Enhancing removal of aromatic compounds using an integrated biofilm–GAC reactor

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Introduction

Recent studies have shown that aerobic granular sludge (AGS) can be adapted for use in high-salinity wastewater environments, such as those found in oil & gas wastewaters and canning and vegetable pickling waste (Ou et al. 2018, Ozaki et al. 2015). The presence of recalcitrant and toxic dissolved organic compounds, such as toluene and other BTEX compounds often found in produced water, can hinder AGS reactor performance (Boyd et al. 1997, Ramos et al. 2015, Sousa et al. 1998). Granular activated carbon has been used extensively in post or tertiary treatment to improve water quality prior to reuse or discharge into the environment (Cozma et al. 2012, Paredes et al. 2018). Utilizing GAC as moving-bed biofilm has also been reported to be an effective way to enhance toxic organics removal (Puyol et al. 2015, Wang et al. 2017). Integration of GAC with a hybrid adsorptive biofilm (Bio-GAC) to treat recalcitrant and toxic organic compounds incorporates both biological and physico-chemical processes to enhance contaminant removal (Loukidou and Zouboulis 2001). The high ratio of surface area to volume of GAC increases the adsorption rate of organic matter to the GAC surface. This reduces the toxicity from these compounds and improves the performance of the biological treatment system (Puyol et al. 2015).

This work addresses the development of a hybrid Bio-GAC reactor that uses GAC as a support medium for the growth of salt-tolerant biofilms. Selected aromatic compounds (benzyl alcohol, o- cresol, and phenol) were fed to these reactors in a synthetic high-salinity wastewater solution (8.5% NaCl) to examine their removal and biodegradation. An aerobic AGS reactor previously adapted for performance under hypersaline conditions is used as a reference case to compare the extent of biodegradation and overall organic removal.

Materials and Methods

Two identical bench scale sequencing batch reactors (SBRs), with a working volume of 3.0 L, were used in the current study. One SBR was run with 125 g of Filtrasorb 400 GAC as the carrier medium and inoculated with 6000 mg L^{-1} of AGS to enhance biomass growth on its surface. The second reactor was inoculated with 6000 mg L^{-1} MLVSS AGS. A synthetic produced water (PW) modeled after that reported in the existing literature was used in the study (Pendashteh et al. 2012, Sharghi et al. 2014). The NaCl concentration was fixed at 85 g L^{-1} throughout the experiment to provide hypersaline conditions. A mixture of benzyl alcohol, o-cresol, and phenol was utilized as the carbon source for the two SBRs. The aromatic compounds content was increased gradually over time to a final concentration of 100, 100, and 250 mg L^{-1} for each compound respectively. The final operation cycle time was 12 hours, comprising all SBR phases (feeding, reaction, settling, and decanting).

To determine the aromatic compounds adsorptive capacity of Filtrasorb 400 GAC, an isotherm study was conducted. Four sets of sealed 250 mL batch reactors were filled with 100-1000 mg of GAC, and 1000 mg L^{-1} of either benzyl alcohol, o-cresol, or phenol. All samples were allowed to shake at 150 rpm for 24 hours at 30 ºC. A control reactor with no GAC was used to account for natural losses due to volatility. Samples from each reactor were filtered through

0.45 um glass-fiber filters and analyzed to determine aqueous phase aromatic concentrations, with the mass of sorbed compound determined by difference.

The volatility, biosorption, and biodegradation of each of the aromatic compounds in contact with aerobic halophilic granules were investigated through running three batch reactors. These reactors were filled with 2 liters of PW containing either benzyl alcohol, o-cresol, or phenol as the only carbon source and injected with air at a rate of 2.2 liter per minute. The first reactor contained only the aromatic solution, to determine compound losses through volatilization. The second reactor included fixed AGS, to stop all biotic activity, to assess aromatic compounds biosorption on biofilm. AGS samples in this reactor were fixed according to the protocol described by Bassin et al. (2012). The third reactor contained active AGS to investigate the biodegradation of the selected aromatic compounds.

The biogrowth on GAC surface was extracted by grinding GAC samples in a mortar for two minutes followed by sonication at 25 Watt for two minutes as well. This new method for biofilm detachment was developed specifically for analyzing the biological content in detached biofilm of the hybrid reactor Bio-GAC. The main purpose of this two-step extraction was to avoid cell lysis and thus avoid over estimated Extracellular polymeric substances (EPS) content. EPS extraction was carried out using the heat method described by Li and Yang (2007). Preparation of AGS and GAC samples and biofilm fixation for SEM microscopic analysis was performed according to Bassin et al. (2012). All studied aromatic compounds were extracted by solid phase extraction using acetone as a solvent. DNA isolation was performed according to manufacturer protocols.

Results and discussion

Aromatic compounds adsorptive capacity

Sorption data for all three aromatics in contact with GAC were best fit by the Freundlich isotherm model (Figure 1). The results indicated that GAC has a high sorption capacity for all three compounds, with benzyl alcohol showing the greatest affinity for GAC. The high adsorption capacity of aromatic compounds plays a crucial role in their removal efficacy because it reduces bulk organic load significantly and keeps microorganisms in intimate contact with the carbon source (Loukidou and Zouboulis 2001).

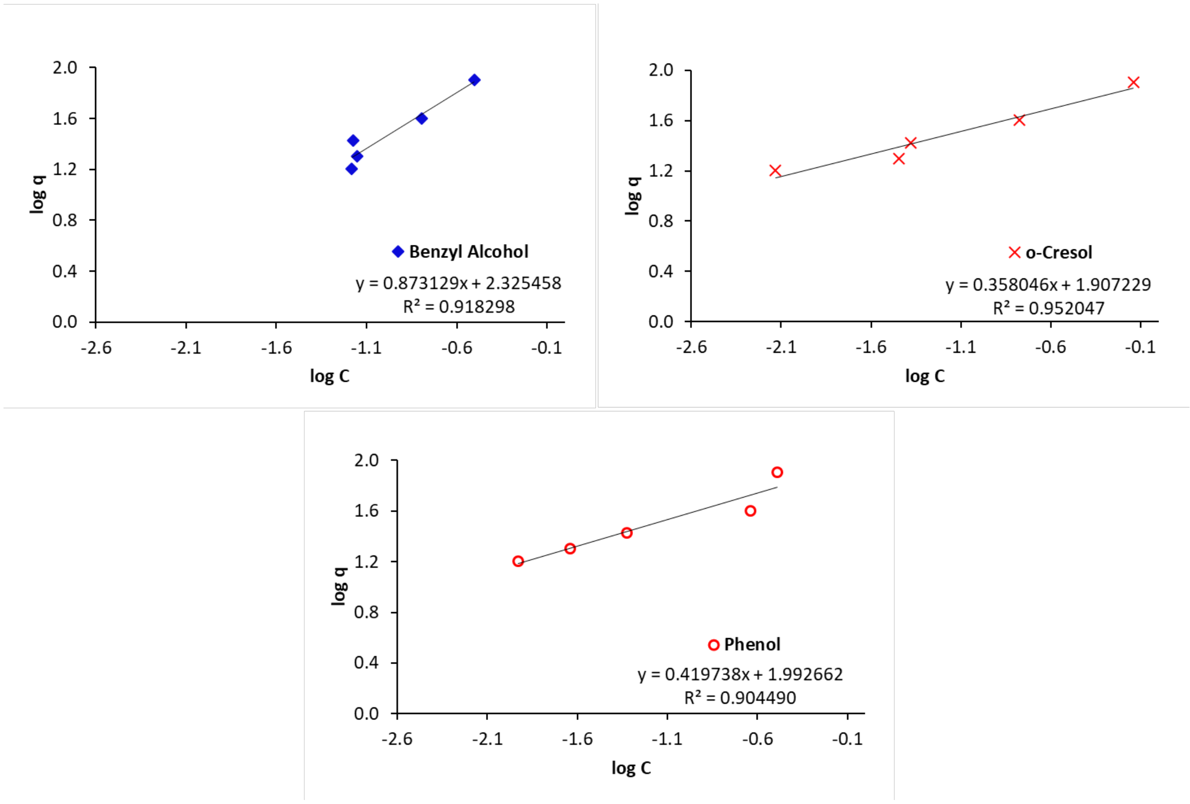

Figure 1: Freundlich adsorption isotherm for selected aromatic compounds, where q is in mg/g and C is in mg/l

Biodegradability of selected aromatic compounds

Aerated batch studies showed that volatile losses of all three compounds were negligible under reactor operating conditions (Figure 2). Benzyl alcohol showed the highest losses due to biosportion and biodegradation, with almost complete removal after 6 hours in the presence of live granules. Phenol showed similar losses due to biosorption, but little differences in concentration between the fixed and live granules, indicating little to no biodegradation. This low biodegradability of phenol may be attributed to phenol toxicity inhibiting biological activity. The o-cresol results showed lower biosorption than either of the other two compounds, and intermediate biodegradation between that for benzyl alcohol and phenol.

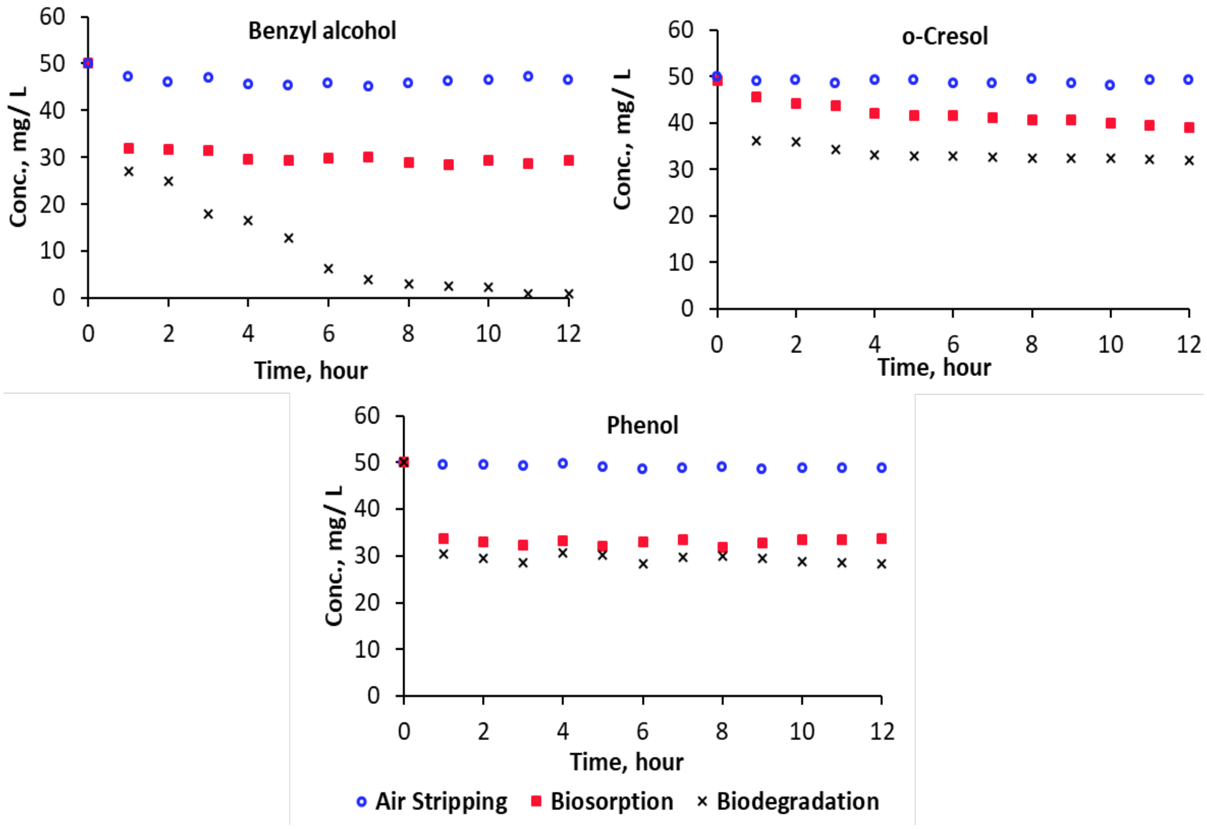

Figure 2: Aerated batch study results for selected aromatic compounds.

Biofilm development on GAC surface

The development of biofilm on the GAC surface was monitored through quantification of DNA and through SEM imaging of the GAC surface (Figures 3 and 4). After 60 days of inoculation, the reactor reached 6000 ng of DNA g^{-1} GAC, the seeded AGS was washed out by gravity separation, and only GAC kept in the SBR. Figure 3 shows that biogrowth on the GAC surface continued to increase after this point. As the quantified DNA in the Bio-GAC reactor reached steady state at 90 days, 20% of the influent acetate (270 mg COD L^{-1}) was replaced by 100 mg L^{-1} of benzyl alcohol. The introduction of benzyl alcohol enhanced the biofilm growth on the GAC surface (Figure 4 b), as it is readily biodegradable. Beginning at 105 days, o-cresol was added in as similar manner. 100 mg L^{-1} of o-cresol (250 mg COD L^{-1}) was added to the influent wastewater and acetate was simultaneously reduced to maintain a constant COD. The impact of adding *o*-cresol on biofilm growth resulted in a significant decrease in the density of the observed biofilm on GAC (Figure 4 c), which may be due to the lower biodegradability of o-cresol as shown in Figure 2. Finally, at 120 days, the remaining acetate was replaced with 640 mg COD L^{-1} of phenol. The performance of both reactors, in terms of EPS production, was impacted by this change in carbon source, but it started to back up after 30 days of phenoladdition (Figure 5).

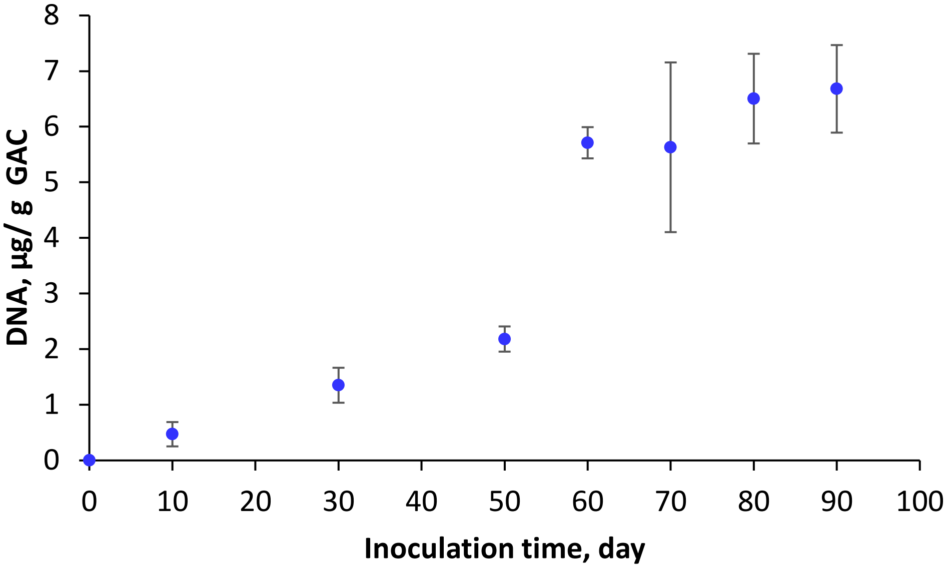

Figure 3: Quantified DNA during startup period.

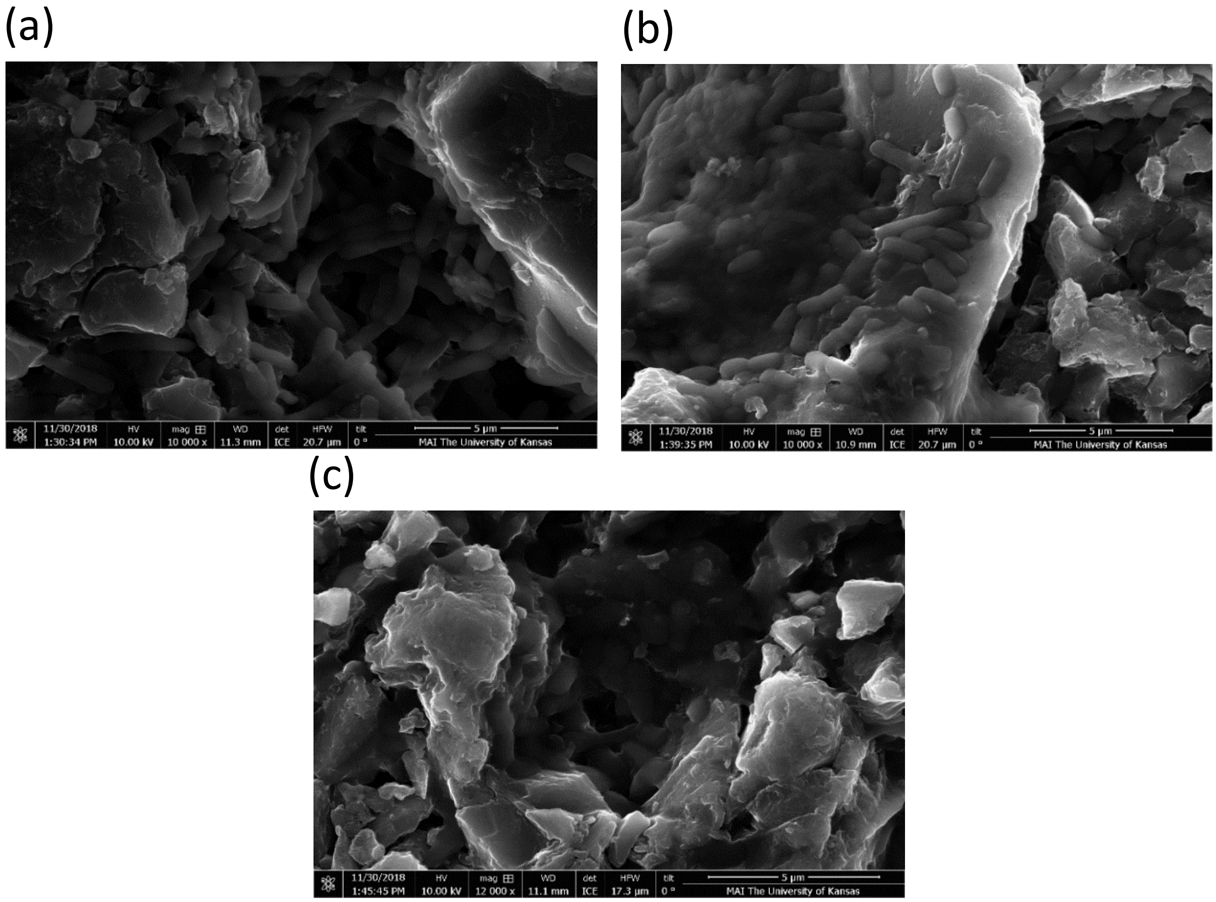

Figure 4: SEM micrographs showing the biofilm development to GAC surface: acetate fed only (a), 80% acetate: 20% benzyl alcohol (b), and 60% acetate: 20% benzyl alcohol: 20% o-cresol *(c).*

EPS production

EPS production in the Bio-GAC and AGS reactors responded very differently to the change in carbon source (Figure 5 a). When benzyl alcohol was introduced to the influent, EPS production increased slightly. The EPS content, however, declined slightly as *o*-cresol was introduced to the system. This finding matches the observed differences in the SEM images (Figure 4). However, the addition of phenol to the wastewater enhanced EPS production. In the AGS reactor, by contrast, EPS production declined significantly when acetate was substituted by benzyl alcohol and then o-cresol (Figure 5 b). EPS production remained consistently lower throughout the introduction of the aromatic compounds as the carbon source. This observation indicates that either the selected aromatic compounds were not as readily biodegradable as acetate or the biomass metabolism has changed due the change in carbon source. EPS production in the Bio-GAC reactor was not affected by adding phenol as a new carbon source. However, this change caused an extensive reduction in EPS production in the AGS system. The adsorption capacity of GAC could be mitigating the toxic impact of aromatic compounds on biogrowth in the Bio-GAC system, in agreement with previous studies that showed the presence of GAC in biological treatment systems reduces the toxic impact of treated wastewater (Loukidou and Zouboulis 2001). In addition, the growing biomass will be in close contact with the adsorbed organic substrate, which improves overall system performance (Puyol et al. 2015).

Aromatic compounds removal efficiency

The performance of the Bio-GAC system was consistently higher in terms of aromatic compounds removal efficiency (Figure 6). Benzyl alcohol and o-cresol were removed entirely, along with 90% of phenol, after about two hours of operation (1.5 hours of aeration) in Bio-GAC system. BY 4 hours, removal of aromatic compounds was essentially complete. Ultimate removal efficiency of aromatic compounds in the AGS reactor was also high, at 99 %, 94 %, and 89 % for benzyl alcohol, o-cresol, and phenol respectively. However, it took much longer to achieve this level of removal. For instance, benzyl alcohol was removed only after six hours of operation while it took ten hours to remove 91% of o-cresol. Phenol took much longer to remove in the granule-only system, with 89 % removal after 12 hours of operation. In general, the performance of Bio-GAC system was higher than AGS system in terms of aromatic compounds removal efficiency.

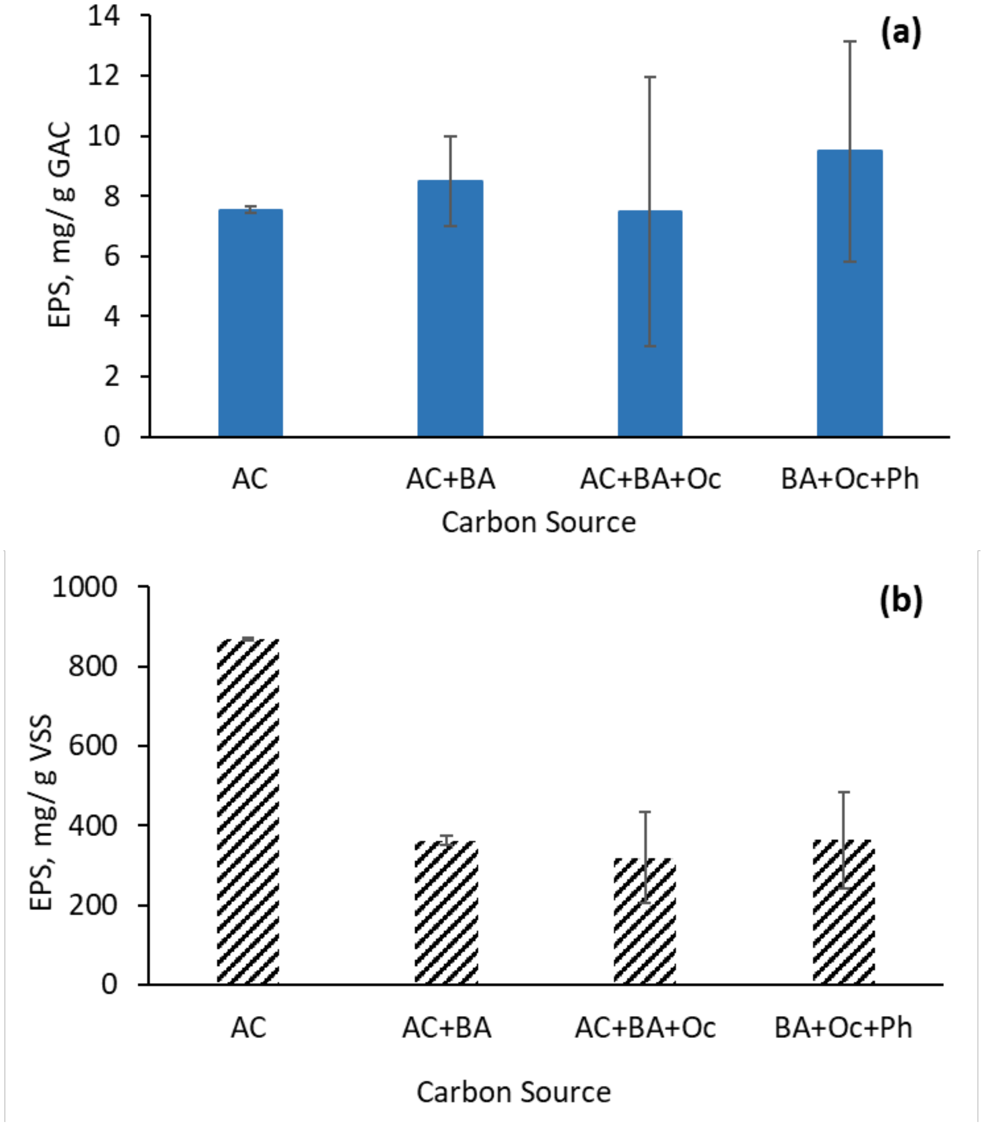

Figure 5: EPS production with different carbon source in integrated biofilm–GAC reactor; Acetate fed only (AC), 80% acetate: 20% benzyl alcohol (AC+BA), 60% acetate: 20% benzyl alcohol: 20% o-cresol *(AC+BA+Oc), 25% benzyl alcohol: 25%* o-cresol: 50 phenol *(BA+Oc+Ph).*

Conclusions

Biofilm growth on GAC surface was established successfully in this study and showed higher tolerance to the change in electron donor and carbon source compared to the self-immobilized biological treatment system (AGS). While the AGS reactor also adapted to the aromatics in the influent, EPS production declined significantly in this system compared to the

Bio-GAC reactor. Additionally, removal of aromatic compounds was rapid and more thorough in the Bio-GAC reactor. Longer-term studies are ongoing to address aromatic biodegradation versus sorption and establish the overall effectiveness of the bio-GAC and AGS system under hypersaline conditions.

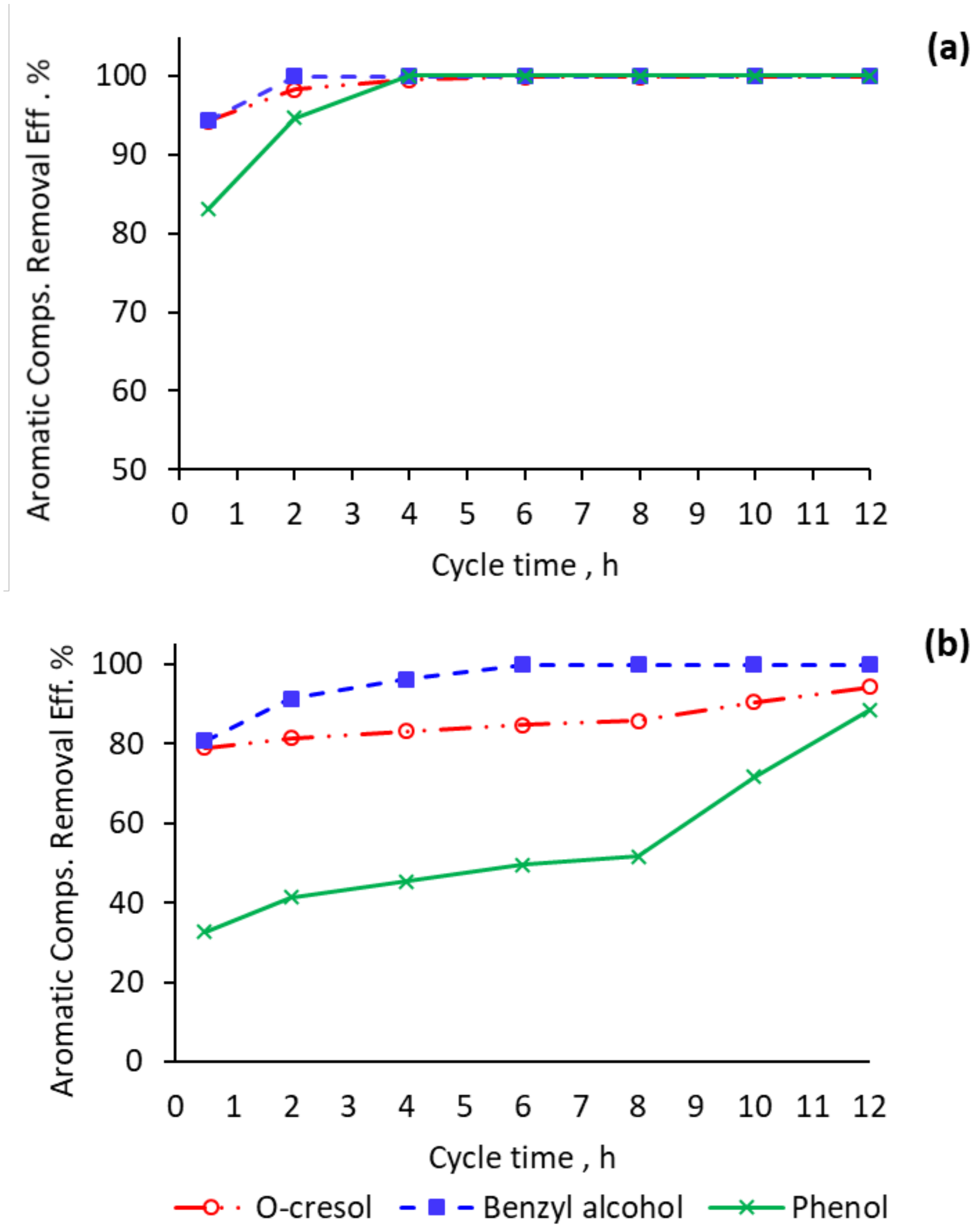

Figure 6: Benzyl alcohol, o-cresol, and phenol removal efficiency in biofilm-GAC system.

Acknowledgements

This study was financially supported by:

- The National Science Foundation EPSCoR Track-2 Research Infrastructure Improvement Program: Track-2 Focused EPSCoR Collaboration award (OIA-1632892).
- Iraqi government scholarship programs/ Ministry of Higher Education and Scientific Research (MOHESR).

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