane content with a specific methane production of 0.26 $m^3_{methane}$/kgCOD$_{removed}$. The overall performance of bioreactor was marginally improved when the system was running with low sulfate enzymatic desizing wastewater instead of oxidative peroxydisulfate-treated desizing wastewater. After further optimization overcoming unsatisfying biomass retention, high H_2S formation, and possible inhibitory effects of detergents used in the desizing process, this technology has the potential for widespread application in the textile sector of semi-arid developing countries.

Keywords: Desizing wastewater; Anaerobic treatment; Organic removal; Biogas production

1. Introduction

The textile industry of Pakistan has a significant impact on the economy of the country. It is contributing about 57% of the total export of the country and 8.5% to the gross domestic product [1,2]. About 45% of the total manpower of the country is working in the textile industry [2]. Textile manufacturing consists of dry processes (i.e. spinning, knitting, weaving and production of the garments) and wet processes (i.e. sizing, desizing, scouring, bleaching, mercerizing, dyeing, printing and finishing) [3]. Wet processes consume large amounts of water and ultimately generate substantial

* Corresponding author.

volumes of wastewater discharged untreated to drains or rivers. The wastewater generated by the wet processes is often well beyond the National Environmental Quality Standards (NEQS) of Pakistan [4] and contains a wide variety of pollutants, for example, dyes, organic matters and other chemicals that can jeopardize human and aquatic life [5,6]. The textile industry has intensified the adoption of treatment technologies to reduce the adverse impacts of wastewater pollutants on the environment. Stringent international standards are demanding for sustainable and environmentally friendly practices. Pakistan's textile sector exporting fabric to international brands in developed countries need to adopt the cost-effective technologies to meet stringent effluent standards, for example, Zero Discharge of Hazardous Chemicals (ZDHC) guidelines [7].

In Pakistan, aerobic activated sludge processes are widely used for textile wastewater treatment which requires aeration to metabolize the suspended and soluble organic matters [8]. The organic matter in aerobic treatment is oxidized into CO_2 as well as in the synthesis of new microbial cells [9]. Due to the high organic pollutant load, the aerobic treatment of textile wastewater requires high amounts of energy for aeration and subsequently produces a higher amount of the excess biomass. The textile wastewater from the desizing unit, which is 5%–10% of the total wastewater volume, accounts for over 50% of the total organic load [10,11]. Regarding organics, desizing wastewater mainly contains sizing agents that are applied to the warp yarn to protect it against the mechanical stress during weaving. After the weaving process, this wastewater has to be discharged completely. In Pakistan, the dominating sizing agent applied is starch but in many cases, the sizing recipes also contain a smaller proportion of synthetic sizing agents, mainly polyvinyl alcohol, in some cases carboxymethyl cellulose or polyacrylates are also used. The addition of wastewater from the desizing unit into the other wastewater streams increases the energy demand for aerobic treatment. Pretreatment of desizing wastewater may be a simple and more economical strategy as compared to combined centralized textile wastewater treatment [12] since energy consumption for aeration and sludge generation is significantly reduced and at the same time, energy is recovered in the form of biogas if pretreated anaerobically [13]. Different technologies have been adopted to treat desizing wastewater such as Fung et al. [14] used UV/US with hydrogen peroxide (H_2O_2) for organic and color removal of desizing/dyeing wastewater. The effects of pH, H_2O_2 dosage and ultrasonication (US) were investigated in this study. They found that the organic and color removal increased by increasing pH and the US when the dosage of H_2O_2 was <0.1 mL/L. Kumar et al. [15] treated the desizing wastewater by using coagulant with and without catalytic thermal treatment. Without catalytic thermal treatment, maximum chemical oxygen demand (COD) removal of 58% was achieved by using 5 g/L of commercial alum at a pH of 4. At the same coagulant dose and pH, COD removal of 88% was achieved with catalytic thermal pretreatment desizing wastewater. Magdum et al. [16] degraded the polyvinyl alcohol-containing textile desizing wastewater by aerobic treatment. They achieved 80%–90% of COD removal at the aeration of 16 L/min/L, stirring speed of 150 rpm and hydraulic retention time of 2 d. These technologies have encountered restrictions due to high operational cost, lower treatment efficiency and high sludge production [13].

Anaerobic pretreatment is an established technology in industries treating effluent with high organic loads, particularly in the beverage and food industry [17]. Anaerobic pretreatment of desizing wastewater can reduce the energy demand as well as the sludge production of subsequent aerobic treatment and also produce energy in the form of biogas. Desizing wastewater is a potential source for renewable energy production as it contains a high concentration of biodegradable substances. Very few studies have been conducted on anaerobic digestion of desizing wastewater [13,18–21], most of which are based on lab-scale reactors. In Germany, there is one plant known for the pre-treatment of desizing liquor at an industrial scale [22]. In Pakistan, so far no anaerobic treatment has been used for the treatment of real desizing wastewater.

In this study, anaerobic moving bed bioreactor (An-MBBR) plant was chosen because in An-MBBR biofilm develops on media retained in the system, utilizing the whole volume of the reactor and no sludge wasted [23]. A pilot-scale An-MBBR plant was commissioned for the treatment of real desizing wastewater at Kohinoor Mills Limited Kasur, Pakistan. In this textile industry, almost 60% of the total COD load is generated from the desizing unit. The pilot treatment plant was designed, manufactured, shipped and operated under the InoCottonGROW project (Innovative impulses reducing the water footprint of the global cotton-textile industry towards the UN Sustainable Development Goals) funded by the German Ministry of Education and Research (BMBF). This study aimed to investigate the performance of an anaerobic MBBR in terms of COD removal and biogas production of desizing wastewater under on-site conditions in Pakistan.

2. Materials and methods

2.1. Experimental setup

The process flow diagram of the pilot-scale An-MBBR is shown in Fig. 1. The containerized plant was manufactured by A3 Water Solutions GmbH, Germany. The anaerobic reactor having a volume of 1,400 L was used for the treatment of desizing wastewater and subsequent production of bioenergy. The system was operated from 21st June 2018 (day 1) to 26th October 2018 (day 122) at Kohinoor Mills Limited Kasur, Pakistan. Wastewater for the anaerobic plant was collected in a container from a drain near the desizing wash boxes and transported to the pilot plant. After overnight cooling, wastewater was filled through a bag filter (pore size of 250 μm) into the feed tank by using a transfer pump (Drum pump Lutz B2 Vario, Germany). A mechanical stirrer was provided in the feed tank to ensure the uniformity of constituents. With an adjustable peristaltic pump (Peristaltic, Series MP2-R, Germany), wastewater was continuously pumped into the An-MBBR.

Plastic carrier (Pearl®, EvU - Innovative Umwelttechnik GmbH, Germany) having a specific surface area and density of 700 m^2/m^3 and 0.98 g/cm^3, respectively was used as a carrier material for the growth of biofilm. Wastewater and carrier material were mixed inside the bioreactor with a double impeller mixer rotating at 70 rpm. A progressive cavity

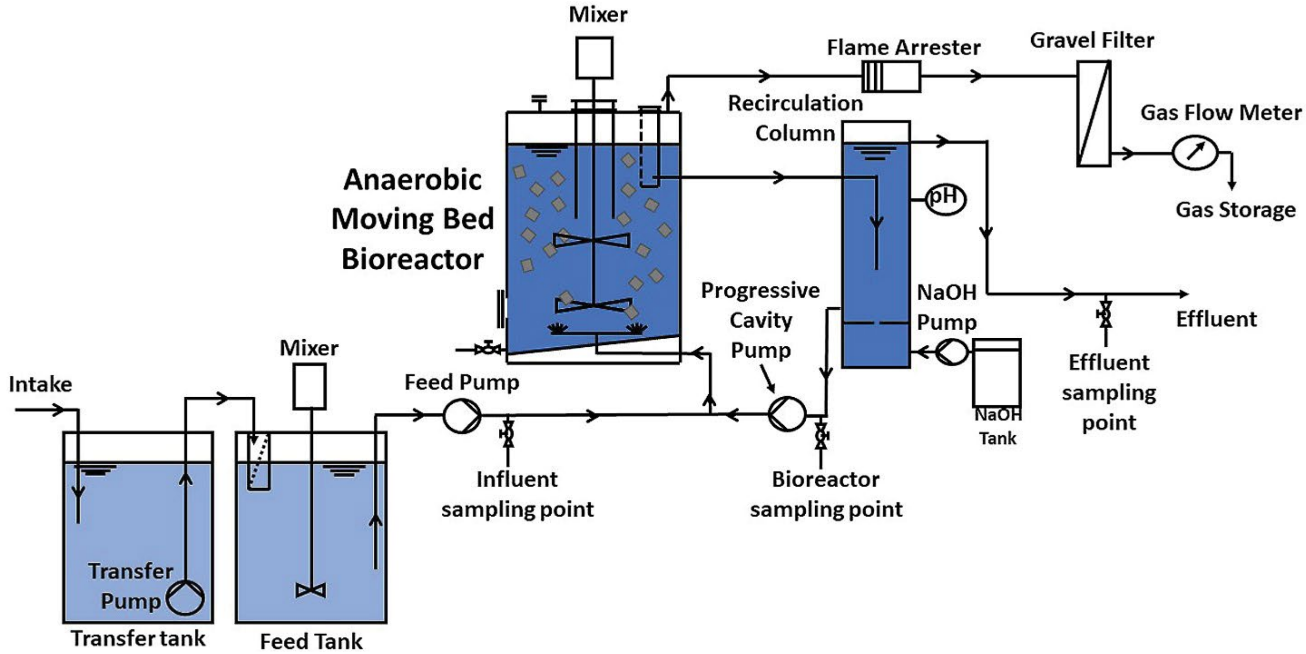

Fig. 1. Process flow diagram of anaerobic moving bed bioreactor.

pump (Cole-Parmer MD 025-6L, Germany) was used for the recirculation of the wastewater from top to the bottom of the bioreactor at a flow rate of 150 L/h. Recirculation was provided for the proper mixing of the influent wastewater and caustic soda (NaOH) which was used for the pH adjustment of the bioreactor. NaOH was pumped with a peristaltic pump (Series MP2-R, Italy) connected with the pH sensor of the recirculation. From the top of the recirculation column, treated wastewater from anaerobic plant exits by overflowing. Biogas generated from the anaerobic plant was dried by a gravel filter and stored into a gas bag (BioGas Backpack, (B) energy GmbH, Germany) having a volume of 1,200 L. Once the biogas bag filled, it was replaced with an empty one and collected gas was burned in a gas stove. The volume of the gas generated from the anaerobic plant was measured by the gas flow meter (G4-RF1, Germany).

2.2. Startup and operation of the reactor

For a startup, the anaerobic MBBR was inoculated with a sieved and filtered emulsion of cow dung and tap water. For this purpose, 75 kg of the cow dung was used as a source of bacteria because no anaerobic sludge was available. During the inoculation period of 20 d, the anaerobic plant was not fed continuously with desizing wastewater. During this period, organic acid production and COD reduction started within 2 d and no biogas production was observed before 16 d, indicating methanogenesis had not started yet. The initial biogas production started on day 16 which increased quickly from 9 to 66 L/d within 4 d.

Continuous feeding was initiated as soon as a significant amount of biogas production was observed. It was performed from day 21 to 122 of the operation. Table 1 shows the operating conditions of anaerobic MBBR during continuous operation.

2.3. Characteristics of wastewater

During the study period, Kohinoor Mills was using two types of desizing processes (oxidative and enzymatic desizing). Out of which 80% of the produced fabric was oxidative desized while the remaining 20% was enzymatic desizied. Characteristics of textile wastewater had been changing day to day or even hour to hour because of the application of different types and composition of sizing and desizing chemicals for the various types of fabric. So, the constituent characterization was very difficult. The measured desizing wastewater characteristics are listed in Table 2.

The high COD is mainly caused by sizing agents. The surfactants used for washing off the sizing agents can have a toxic effect on the anaerobic bacteria [24]. The high sulfate concentration was due to the use of sodium peroxydisulfate for oxidative desizing. This is of relevance as sulfate is converted to hydrogen sulfide which has the potential to inhibit the anaerobic process.

Table 1
Anaerobic MBBR operating conditions during continuous operation

Time (d)	Average OLR (kgCOD/m^3/d)	Media filling (% of reactor volume)	Mixing ratio
21–50	0.58	20	Mixing 20 s after every 20 min
51–66	0.96		
67–76	0.72	35	Mixing 20 s after every 24 h
77–110	1.07		
111–122	0.70		

Table 2
Characteristics of desizing wastewater

Parameters	Range	Average
COD, mg/L	8,500–20,000	14,250.0
pH	9.8–12.0	10.9
Sulfate, mg/L	600–1,300	950.0
Temperature, °C	75–88	81.5
Total nitrogen, mg/L	41–212	126.5
Total phosphorus, mg/L	6.4–17.2	11.8

2.4. Analytical methods

COD, organic acid, pH, oxidation-reduction potential (ORP), biogas production and temperature were the parameters tested daily and nitrogen (TN), phosphorus (TP), and sulfate (SO_4^{2-}) were measured intermittently. pH, ORP and temperature were measured by using a portable multiparameter meter (HI98194, Hanna, USA). COD, organic acid, nitrogen, phosphorus, and sulfate were measured by using a portable spectrophotometer (DR1900, Hach, USA) and Dry Thermostat (LT200, Hach, USA) was used for heating and special digestion of the samples.

The volume of biogas generated from the bioreactor was measured by the gas meter (G4-RF1, Germany) and biogas composition was analyzed with the biogas analyzer (Geotech Biogas 5000 Gas Analyzer, UK). For the test of pH, ORP and temperature, samples were taken from the influent, effluent and the recirculation of the bioreactor. COD was measured from both influent and effluent samples. Organic acid, nitrogen, and phosphorus were measured in the recirculation samples and sulfate was only measured in the influent samples.

3. Results and discussion

3.1. Influent and effluent characteristics

As compared to aerobic treatment, anaerobic treatment is highly sensitive to environmental conditions such as temperature, pH and ORP. The optimum temperature for anaerobic mesophilic treatment is 35°C [25]. The anaerobic MBBR was operated under ambient temperature and no additional heating was provided to the bioreactor. Fig. 2a shows the wastewater temperature in influent and effluent. The first 20 d was the inoculation period of the anaerobic MBBR and wastewater was not continuously fed into the bioreactor. During the acclimatization period, only bioreactor parameters were tested. Once a significant amount of the biogas production was observed, continuous feeding of the system was started from day 21 and all the wastewater samples (influent and effluent) were tested continuously. The actual temperature of the fresh wastewater batch was in the range of 75°C–88°C. The batch was fed into the feed tank when the temperature reached below 45°C (after 16–20 h of the collection). As depicted in Fig. 2a temperature of the feed tank was in the range of 27.5°C–40°C and effluent temperature was in the range of 22°C–36°C (mesophilic range).

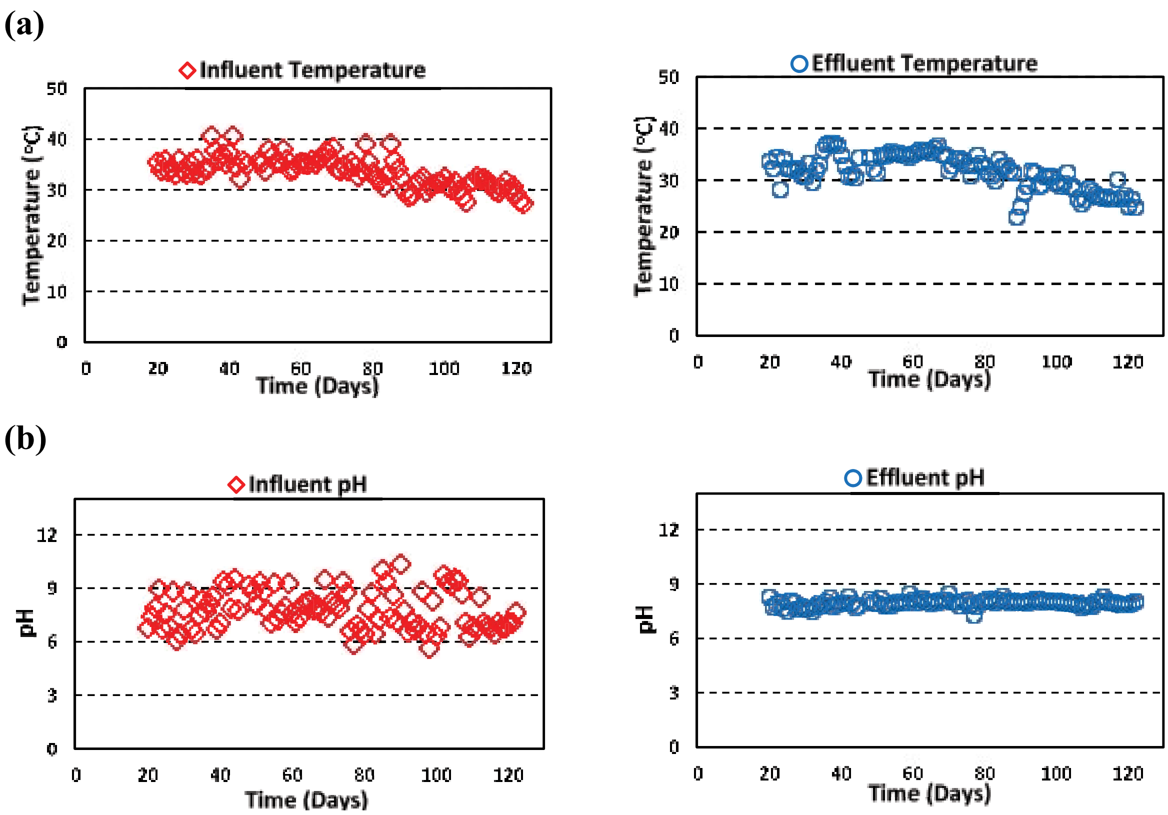

Fig. 2. (a) Temperature and (b) pH in influent and effluent.

Anaerobic treatment is also affected by the pH of the system, which affects the enzymatic activity of bacteria. Fig. 2b shows the pH of the influent and effluent wastewater samples. After filling a fresh batch into the feed tank, the high pH of the wastewater (pH of 10–11) was adjusted to 9.0–9.5 with HCl. The pH in the feed tank then gradually dropped to 7.0–7.5 in a few hours due to bacterial activity. To ensure the continuous feeding to the bioreactor, every fresh batch of the wastewater was always mixed with the previous wastewater in the feed tank. Due to this mixing of the fresh wastewater batch with the remaining wastewater of the feed tank, HCl was only used in a few cases. The anaerobic MBBR was operated at pH 7.7–8.0 and the pH in the bioreactor were maintained by NaOH. The optimum pH for the anaerobic reactor is 6.8–7.2 [26] but the anaerobic process can tolerate pH in the range of 6.5–8.0 [25]. The bioreactor was operated at slightly higher pH as compared to these optimum value, because at pH 8.0, H_2S and organic acid are expected to have less inhibiting effect on the anaerobic process [27].

After startup, the ORP value of the bioreactor was in the range of –580 to –630 mV which is suitable for the anaerobic process and methane-producing bacteria (MPB) because methanogens need an extremely reducing environment. As it was reported in the literature that the value of ORP for the methanogens should be lower than –400 mV [28].

Fig. 3 shows the COD of the influent and effluent of the bioreactor. During the study, the transfer tank was filled 25 times with desizing wastewater from the desizing drain of the bleaching plant and transferred to the feed tank. The level of the feed tank was maintained above 600 L, as much as possible, to reduce the mixing of the air with wastewater in the feed tank and for the continuous supply of the wastewater to the bioreactor. Due to bacterial activity in the feed tank, the COD in the feed tank dropped with time. As shown in Fig. 3, the COD of the feed tank varied from 4,200–16,000 mg/L while it was in the range of 2,200–8,000 mg/L in the effluent. Approximately 50% of average COD removal was achieved as shown in Fig. 4. The nature of the wastewater coming from the textile industry changed day to day or even hour to hour due to batch-wise processes. Downward arrows in Fig. 3 shows the days on which a fresh batch of the wastewater was added into the bioreactor. Sometimes the

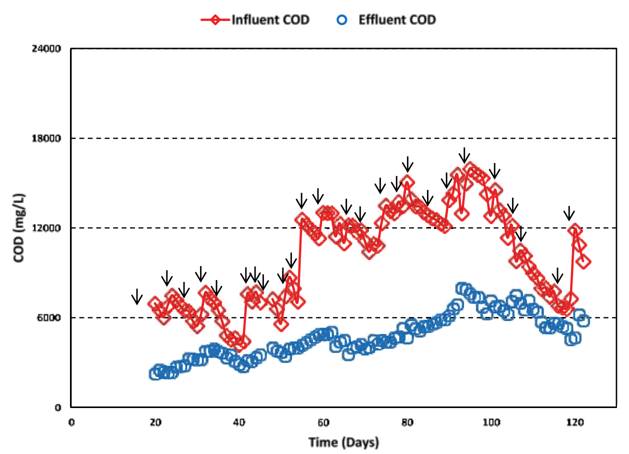

Fig. 3. COD of the influent and effluent of the An-MBBR.

COD concentration of the existing wastewater in the feed tank was diluted by the addition of the fresh batch having a lower COD concentration and sometimes the fresh batch increased the COD in the feed tank due to its higher COD concentration.

3.2. Organic (COD) removal efficiency of An-MBBR at different organic loading rate

Fig. 4 shows the organic loading rate (OLR) to the bioreactor and organic removal from the bioreactor. The variation in the OLR was due to the change in COD concentration in the feed tank as well as the flow rate to the bioreactor. COD of the feed tank changed due to bacterial activity and the addition of fresh batch into the existing one. Moreover, the feeding flow rate was changed to adjust the bioreactor load according to bacterial activity assessed by the biogas production and organic acid concentration (Fig. 5). The vertical lines in the graph (Fig. 4) show the average OLRs applied to the bioreactor during continuous feeding.

The An-MBBR was operated with 20% and 35% of the media filling. The media filling used in this study was based on the media filling ratio range of 20%–50% as reported in a previous study [29]. At the time of 20% media filling, average OLR to the bioreactor was 0.58 and 0.96 kg COD/m^3/d from days 21 to 50 and days 51 to 66, respectively resulting in average organic removal efficiency of 48% and 59%. At the time of 35% medial filling, average OLR to the bioreactor was 0.72, 1.07 and 0.7 kg COD/m^3/d from days 67 to 76, 77 to 110 and 111 to 122 respectively, resulting in average organic removal efficiency of 63%, 50%, and 31%. During 20% media filling, at OLR of 0.58 kg COD/m^3/d, the bioreactor was still in the acclimatization phase, so the COD removal efficiency was low. However, the removal efficiency increased with time through OLR of 0.96 kg COD/m^3/d. During operation at 35% media filling, organic removal decreased from 63% to 50% with an increase in OLR from 0.72 to 1.07 kg COD/m^3/d. The removal continued to decrease further up to 31%. In the end, reduction in the influent COD reduced the OLR again to 0.7 kg COD/m^3/d, which led the bioreactor to recover the COD removal towards an increasing trend near the end of its operation. It is noteworthy to mention here that being biological, the anaerobic treatment takes time to adjust to the change in operating conditions, particularly the OLR. The reduction in organic removal, in the end, might also be due to the continuous decrease in the ambient temperature.

3.3. Organic acid and biogas production from anaerobic plant

As shown in Fig. 5, (a) biogas production and (b) organic acid production were measured to analyze the activity of the methane-producing and acidifying bacteria and according to these two parameters, OLR to the bioreactor was adjusted. On the 33rd day, the organic acid concentration increased to over 1,000 mg/L for the first time, so that the OLR was reduced by reducing the feed flow rate. Biogas production also reduced with a reduction in the OLR (as depicted in Fig. 5a). It was expected that the reduction in organic acid concentration would be faster than the decline of the biogas production (but the results showed the opposite). When the organic

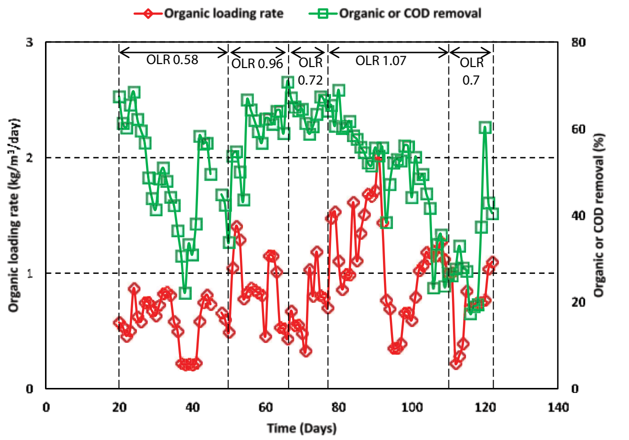

Fig. 4. Organic loading rate to the bioreactor and organic removal efficiency.

acid concentration reached near to 550 mg/L, the potentiometer of the feed pump was set back to the initial level and an increase in biogas production was observed until a defect of the feed pump. The feed was stopped for 2 d and during this time only the bioreactor parameters (organic acid and biogas production) were tested.

As mentioned earlier, the textile industry was using 2 types of desizing processes (oxidative and enzymatic). The batch of enzymatic desizing wastewater was collected on days (54, 58, 77 and 108) and fed to the An-MBBR. Biogas production results were slightly better when the system was running with enzymatic desizing wastewater with less sulfate content. The specific biogas production was 0.35 $m^3_{biogas}/kgCOD_{removed}$ (measured by the total biogas production during the pilot plant operation divided by the total COD removed). As compared to enzymatic desizing, oxidative desizing has higher sulfate concentration in wastewater due to the use of hydrogen peroxide or sodium peroxidisulfate as an oxidative desizing agent. Biogas production rose quickly from 9 to 150 L/d within a few days. From day 1 to day 65 anaerobic MBBR was operated with 20% of the volume filling with carrier material and on day 66 carrier material was increased up to 35% of the bioreactor volume to increase the biomass growth. However, there was no sufficient increase in the biomass which might be due to high shear force caused by the mixer which could inhibit the bacteria from immobilizing on the carrier that was also confirmed by the microscopic examination of the carrier. Consequently, the mixer was set to mix for 20 s every 24 h (previously it was set to 20 s after every 20 min). After increasing the carrier material and reducing the mixing ratio, the biogas production increased up to 386 L/d then decreased to 234 L/d. The reason for the sudden decrease in biogas production might be the increase in the pH (up to 8.5) of the bioreactor during the night time. Furthermore, a drop in the biogas production was observed on day 89, probably due to a decrease in the bioreactor temperature (below 26°C) as the weather cooled down. Before this, the temperature of the bioreactor was in the range of 30°C–35°C (Fig. 2). On the same day, organic acid concentration reached up to 2,400 mg/L, which might be another reason for the reduction of biogas production. The flow rate was reduced again to minimize organic acid accumulation. The gas production did not rise significantly till the end of the study may be due to the following reasons; (a) continuous decrease in the influent COD concentration, (b) decrease in ambient temperature, (c) the domination of acidifying bacteria and (d) inhibition of methanogenic bacteria, both by H_2S and surfactants, especially by fatty alcohol ethoxylates.

3.4. Nutrient concentrations in the An-MMBR process

Nutrients are essential for the microbes for their cell synthesis and to obtain energy. The minimum demand for the macronutrients in anaerobic system should be between 350:5:1 (COD:N:P) and 1,000:5:1 (COD:N:P) depending on the substrate availability [30]. To examine the potential nutrient limitations inside the bioreactor, COD, nitrogen and phosphorus were measured intermittently from the bioreactor samples. Table 3 shows the COD, nitrogen, and phosphorus value with COD:N:P ratio. The ratio of COD:N:P varied from 129:4:1 to 834:30:1, confirming that the nutrient concentrations for the anaerobic bacteria were sufficient.

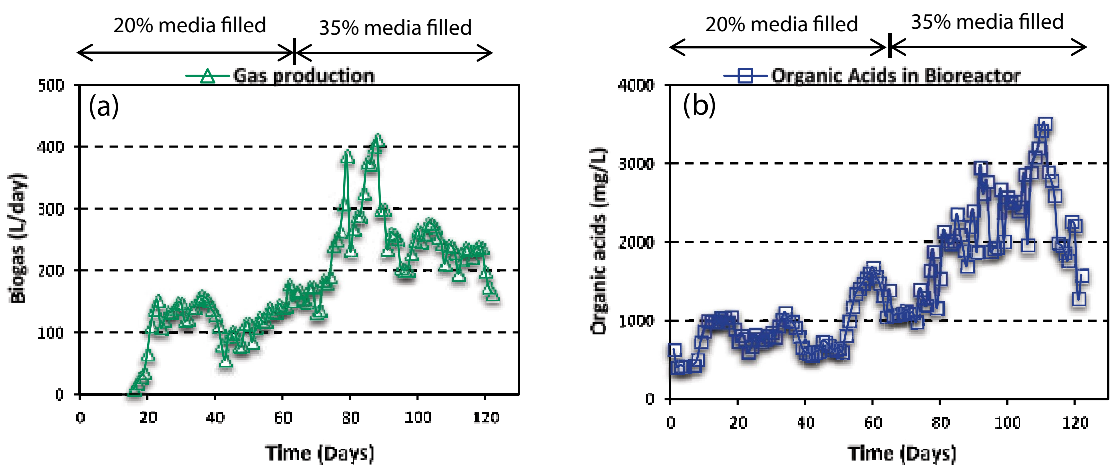

Fig. 5. (a) Biogas and (b) organic acid production from the bioreactor.

Table 3
COD, nitrogen, and phosphorus concentrations inside the bioreactor

Days	COD (mg/L)	Total nitrogen (mg/L)	Total phosphorus (mg/L)	COD:N:P
8	2,222	65.9	17.19	129:4:1
22	2,400	96.4	16.44	146:6:1
30	3,192	127	14.15	226:9:1
35	3,774	139	17.18	219:8:1
44	3,348	157	13.3	251:11:1
50	3,708	127	10.6	350:12:1
55	4,188	169.4	9.54	440:17:1
60	4,914	175.4	12.8	384:13:1
78	4,752	158	7.5	634:21:1
99	6,292	212	7.56	832:28:1
106	7,516	158.6	8.52	882:18:1
113	5,372	197.2	6.44	834:30:1

3.5. Biogas yield and compositions

All of the produced biogas was burned in a gas stove, indicating a sufficient methane content. For biogas analysis, biogas samples were taken in gas bags (Devex Multilayer Foil Gas Bag NDEV31_1, China) from the pilot plant (one when the system was running with oxidative desizing wastewater and other when the system was running with enzymatic desizing wastewater). Table 4 shows the results of the biogas samples. Analysis confirmed that the biogas had high methane content, most of the time the textile industry was using oxidative desizing, under such conditions, on an average 75% of methane content was produced. So the specific methane production from the anaerobic plant was 0.26 $m^3_{methane}/kgCOD_{removed}$ which is lower than the theoretical methane production value of 0.35 $m^3_{methane}/kgCOD_{removed}$ as previously reported in the literature [31].

The analysis data also confirmed that H_2S concentration in the biogas was very high as provided in Table 4. H_2S (unionized sulfide) is a more toxic form of sulfide for anaerobic microorganisms that penetrates through the cell membrane and denatures the proteins or metabolizes enzymes by the formation of sulfide and limits the activity of MPB [32]. As it was reported in the literature [32,33], hydrogen sulfide imposed toxicity to MPB if the level is above 228 mg/L. H_2S production can be mitigated by (i) varying the operating pH of anaerobic system, (ii) by increasing the acclimatization period because MPB can tolerate higher sulfide level (up to 1,000 mg/L) at longer acclimatization period and (iii) by varying the type of organic substrate [32]. Stoichiometry of the H_2S generation due to the presence of sulfate in desizing wastewater is shown in equation (1) and (2). For the use of the biogas in combined heat and power plants, it requires treatment to remove the H_2S before being used to avoid corrosion.

$$SO_4^{2-} + \text{Organic Matter} \xrightarrow{\text{Anaerobic Bacteria}} S^{2-} + H_2O + CO_2 \quad (1)$$

$$S^{2-} + 2H^+ \rightarrow H_2S \quad (2)$$

Table 4
Composition of the biogas produced during oxidative and enzymatic desizing

Compound	Formula	Unit	Oxidative desizing	Enzymatic desizing
Methane	CH_4	%	78.7	87.2
Carbon dioxide	CO_2	%	9.6	5.1
Oxygen	O_2	%	1.3	0.3
Others	–	%	10.3	7.5
Hydrogen sulfide	H_2S	Ppm	6,295	2,169

The results of this study especially COD removal and CH_4 content of biogas is quite similar to the results of full-scale anaerobic desizing wastewater treatment plants installed in Germany [22]. While the production of biogas and H_2S varied in this study. High H_2S production in this study significantly inhibited biogas production as compared to the results of the full-scale study.

4. Conclusions

The pilot-scale anaerobic MBBR (An-MBBR) operated under on-site conditions in Pakistan showed that despite relatively short adaptation time of the biomass, the organic load of the desizing wastewater was significantly reduced while producing biogas with a high calorific value. This study results showed that by increasing the percent media filling in the bioreactor and reducing the frequency of the mixing, the performance of the bioreactor improved in terms of organic removal and biogas production. High H_2S formation and possible inhibitory effects of H_2S and detergents applied in the desizing process may have contributed to limit the total organic removal to 50% on an average. Nevertheless, 0.35 $m^3_{biogas}/kgCOD_{removed}$ of specific biogas production was achieved. The estimated specific methane production was 0.26 $m^3_{methane}/kgCOD_{removed}$. The performance of the bioreactor was also slightly better, in terms of biogas, CH_4 and H_2S production when the system was running with enzymatic desizing wastewater which is very low in sulfate. A cost-benefit analysis of an optimized full-scale anaerobic MBBR pretreatment plant considering Pakistani investment, operation, and maintenance costs is needed to demonstrate that monetary benefits from biogas production (and energy savings in terms of reduced aeration in a subsequent activated sludge treatment) warrant its application in the Pakistani textile sector.

Acknowledgments

The project "Innovative impulses reducing the water footprint of the global cotton-textile industry towards the UN Sustainable Development Goals (InoCottonGROW)" on which this publication is based on is funded by the German Federal Ministry of Education and Research (BMBF) under funding code 02WGR1422A. The responsibility for its content rests with the authors. Authors would also like to acknowledge the management and technical staff of the Kohinoor Mills Limited Kasur, Pakistan for their support during this study. Authors would also like to acknowledge the Higher Education Commission of Pakistan for financial support (Pin No. 213-57748-2EG2-009) to the Ph.D. student.

References

[1] Facts on Pakistan's Garment Industry, Available at: https://cleanclothes.org/resources/publications/factsheets/pakistan-factsheet-2-2015.pdf (accessed on 03.04.2019).

[2] Textile Industry in Pakistan, Available at: https://en.wikipedia.org/wiki/Textile_industry_in_Pakistan#cite_note-2 (accessed on 03.04.2019).

[3] V. Srebrenkoska, S. Zhezhova, S. Risteski, S. Golomeova, Methods for Wastewaters Treatment in Textile Industry, International Scientific Conference, Gabrovo, 2014.

[4] S. Imtiazuddin, M. Mumtaz, K.A. Mallick, Pollutants of wastewater characteristics in textile industries, J. Basic Appl. Sci., 8 (2012) 554–556.

[5] S. Mani, P. Chowdhary, R.N. Bharagava, Textile Wastewater Dyes: Toxicity Profile and Treatment Approaches, Emerging and Eco-Friendly Approaches for Waste Management, Springer, 2019, pp. 219–244.

[6] S. Lorena, C. Martì, S. Roberto, Comparative study between activated sludge versus membrane bioreactor for textile wastewater, Desal. Wat. Treat., 35 (2011) 101–109.

[7] ZDHC, Textile Industry Wastewater Discharge Quality Standards, Zero Discharge of Hazardous Chemicals Programme Literature Review, 2015.

[8] M. Irfan, Wastewater treatment in textile, tanneries and electroplating industries especially by activated sludge method-a technical report, J. Pak. Inst. Chem. Eng., 37 (2009) 4–5.

[9] A. Ghaly, R. Ananthashankar, M. Alhattab, V. Ramakrishnan, Production, characterization and treatment of textile effluents: a critical review, J. Chem. Eng. Process Technol., 5 (2014) 1–19.

[10] A.R. Choudhury, Pre-treatment and Preparation of Textile Materials Prior to Dyeing, Handbook of Textile and Industrial Dyeing, Elsevier, Cambridge, 2011, pp. 64–149.

[11] H. Feitkenhauer, Anaerobic digestion of desizing wastewater: influence of pretreatment and anionic surfactant on degradation and intermediate accumulation, Enzyme Microb. Technol., 33 (2003) 250–258.

[12] G. Pei, F. Yu, J. Liu, Feasibility study of individual treatments of desizing wastewater, J. Residuals Sci. Technol., 12 (2015), doi:10.12783/issn.1544-8053/12/S1/13.

[13] C.-Y. Lin, M.-L.T. Nguyen, C.-H. Lay, Starch-containing textile wastewater treatment for biogas and microalgae biomass production, J. Cleaner Prod., 168 (2017) 331–337.

[14] P. Fung, Q. Huang, S. Tsui, C. Poon, Treatability study of organic and colour removal in desizing/dyeing wastewater by UV/US system combined with hydrogen peroxide, Water Sci. Technol., 40 (1999) 153–160.

[15] P. Kumar, B. Prasad, S. Chand, Treatment of desizing wastewater by catalytic thermal treatment and coagulation, J. Hazard. Mater., 163 (2009) 433–440.

[16] S.S. Magdum, G.P. Minde, U.S. Adhyapak, V. Kalyanraman, An efficient biotreatment process for polyvinyl alcohol containing textile wastewater, Water Pract. Technol., 8 (2013) 469–478.

[17] J.B. Van Lier, High-rate anaerobic wastewater treatment: diversifying from end-of-the-pipe treatment to resource-oriented conversion techniques, Water Pract. Technol., 57 (2008) 1137–1148.

[18] R. Dinsdale, K. Bryne, D. Tucker, The Anaerobic Digestion of Textile Desizing Wastewater, Ecotextiles, Elsevier, Cambridge, 2007, pp. 163–167.

[19] M. Javaid, A.R. Saleemi, S. Naveed, M. Zafar, N. Ramzan, Anaerobic treatment of desizing effluent in a mesophilic anaerobic packed bed reactor, J. Pakistan Inst. Chem. Eng., 39 (2011) 61–67.

[20] K. Opwis, T. Mayer-Gall, J.S. Gutmann, C. Dammer, T. Titscher, A. Nickisch-Hartfiel, O. Grün, C. Spurk, C. Schloderer, A. Köppe, Semi-industrial production of methane from textile wastewaters, Energy, Sustainability and Society, 2 (2012) 1.

[21] L. Rongrong, L. Xujie, T. Qing, Y. Bo, C. Jihua, The performance evaluation of hybrid anaerobic baffled reactor for treatment of PVA-containing desizing wastewater, Desalination, 271 (2011) 287–294.

[22] C. Baumann, H.M.A. Shahzad, R. Minke, Anaerobic Pre-treatment of Desizing Liquor - Experience from Germany and Pakistan, Proceeding of the Colloquium on Integrated Best Available Wastewater Management in the Textile Industry, Vulkan-Verlag GmbH, Essen, Stuttgarter Berichte zur Siedlungswasserwirtschaft, Band 241, Stuttgart, 2018, pp. 101–119.

[23] A. di Biase, T. Devlin, M. Kowalski, J. Oleszkiewicz, Performance and design considerations for an anaerobic moving bed biofilm reactor treating brewery wastewater: impact of surface area loading rate and temperature, J. Environ. Manage., 216 (2018) 392–398.

[24] H.-U. Lerch, Biologische Abwasserreinigung von schlichtehaltigen Textilabwässern mittels eines zweistufigen anaeroben Systems (Biological wastewater treatment of plain textile wastewater using a two-stage anaerobic system), ETH Zurich, Zurich, 2000.

[25] A.E. Cioabla, I. Ionel, G.-A. Dumitrel, F. Popescu, Comparative study on factors affecting anaerobic digestion of agricultural vegetal residues, Biotechnol. Biofuels, 5 (2012) 39.

[26] P. Boonsawang, A. Rerngnarong, C. Tongurai, S. Chaiprapat, Effect of pH, OLR, and HRT on performance of acidogenic and methanogenic reactors for treatment of biodiesel wastewater, Desal. Wat. Treat., 54 (2015) 3317–3327.

[27] K.-H. Rosenwinkel, H. Kroiss, N. Dichtl, C.-F. Seyfried, P. Weiland, Anaerobtechnik: Abwasser-, Schlamm-und Reststoffbehandlung, Biogasgewinnung (Anaerobic technique: sewage, sludge and residue treatment, biogas production), Springer-Verlag, Berlin, 2015.

[28] ORP Management in Wastewater as an Indicator of Process Efficiency, YSI, Yellow Springs, OH Available at: https://www.ysi.com/File%20Library/Documents/Application%20Notes/A567-ORP-Management-in-Wastewater-as-an-Indicator-of-Process-Efficiency.pdf (accessed on 15.08.18), (2008).

[29] S. Azizi, A. Valipour, T. Sithebe, Evaluation of different wastewater treatment processes and development of a modified attached growth bioreactor as a decentralized approach for small communities, Sci. World J., 2013 (2013), doi: 10.1155/2013/156870.

[30] B.S. Yildiz, Water and Wastewater Treatment: Biological Processes, Metropolitan Sustainability, Elsevier, Cambridge, 2012, pp. 406–428.

[31] W. Douglas, D. Hamilton, Methane Production Potential of Waste Materials, Oklahoma Cooperative Extension Fact Sheets, Oklahoma, 2015.

[32] S.K. Khanal, Anaerobic Biotechnology for Bioenergy Production: Principles and Applications, John Wiley & Sons, Ilowa, 2011.

[33] S.K. Khanal, J.C. Huang, Effect of high influent sulfate on anaerobic wastewater treatment, Water Environ. Res., 77 (2005) 3037–3046.