Acclimatized Activated Sludge for Enhanced Phenolic Wastewater Treatment Using Pinewood Biochar

Mohammadreza Kamali[a], Tejraj M. Aminabhavi[b,*], Luis Tarelho[c], Rens Hellemans[a], Joren Cuypers[a], Isabel Capela[c], Maria Elisabete V. Costa[d], Raf Dewil[a], Lise Appels[a,*]

[a] KU Leuven, Department of Chemical Engineering, Process and Environmental Technology Lab, J. De Nayerlaan 5, 2860 Sint-Katelijne-Waver, Belgium

[b] Pharmaceutical Engineering, Soniya College of Pharmacy, Dharwad, 580-002, India

c Department of Environment and Planning, University of Aveiro, 3810-193 Aveiro, Portugal

d Department of Materials and Ceramics Engineering, Aveiro Institute of Materials, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

Abstract

Activated sludge acclimatization was assessed for pinewood biochar to study phenol biodegradation from synthetic effluents. The biochar was produced in a continuous pyrolysis system (auger reactor) at 525°C and was characterized by scanning electron microscopy (SEM), X-ray diffraction, Fourier Transform Infrared (FTIR), elemental analysis, and particle size evaluation. Sludge acclimatization greatly facilitated the phenol biodegradation rate, especially in the presence of biochar. Specific biodegradation rates increased from 0.0017 (g phenol/g VSS/h) for as-received activated sludge to 0.0184 (g phenol/g VSS/h) and 0.041 (g phenol/g VSS/h) for activated sludge acclimatized without (control) and with biochar, respectively at pH ~6.5, for a phenol concentration of 250 mg/L and at room temperature (T = 15-18 °C). The results furthermore demonstrated the positive effects of biochar on microbial colonization and growth. The volatile suspended solids (VSS) increased from 1 g/L for as-received sludge to 1.97 g/L and 2.96 g/L for control and activated sludge acclimatized in the presence of biochar. The sludge volume index decreased from 108 (mL/g MLSS) to 60, while it increased to 298 (mL/g MLSS) for the control. The system studied showed a high degree of stability and resistance to the load shock loading when the initial phenol concentration was increased from 250 to 500 mg/L.

Keywords: *Biochar, activated sludge, acclimatization process.*

1. Introduction

Water pollution is considered to be one of the most challenging environmental issues worldwide [1]. A wide range of environmental contaminants including heavy metals and phenolic organics are generally present as emerging effluents from various industrial activities; these can cause severe ecotoxicological and health-related problems if they are released into the environment without proper treatment [2,3]. There is thus a need for developing sustainable treatment technologies with acceptable efficiencies while being environmentally friendly and cost-effective [4,5].

Among the various technologies developed to deal with highly polluted effluents, the activated sludge system (AS) has been widely implemented for the treatment of both sewage [6] and industrial waste effluents [7] due to its inherent advantages over the other physico-chemical and biological treatment methods in view of simplicity and cost-effectiveness. However, its relatively low efficiency to deal with high concentrations of phenolic effluents has been the main challenge to apply this method for treating high strength phenolic effluents [8]. Acclimatization has been employed to gradually adjust microbial communities to harsh environmental conditions such as pH, temperature, and pollution load [9]. Reports in the literature show that acclimatization can lead to microbial communities capable of degrading relatively high concentration of phenolics [10]. In many cases biodegradation kinetics of acclimatized AS are relatively low for the phenolic wastewaters. Therefore, the development of an acclimatization process that promotes the microbial communities for an efficient treatment of phenolic effluents is highly desired.

Biochar is a carbon-rich product of biomass pyrolysis at temperatures above 250°C under oxygen-free (or limited oxygen content) conditions [11]. This low-cost material that can satisfy the sustainability considerations by sequestrating carbon [12] has been recently employed in several areas, including as soil amendment to improve the soil properties [13] and crop production [14], and in wastewater treatment to adsorb inorganic pollutants such as heavy metals [15] and nutrients [16] or catalyse the degradation of various types of organic and inorganic pollutants via advanced oxidation processes (AOPs) [17]. In anaerobic wastewater treatment systems, the biochar (as a conductive material) furthermore can facilitate interspecies electron transfer between electron-donating bacteria and electron-

accepting methanogens to promote anaerobic digestion processes [18]. In this study, biochar was prepared through the pyrolysis of pinewood. The acclimatization of the as-received sludge was performed in the presence of biochar to investigate biodegradation of synthetic phenolic wastewater and the study was developed to address the need for efficient as well as low-cost technologies to treat the phenolic wastewaters. Since the activated sludge is considered a cost-effective treatment method, further improvements in its performance can promote the applicability of this process to deal with highly polluted effluents.

2. Materials and methods

2.1 Biochar production

Biochar was produced in a continuous pyrolysis system (auger tubular reactor) using pinewood as the feedstock. The reactor was operated at steady-state conditions with continuous feeding of the biomass employing a rotating screw. The maximum pyrolysis of 525 °C and pyrolysis time of 8 min was selected as the operating conditions.

2.2 Biochar characterization

X-ray powder diffraction (XRD) (Panalytical X'Pert PRO 3, Netherlands) analysis was performed to examine the crystallinity of the biochar. A continuous scan from 10° to 100° of 2θ was conducted at a scan rate of 2° 2θ/min. The elemental composition of the biochar was determined using a Philips PW-1400 sequential x-ray fluorescence spectrometer (XRF). Scanning electron microscopy (SEM) was performed using a Hitachi SU-70 SEM. The slurry containing the as-prepared materials suspended in ethanol was ultrasonically irradiated for 10 min to allow the separation of particles. A drop of the slurry was then placed on the grid and was dried before the microscopic analysis. The carbon, hydrogen, nitrogen, and sulfur (CHNS) contents of the produced biochar were determined using an organic elemental analyzer (Thermo Finnigan, Flash 2000, Thermo Scientific). For the analysis, biochar sample was weighed into tin capsules and introduced sequentially in the equipment. Fourier Transform Infrared (FTIR) analysis was performed using a Bruker Tensor 27 system. The spectrum was obtained from 256 scans with a resolution of 4 cm^{-1} under trans-

mittance mode in the range of 4000–400 cm^{-1}. A laser diffraction particle size analyser (model CILAS) was also utilized to identify the average size of the biochar particles.

2.3. Phenol volatilization

Volatilization of phenol was first assessed by introducing 500 mL of the synthetic effluent containing 25, 50, 100, 250, and 500 of mg/L phenol in 1000 mL batch reactor without activated sludge (mixed liquor volatile suspended solids (MLVSS)=0 mg/L) [19]. Samples were collected at specific sampling points from the top of the reactors to determine any loss of phenol during the volatilization.

2.4 Acclimatization process

Acclimatization of as-received activated sludge from a full-scale municipal wastewater treatment plant (Aquafin, Mechelen-Noord, Belgium) to increasing phenol concentrations including 250 mg/L (days 1-7), 50 mg/L (days 8-14), 100 mg/L (days 15-21), and 250 mg/L (days 22-28) of phenol (purchased from Acros Organics >98%) was carried out using two 5 L cylindrical reactors equipped with an air diffusion. One of the reactors was fed by the activated sludge only (reactor 1) and the second (reactor 2) with the activated sludge and the biochar (1.5 g). Both were operated in batch mode. Samples were collected at specific sampling points from the top of the reactors. The phenol concentrations profiles attained during the acclimatization process was based on the literature search [20–22]. Both reactors were daily charged with the pre-determined concentration of phenol. The AS with an initial MLVSS of 1 g/L was acclimatized in both reactors with the nutrients as reported by the composition of peptone (188 mg/L), ammonium chloride (172 mg/L), magnesium sulfate (49 mg/L), dipotassium hydrogen phosphate (250 mg/L) and sodium bicarbonate (14.7 mg/L) as per our earlier study [23]. The acclimatization process was conducted at room temperature (T = 15-18 °C) without applying external heating or/cooling.

2.5 Analytical methods

Microscopic images of the sludge were taken using a ZEISS (imager A.2) microscope at various stages of the acclimatization process. The phenol concentration was

determined using an Agilent 1100 HPLC system (Agilent Technologies, Waldbronn, Germany). The system consisted of a binary pump (G1312A), as well as a thermostatted column compartment (G1316A), an auto-sampler (G1367A) and a VWD detector (G1314A). A C18 column (Agilent Eclipse Plus, 4.6 × 100 mm; particle size (dp) 3.5 µm) was utilized for the analysis. Total suspended solids (TSS), volatile suspended solids (VSS), and sludge volume index (SVI), defined as the volume (in mL) occupied by 1 g of activated sludge after settling the aerated liquid for 30 min, were measured according to the standard methods [24].

3. Results and discussion

3.1 Biochar characterization

The XRD pattern of the prepared pinewood biochar is presented in Fig. 1. As observed, a broad pattern without sharp peaks was obtained, thus indicating an amorphous structure of the prepared powders which is typical for the biochars prepared under low to moderate pyrolysis temperatures [25]. The results of CHNS elemental analysis indicated that the prepared materials consist of 72% carbon and 4% hydrogen. No sulphur and nitrogen were detected in the structure of the biochar prepared. Furthermore, XRF and elemental analysis confirmed that biochar is mainly composed of C (72%), O (14%), H (4%) as well as metallic elements including Ca (8%), and K (2%). Trace amounts (>1%) of Al, Si, P, S, Cl, Ti, Mn, Fe, Ni, Cu, Zn, and Sr were also detected in the composition of the biochar.

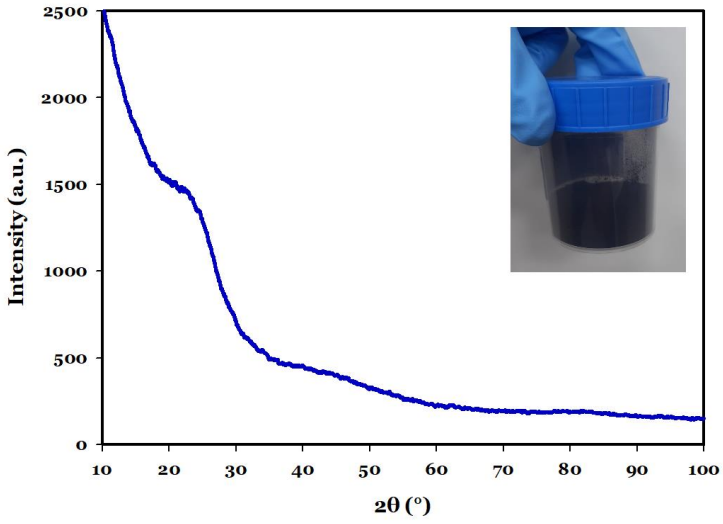

Fig. 1.
X-ray diffraction pattern of the prepared pinewood biochar

SEM images of the biochar samples are depicted in Fig. 2. The particles represent an irregular shape (Fig. 2, a) with smooth surfaces (Fig. 2,b) as previously reported in the literature for the biochar prepared from various feedstock materials [26,27]. One can see some smaller size particles (Fig. 2, b) and the prepared powder represents an average particle size of 53.8 μm.

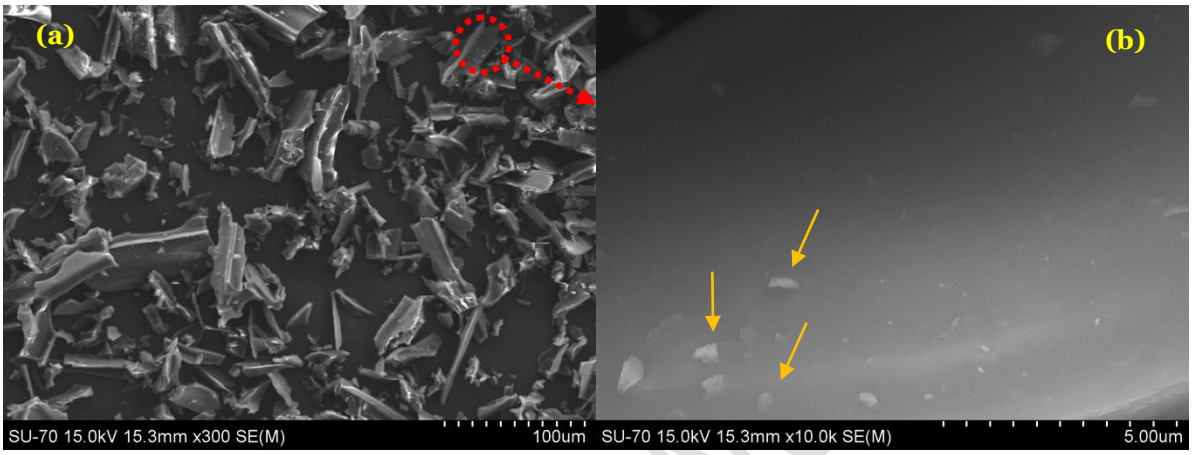

Fig. 2.
SEM of the prepared biochar powder with different magnifications demonstrating the formation of micro-size particles (right) with a smooth surface (left)

Figure 3 represents the FTIR spectra of the biochar sample. The low-intensity peak that appeared at 420 cm^{-1} confirms the presence of oxygen bonded to metals such as Ca and K. The representative peak at 812 cm^{-1} is also originated from the aromatic structure of the biochar [28]. The presence of C-N stretching can be confirmed at 1187 cm^{-1} [34]. Also, the peak at 1576 cm^{-1} can be related to the C=C grouping vibrations in an aromatic ring, coupled with the C=O carbonyl group indicating the formation of organooxygen containing products [30]. The presence of CO_2 which remained at the surface of the product from the reaction, can also be confirmed by the appearance of the C-O band at 2342 cm^{-1} [31].

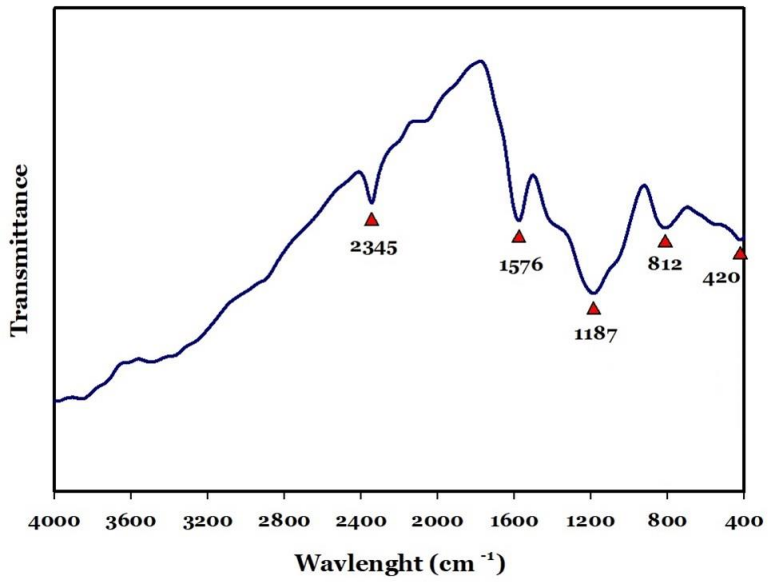

Fig. 3.
FTIR spectra of the prepared pinewood biochar

3.2 Phenol biodegradation

3.2.1 Phenol volatilization

The results of the phenol volatilization demonstrate that the loss of phenol at the investigated phenol concentrations seems to be negligible (< 5% in all the cases). The results are in agreement with the previous reports for the volatilization of phenol [23,32,33].

3.2.2 As-received sludge without acclimatisation

Figure 4 indicates the potential of non-acclimatized as-received AS for the removal of phenol as well as the respective specific phenol biodegradation rate and reactors were inoculated with 1 g/L MLVSS of the as-received sludge.

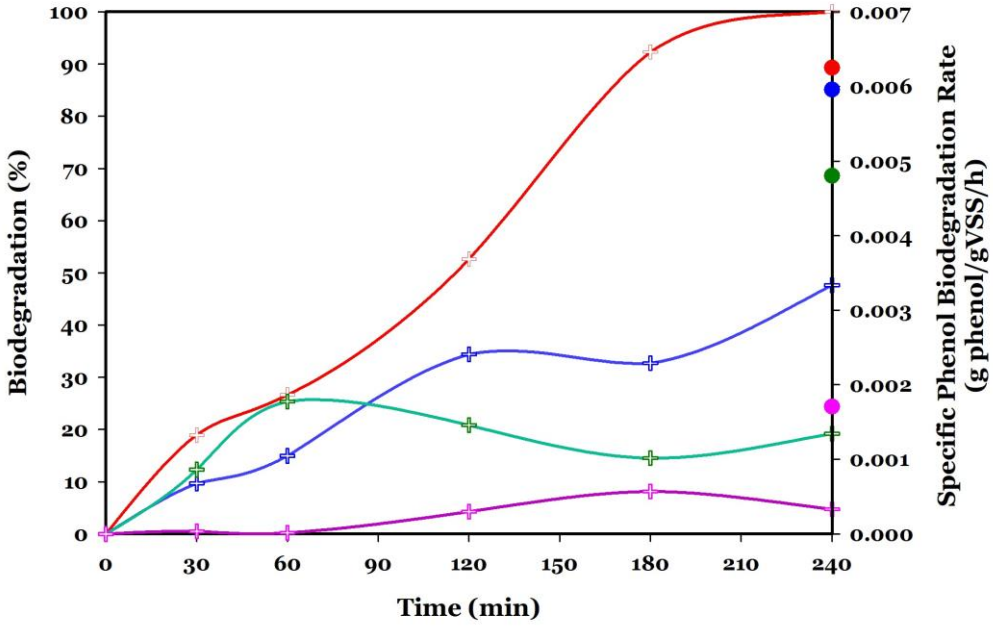

Fig. 4.
Phenol biodegradation potential of the as-received sludge (%) under different initial phenol concentration, and the respective specific phenol biodegradation rate (g phenol/g VSS/h), MLVSS: 1 g/L.

Phenol was only completely degraded for the initial concentration of 25 mg/L owing to the highest specific phenol biodegradation rate (SPBR) achieved in the case of as-received sludge (0.0065 g phenol/g VSS/h). The SPBR represents a decreasing trend when increasing the initial phenol concentrations, equalling 0.0059, 0.0048, and 0.0017 for the initial phenol concentrations of 50 mg/L, 100 mg/L, and 250 mg/L, respectively. The results demonstrate the low tendency for phenol degradation for the as-received AS.

3.2.3 Effects of biochar supplementation

3.2.3.1 Microbial growth

During the acclimatization process, the biomass concentration (expressed as MLVSS) increased both in the absence (reactor A) as well as the presence of the biochar (reactor B) as displayed in Fig. 5. For reactor B, the increase was much more outspoken. After 7 days of acclimatization ($[phenol]_0$=25 mg/L), the MLVSS in reactor A showed a slight increase to 1.06 g/L, while reactor B experienced a faster mi-

crobial growth, reaching to 1.49 g/L. Between days 8-14 ([phenol]$_0$=50 mg/L), the increase in MLVSS continued and reached to 1.21 g/L and 1.7 g/L in reactor A, and reactor B, respectively.

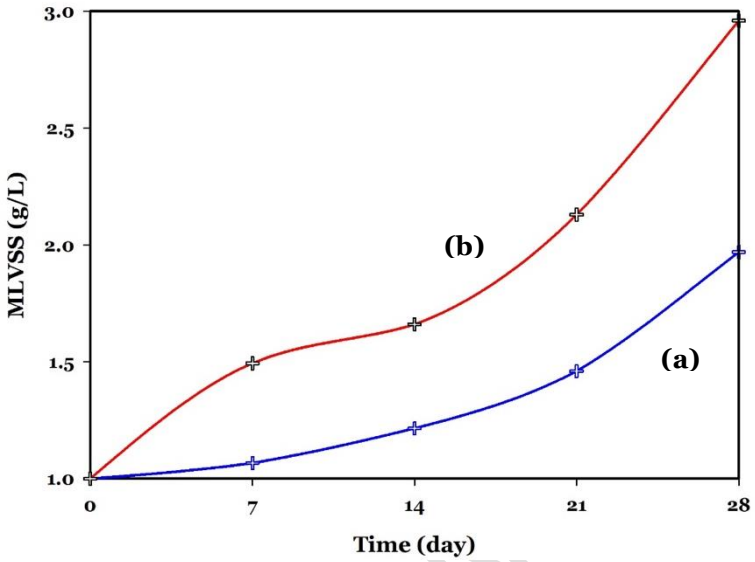

Fig. 5.
The changes in MLVSS of the reactor without biochar supplementation (a), and with biochar supplementation (b).

By increasing the initial phenol concentration to 100 mg/L between days 15-21, microbial growth was accelerated in both reactors and reached to 1.46 g/L and 2.13 g/L in reactor A, and reactor B, respectively. The highest microbial growth rate occurred during the final phase of the acclimatization (days 22-28) in response to an increase in the initial phenol concentration to 250 mg/L. MLVSS in the presence of biochar (reactor B) finally reached 2.96 g/L vs 1.97 g/L for the non-biochar supplemented reactor (reactor A). The results thus confirm positive effects of the biochar on microbial growth. Figure 6 indicates the microscopic image of the acclimatized sludge without (a) and with (b) biochar supplementation on the final day of the acclimatization process. As can be observed, biochar (black) particles acted as the nucleation cores for biomass growth during the acclimatization process. This has potentially led to the promotion of the growth of the microorganisms, especially under the elevated concentration of a hardly-biodegradable compound. These findings suggest that activated sludge after the acclimatization process mainly consisted of flocks of phenol-degrading microorganisms forming the denser colonies in the sludge containing biochar compared to sludge that did not contain biochar. Only a very limited

number of reports can be found in the literature discussing the effects of carbonaceous materials on the promotion of microbial growth. According to Cheng et al., [34] functional graphene materials can promote microbial colonization by creating suitable microenvironments for the adhesion of microbes and their growth. The results of the present study thus confirm the applicability of biochar as a low-cost material for the promotion of efficiency of the biological treatment process.

In the literature, some reports can be found stating that microbial strains such as *Arthrobacter citreus* [35], *Pseudomonas putida* [36,37], *Serratia marcescens* [38], *Acinetobacter* [39], *Bacillus subtilis* [40], *Rhodococcus erythropolis* [41], *Sphingomonas* [42], *Alcaligenes faecalis* [43], and *Bacillus brevis* [44] are able to degrade phenol present in polluted wastewaters. From the micrographs of the present study, strains such as *Acinetobacter calcoaceticus* [45] as well as stalked ciliates such as *Paramecium sp.*, *Epistylis sp.*, *Opercularia sp.*, and *Vorticella sp.* can be distinguished in the acclimatized sludge with biochar [23,46,47]. The synergistic effects of such species can further improve the biodegradation of aromatic hydrocarbons from wastewater [23,47].

The enhanced microbial growth in the presence of biochar can be also considered as a sign of the non-toxic nature of the biochar towards microbial communities. This can be correlated with the type of feedstock (pinewood) used in this study and the applied pyrolysis conditions. The origin of the biochar can also play a significant role in the presence of toxic elements in its chemical structure. For instance, biochar prepared from the pulp and paper mill effluent treatment plant sludge may contain relatively high heavy metal concentrations [48,49].

As per the results achieved in this study, the biochar prepared from pinewood, which contains low concentrations of metallic elements. In addition, hazardous elements such as Cd and Pb, which can cause toxic effects [50] were not detected in the biochar. Notice that some published reports also confirm the effects of pyrolysis temperature on the composition and hence, toxic effects from the biochars since they were produced at elevated temperatures (>500°C) [51,52] and may contain less toxic compounds.

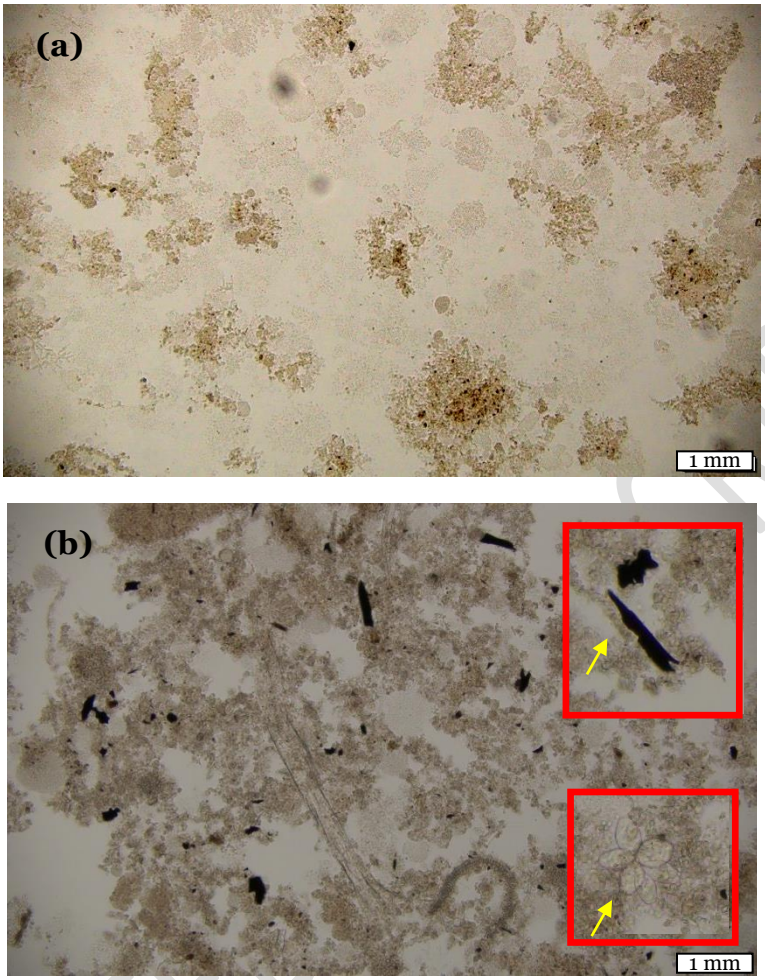

Fig. 6.
Micrographs of the acclimatized activated sludge with (a) and without biochar (b) supplementation

3.2.3.2 Specific biodegradation rate

Batch reactors were utilized to test the phenol biodegradation potential of the activated sludge during the acclimatization process with and without the biochar supplementation under the initial phenol concentrations of 25-250 mg/L, at pH≈6.5 and room temperature conditions. The results are presented in Figures 7 and 8; Figure 9 illustrates SPBRs over the acclimatization period. After 7 days of acclimatization, both the reactors exhibited enhanced SPBRs compared to as-received AS. Reactor A was able to degrade the phenol at an initial concentration of 25 mg/L within 120 min (SPBR=0.0117 g phenol/g VSS/h, Fig. 9). The microbial community in reactor B also

showed a higher SPBR (0.008 g phenol/g VSS/h) compared to non-acclimatized sludge, and complete phenol biodegradation was achieved within 150 min.

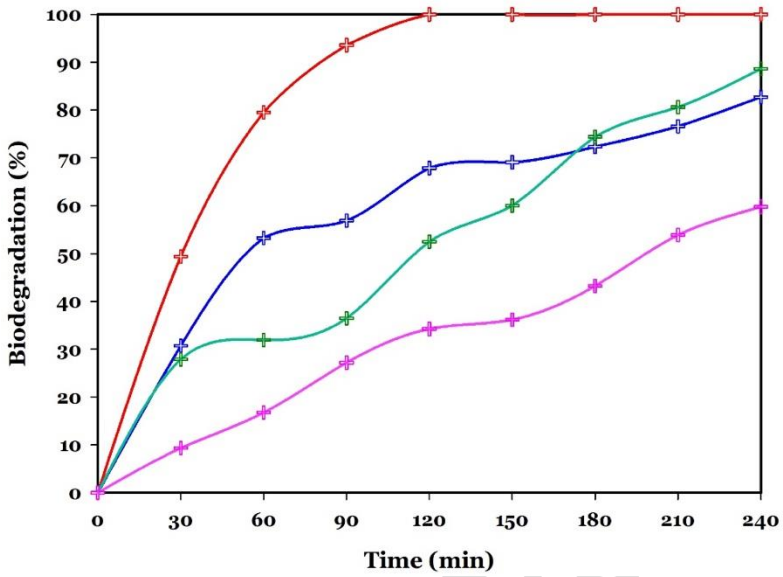

Fig. 7.
Phenol biodegradation potential of the acclimatized sludge (%) under different initial phenol concentration, MLVSS values have been presented in Fig. 5.

25 mg/L, 50 mg/L, 100 mg/L, 250 mg/L

At the initial concentration of 50 mg/L (day 14), an increase in SPBR was observed from 0.0059 g phenol/g VSS/h in the case of as-received sludge to 0.0085 and 0.015 for reactor A and reactor B, respectively, demonstrating an enhancement in the performance of the microbial community towards phenol biodegradation, especially for those acclimatized in the presence of the biochar. However, reactor A (without biochar-supplementation) failed to complete the degradation of phenol within 4 h (82 %, Fig. 7), while the biochar-containing reactor reached 100 % of phenol biodegradation after 120 min (Fig. 8). Between days 15-21, the initial concentration of phenol in both the reactors increased to 100 mg/L. Although SPBRs was increased in reactor A up to 0.015 g phenol/g VSS/h (Fig. 9) at day 21 compared to that of the as-received sludge (0.0048 g phenol/g VSS/h), the reactor was not able to completely degrade the phenol (88% after 240 min). On the other hand, reactor B demonstrated a 0.023 g phenol/g VSS/h phenol biodegradation rate and 100% phenol biodegradation within 150 min. When the initial phenol concentration was increased between days 22-28 to 250 mg/L, only a moderate biodegradation efficiency

of 59% was obtained after day 28 in reactor A, corresponding to an SPBR of 0.018 g phenol/g VSS/h. However, reactor B represented the highest SPBR of 0.041 g phenol/g VSS/h, resulting in 100% degradation of phenol within 150 min.

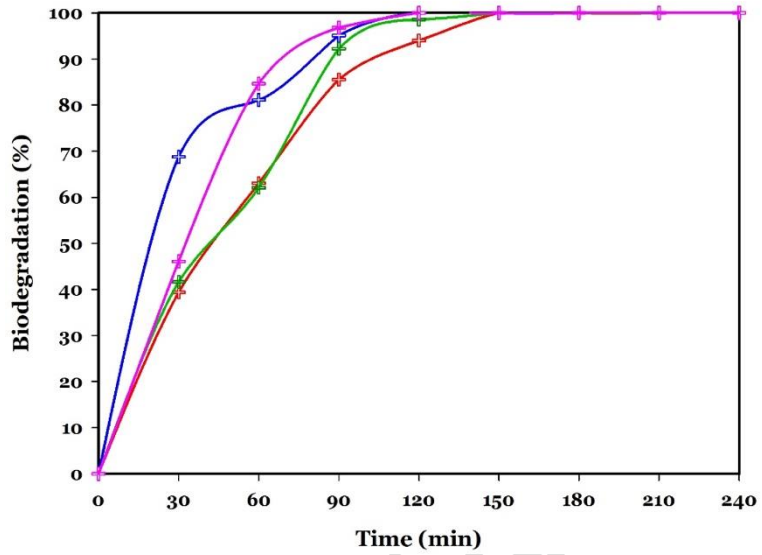

Fig. 8.

Phenol biodegradation potential of the biochar supplemented acclimatized sludge (%) under different initial phenol concentration.

Currently, the biological treatment of phenolic effluents does not comply with sustainability requirements mainly due to the treatment efficiency and costs associated to the relatively long hydraulic retention time [1]. However, studies have suggested the effectiveness of acclimatization for the promotion of AS process to deal with phenolic effluents. For instance, Rajan [53] and Marrot et al., [54] achieved a phenol biodegradation rate of 0.011 g phenol/g VSS/h and 0.036 g phenol/g VSS/h, respectively. In any case, the results of this study demonstrated the possibility of enhancing the treatment efficiency with a reduction of treatment time, which can enhance the capacity of the respective treatment plants along with the overall treatment costs [45,55].

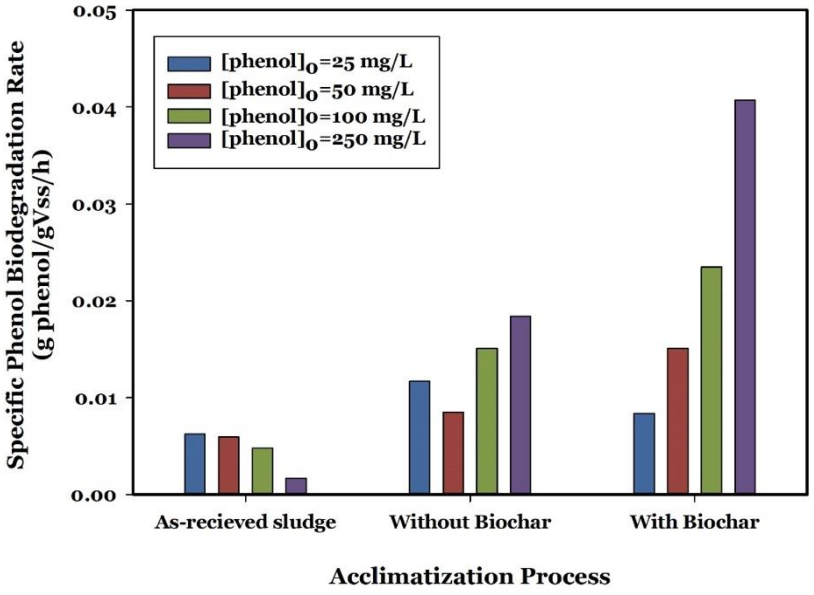

Fig. 9.
Specific phenol biodegradation rate of biochar supplemented acclimatized sludge and the control (without biochar supplementation).

3.2.3.3 Sludge volume index

Sludge volume index (SVI) is an important parameter to determine the quality of the sludge. This parameter can directly influence the performance cycle of the aerobic biological treatment systems (such as aerobic sequencing batch reactors (SBRs) [56]. SVI is also an important parameter determining the sludge settlability in the secondary clarifiers after biological treatment. The lower the SVI, the better for the separation of the sludge from the treated water. As illustrated in Fig. 10, the SVI was changed during the acclimatization process in both reactors, especially after day 14 when the initial phenol concentration was raised to 100 mg/L. In the non-biochar supplemented reactor, an increase in SVI was observed from 109 mL/g to 168.21 mL/g between days 14 and 21, which further continued to increase to 298.08 mL/g at day 28. This can be attributed to both an increase in the F/M ratio and phenol biodegradation inhibition at higher phenol concentrations [57,58]. On the contrary, in reactor B, SVI decreased to 60.45 at day 28, which falls within the optimum SVI for the AS systems (40-70 mL/g) [59]. According to Figure 5 and Figure 10, reactor B shows an increase in the biomass concentration (MLVSS from 1 to 2.96) during the acclimatization process, while decreasing the SVI from 108.74 to 60.45, which is evi-

dence of strong colonization in this reactor. Figure 11 shows the settling properties of the sludge after acclimatization with and without the biochar.

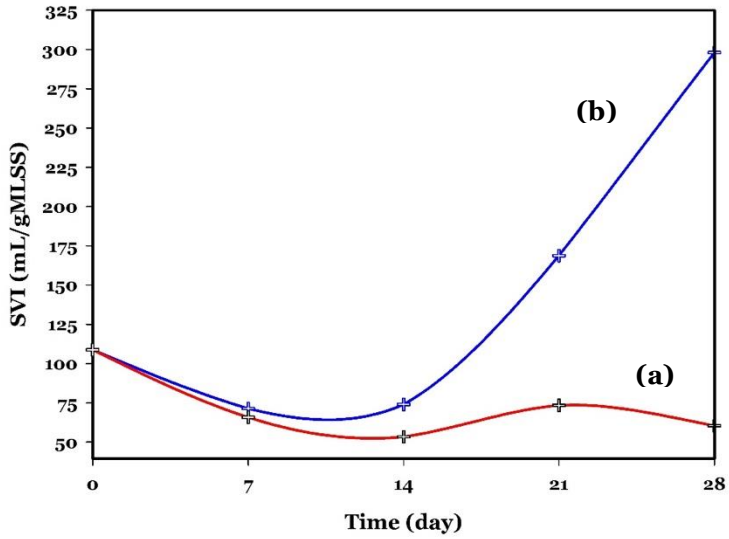

Fig. 10.

The changes in the SVI of the reactor without biochar supplementation (a) and with biochar supplementation (b).

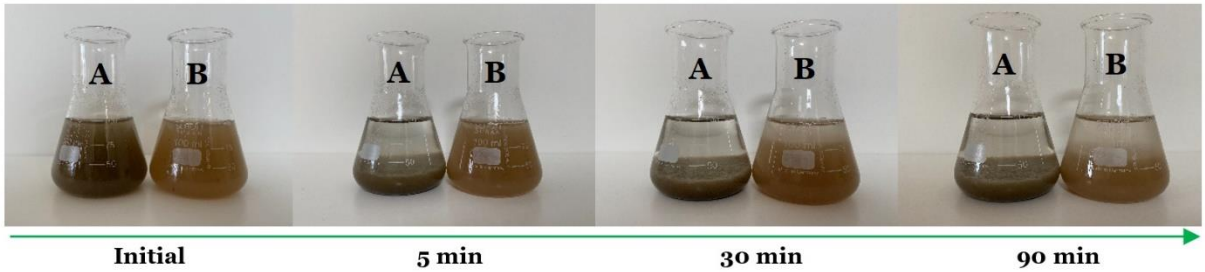

Fig. 11.

The settling properties of the sludge after acclimatized process with (A) and without (B) biochar after 5, 30, and 90 min.

3.2.3.4 The effects of phenol shock

The impact of phenol stress on the performance of AS process was also studied by a sudden increase in initial phenol concentration from 250 mg/L (day 28) to 500 mg/L (day 29); these data are shown in Figure 12. After 240 min, the efficiency of reactor A dropped from 59% to 31% (Fig. 7), while in the biochar B still a in the complete phenol biodegradation was observed within 210 min. In addition, SPBR in reactor B continued to increase from 0.041 g phenol/g VSS/h [pheno]=250 mg/L] to 0.054 g phenol/g VSS/h. In contrast, no significant change was observed in the SPBR

of reactor A. It may thus be concluded that both the reactors were able to continue their performances under the initial phenol shock. However, the biochar-supplemented reactor represented an enhanced performance compared to initial phenol concentration of 250 mg/L.

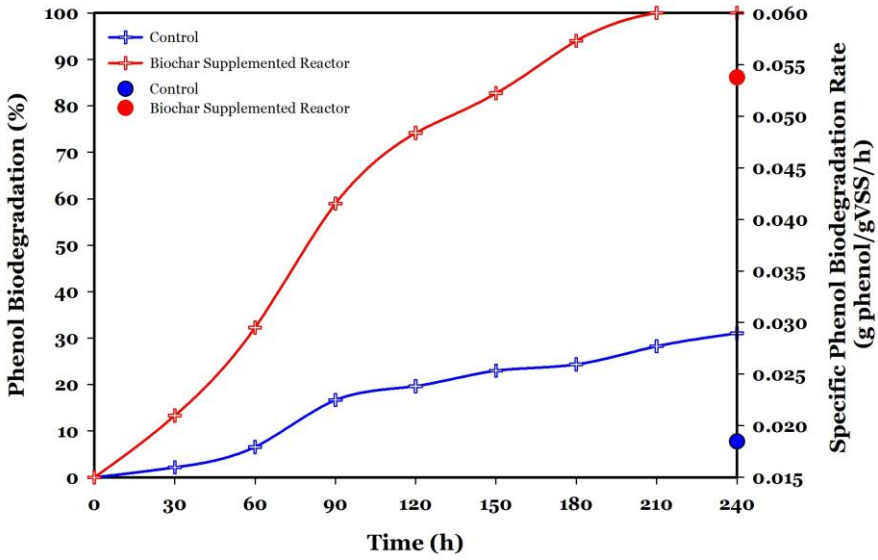

Fig. 12.
The performance of the anaerobic sludge acclimatized in presence of pinewood biochar compared to control (without biochar supplementation) under initial phenol concentration shock (to 500 mg/L).

4. Research challenges and future considerations

Various feedstocks have so far been used for the production of biochar with various compositions and properties. For instance, biochars from sludge are normally rich in phosphorous and nitrogen [60,61]), and woody biochars are of high carbon content [62], as reported in the present study for the biochar from pinewood. The produced biochars have been used for several applications such as (waste)water treatment [11], soil applications [49], and recovery of valuable compounds such as P, and N [63]. They have been also recently applied to enhance the methane production yield in anaerobic digestion processes via mechanisms such as promoting the direct electron transfer among the microorganisms responsible for the decomposition of the organic compounds [64]. To our best knowledge, the present study is the first report on the applicability of biochar for the promotion of activated sludge, as the widely used technique to deal with effluents from various origins. The results indi-

cated that biochar addition promotes microbial colonization and growth, reflected in the VSS of the biochar supplemented activated sludge process, and enhancing the phenol specific biodegradation rate. The acclimatized sludge in the presence of biochar also represented a low SVI which can result in a shorter treatment time, and hence higher capacity for the treatment system, and higher quality for the treated effluents. The potential of the biochar to tolerate the load shock can also indicate the stability of the process which together with the enhanced efficiency and higher quality of the treated effluents can satisfy the sustainability considerations [65].

For future studies, it can be recommended to use biochar from various feedstock and properties (such as magnetic biochar [66]) to reach the optimum conditions for the application of these technologies for real applications. The possibility of release of specific compounds such as metallic compounds, which can be originated from some biochar feedstocks such as sewage sludge [67], and its effects on the microbial communities and the final quality of the treated are also of high importance to be investigated by the future studies. The development of economic methods for the treatment of highly polluted effluents is also another research challenge. Although biochar is an expensive material, some measures can be still adopted to decrease the production cost and push the technologies for commercialization. For instance, renewable sources of energy can be used to provide the energy required for the pyrolysis process under relatively high temperatures [68].

4. Conclusions

This study reports the application of pinewood biochar for the promotion of activated sludge properties including the microbial growth, specific biodegradation rate, and sludge volume index during the acclimatization process. The addition of biochar promoted the colonization of the microorganisms and hence, enhanced the microbial growth as well as phenol biodegradation capacity. The highest specific phenol biodegradation rate of 0.041 g phenol/g VSS/h was observed after 28 days of the acclimatization process under an initial phenol concentration of 250 mg/L. In addition, the system could efficiently tolerate the shock load in phenol concentration of 500 mg/L, thereby showing a specific phenol biodegradation rate of 0.054 g phenol/g VSS/h. Furthermore, the sludge volume index of the biochar supported that the ac-

climatized sludge decreased to 60.45 compared to 108.74 for the as-received activated sludge. Since the produced biochar is a low-cost and non-toxic material, the method developed here may offer a sustainable option for enhancing the performance of the biological methods for the efficient treatment of phenolic wastewaters.

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