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Offline bioregeneration of spent activated carbon loaded with real Produced Water and its adsorption capacity for benzene and toluene

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ABSTRACT

The disposal of water produced during the petroleum extraction (Produced Water) is a relevant issue due to the occurrence of contaminants. Adsorption on activated carbon is one of the best available technologies for the removal of synthetic organic chemicals from water. However, the replacement and disposal of exhausted carbon is quite expensive and the spent carbon may have to be handled as hazardous waste. The bioregeneration of spent carbon could be a feasible solution; however, hypersaline wastewaters, like Produced Water, are often recalcitrant to biological process due to the strong inhibition by salts (mainly NaCl), elevated temperature, and presence in solution of biocides. In this study, adsorption kinetics, isotherms, and rapid small-scale column tests have been performed to select the type of granular activated carbon (GAC) with the best adsorption capacity of target monoaromatic compounds (benzene and toluene). Continuous-flow pre-loaded GAC biological regeneration experiments were conducted with both synthetic and actual hypersaline wastewaters (oily Produced Water), using solutions containing selected micro-organisms. GAC adsorption was found very effective to remove target compounds (benzene and toluene) from both the synthetic hypersaline water and the real Produced Water. A preferential adsorption of toluene was observed from batch and dynamic adsorption experiments. This study demonstrates that GAC loaded with either synthetic or real Produced Water can be regenerated by offline bioregeneration. Indeed, about 57% and 50% of the GAC regeneration capacities were achieved for benzene and toluene, respectively, during experiment with real Produced Water. The genetic characterization of the isolated bacteria has shown the presence of species which are well known for the degradation of hydrocarbons. The maximum values of optical density, CFU, and CO_2, indicating the highest biomass growth, have been found simultaneously with the maximum bioavailability of benzene and toluene. These results clearly demonstrate that biological regeneration occurs.

Keywords: Adsorption; Benzene; BTEX; Oily Produced Water; Petroleum Industry; Rapid small-scale column tests; Toluene; Volatile organic carbon (VOC)

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1. Introduction

The onshore and offshore extraction of crude oil and natural gas is associated with the co-production of significant quantities of wastewater, namely "Produced Water." This is the largest waste product associated with the oil and gas industry [1]. For instance, Produced Water accounts for about 90% of the total volume of exploration and production material brought to the surface by the oil and gas industry [2,3]. Overall, the total volume of Produced Water generated is estimated as thousands of meter cubes per day [4].

Usually, Produced Water is re-injected into producing reservoir to maintain formation pressure and increase output. This type of secondary recovery for petroleum production is generally called "waterflood" and accounts for about 50–60% of the total amount of Produced Water [5]. Another big fraction (about 40%) of Produced Water is re-injected into non-producing formations for storage, while a smaller fraction (about 4%) is discharged in surface water [2]. In many countries, the current regulations do not permit the disposal of Produced Water into deep geological units or in surface water [e.g. 6]. Indeed, Produced Water contains several contaminants which can cause adverse effects to the environment [7–10].

The physical, chemical, and biological properties of Produced Water from oil fields depend on both the geological formation and the geographical location of the reservoir [11,12]. These two factors affect the type and concentration of inorganic species (silt, salts, scale salts, radionuclide, and metals) as well as the type of hydrocarbons. Sulfate-reducing bacteria (SRB) and/or other anaerobic bacteria can also be present in Produced Water. Algae, fungi, and residual production chemicals such as corrosion inhibitors, emulsion breakers, scale inhibitors and dissolvers, and biocides further complicate the properties of Produced Water [12]. Qualitatively, dissolved organic matter in Produced Water is similar to that reported in oceans and freshwater, except that it contains much more sulfur and is less aromatic [13]. Produced Water contains high concentrations of total n-alkane, polycyclic aromatic hydrocarbons, minerals, radioactive substances, benzenes, and phenols [14]. The salt concentration of Produced Water may range from a few mg/L to 300,000 mg/L and a significant level of heavy metals is also present [15]. Produced Water has total organic carbon concentrations between 0 and 1,500 mg/L and oil and gas concentrations between 2 and 565 mg/L [16].

Produced Water is conventionally treated through different physical, chemical, and biological processes. No single technology to treat Produced Water can meet the required effluent standard quality, thus two or more treatment processes might be used in a treatment train. The choice of the best technology is based on Produced Water chemistry, cost effectiveness, space availability (off-shore vs. on-shore), reuse and discharge plans, durable operation, and byproducts formation [15]. Recently, most research has been carried out on the use of biological and/or membrane processes for Produced Water treatment [3,15,17–19]. Adsorption on activated carbon has been demonstrated in numerous studies to represent one of the best available technologies for the removal of synthetic organic chemicals from water; it has also been acknowledged as a very efficient unit process for removing refractory organic compounds that persist in the environment or resist to conventional treatments [20]. Therefore, granular activated carbon (GAC) adsorption is also used to treat oily wastewaters from petrochemical industry to reduce its overall organic content and minimize its toxicity [15].

Replacement and disposal of exhausted carbon is quite expensive and the spent carbon may have to be handled as hazardous waste. This could create a problem for treatment facilities where the amount of spent GAC generated is not large enough to justify the regeneration and where hazardous waste landfills are not available locally. Degradation of adsorbed organics by microbial activities, termed bioregeneration, represents an alternative treatment to regenerate exhausted carbon; biological treatment has the potential to completely destroy the contaminants and is generally less expensive than physical–chemical treatment process. Bioregeneration can be achieved either by mixing bacteria with saturated activated carbon in systems [21–25] or in the course of biological-activated carbon systems [26–32]. However, most of the conclusions that can be drawn on the bioregeneration process were obtained from investigations involving offline bioregeneration (OBR), because in simultaneous processes, it is very difficult to differentiate between adsorption/desorption and biodegradation [33]. Since the hypersaline wastewaters, like Produced Water, are often recalcitrant to biological process due to the strong inhibition by salts (mainly NaCl), high temperature and the presence in solution of biocides, OBR is the only possible way to regenerate with microbial activities the carbon saturated with the organic substances present in the water. OBR involves removal of adsorbed organic matter from contaminated carbons through desorption and biodegradation occurring inside a closed batch system [34]. It consists of regenerating spent activated carbon in a column in which a mixture of acclimated bacteria, nutrients, and dissolved oxygen are re-circulated to remove adsorbed

organic matter. Bioregeneration processes depend on numerous factors including reversibility of adsorption, presence of microbial organisms capable of metabolizing the adsorbate, settings of optimal microbial growth conditions such as nutrients, temperature, dissolved oxygen, and optimization of microbial and adsorbate concentration ratios.

In literature, there is a lack of comprehensive understanding of this phenomenon especially for hypersaline wastewater contaminated with hydrocarbons. The aims of the present study are (i) to verify the effectiveness of the adsorption process onto GAC at laboratory scale for the removal of hydrocarbons (benzene and toluene as target compounds) from both synthetic hypersaline water and real Produced Water and (ii) to investigate the feasibility of OBR of the saturated carbon.

2. Material and methods

2.1. Waters and materials

Tested waters include a synthetic hypersaline water and a Produced Water sampled at a real oily Produced Water treatment facility. The synthetic water was made with 12.04 g/L of $CaCl_2$, 3.13 g/L of $MgCl_2$, 0.57 g/L of $CaSO_4$, 52.07 g/L of NaCl, and 2.46 g/L of KCl in deionised water. The Produced Water used in this study was characterized by analyzing the main organic and inorganic compounds usually found in this kind of waste. Table 1 reports the concentration of the chemical contaminants analyzed. The analysis by GC/MS of the crude oil removed from the Produced Water at the water treatment facility has demonstrated the presence of saturated hydrocarbons (the most abundant constituents in crude oils), with prevalence of alkanes which are well-known abundant constituents in the Produced Water [35] and aromatic hydrocarbons, while the GC/MS analysis of the Produced Water has shown the presence of several carboxylic, aliphatic, and cyclic acids. The latter result indicates the occurrence of the biodegradation of the oily fractions in Produced Water by SRB at the production site. This hypothesis is confirmed by the microbiological analysis of the investigated Produced Water which has shown the occurrence of several SRB such as *Thermotoga*, *Alkalibacterium*, *Desulfotomaculum*, *Petrotoga*, *Clostridium*, and *Bacillus*.

Both synthetic hypersaline water and Produced Water were spiked with 40–50 mg/L of benzene and toluene, which were selected as target compounds to be investigated because they are usually present in Produced Water. All reagents used were ACS grade or better.

Table 1
Chemical characterization of the investigated Produced Water

Parameter	Unit	Value
pH	–	6.4
Total alkalinity	mg/L	1,151
Salinity	mg/L	51,350
Total dissolved solids (TDS)	mg/L	53,500
Electrical conductivity at 20°C	µS/cm	93,366
TSS	mg/L	167
BOD_5	mg/L	60
COD	mg/L	3,400
Fe	mg/L	0.3
SO_4^{2-}	mg/L	391
Cl^-	mg/L	43,080
F^-	mg/L	2.5
Br^-	mg/L	221
NH_4^+	mg/L	819
K	mg/L	1,290
Ca	mg/L	4,516
B	mg/L	70
Mg	mg/L	798
Na	mg/L	20,810
Li	mg/L	9
Total hydrocarbons	mg/L	3.6
Benzene	µg/l	273
Ethylbenzene	µg/l	3
Toluene	µg/l	266
Xylenes	µg/l	4

Four types of GACs were investigated, namely PICACARB 830, PICABIOL, NORIT PK1-3, and NORIT ROW 0.8 SUPRA. These GAC were crushed and sieved in order to reach 40 × 70 mesh (0.25 × 0.425 mm) dimension which allowed the use of a smaller amount of water by the application of the rapid small-scale column tests (RSSCT) [36].

2.2. Adsorption experiments

Adsorption kinetics and isotherms were performed using the synthetic hypersaline water to investigate the adsorption capacity of target monoaromatic compounds (benzene and toluene) onto selected type of GAC. The kinetic experiments were conducted using two different doses (100 and 500 mg/L) of GAC in batch systems with contact time varying from few minutes to 24 h. Adsorption isotherms were determined by dosing different amounts of GAC (0.01–2.0 g) in batch reactor containing 100 mL of the tested water.

The RSSCT was employed for continuous flow adsorption experiments of synthetic hypersaline water. Fig. 1 illustrates the experimental setup used in this study. A 1 cm inner diameter column was used with a

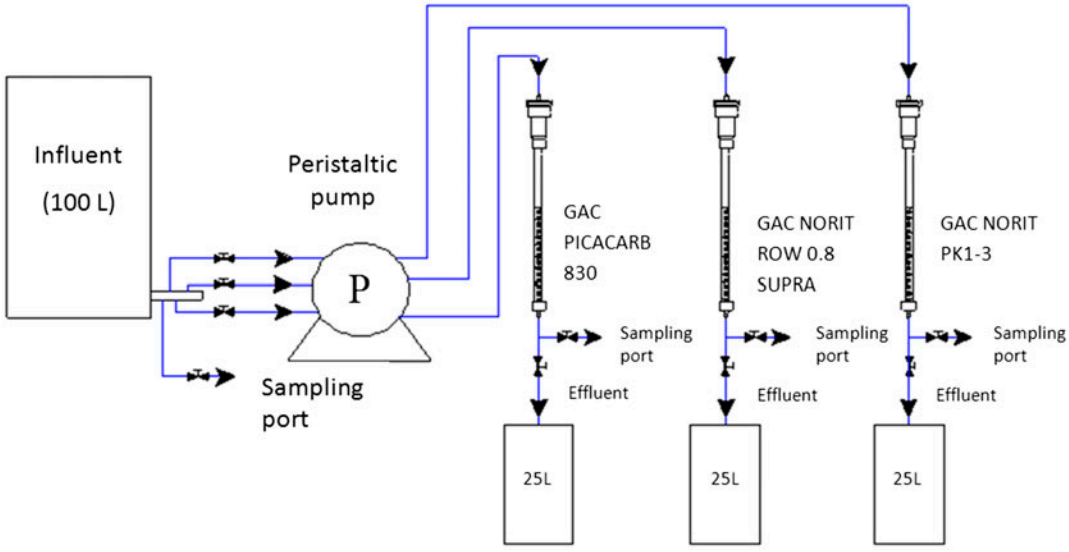

Fig. 1. Experimental setup used for dynamic adsorption experiments.

small-scale empty bed contact time ($EBCT_{SC}$) of 0.45 min, which corresponds to 10 min of EBCT at full scale.

The continuous flow adsorption experiments using the real Produced Water were carried out with an EBCT of 5 min to further reduce the amount of water required.

2.3. Bioregeneration experiments

Pre-loaded GAC columns with synthetic water or Produced Water were bioregenerated by OBR using solutions containing selected micro-organisms. The experimental setup for OBR is shown in Fig. 2. The biological solution was circulated up-flow throughout the GAC column using a peristaltic pump in order to fluidize the packed GAC and, therefore, allowing a better contact between the biological solution and the GAC. Air was bubbled into the biological solution in order to maintain a dissolved oxygen concentration >2.0 mg/L which is required for the aerobic micro-organisms. The OBR setup was employed using three different conditions: (i) the GAC saturated column and the use of a biological solution continuously re-circulated (setup A), (ii) the saturated GAC column and the use of a culture medium without biomass continuously re-circulated (setup B), and (iii) a fresh GAC column and the use of a biological solution continuously re-circulated (setup C).

The biological solution was enriched using a culture medium M9 spiked with benzene and toluene as the sole carbon source for the synthetic water experiments, and an ONR culture medium spiked with Produced Water for the experiments performed with the Produced Water. The CO_2 produced by the biological degradation of the adsorbed compounds was collected in two flasks placed in series containing a solution with $Ba(OH)_2$.

2.4. Analytical methods

Benzene and toluene were analyzed by a GC/MS with a head space system (Agilent) employing a capillary column HP-5 (30 m; $d = 0.25$ mm; and $s = 0.25$ μm) with helium as carrier gas and a flowrate of 1.5 mL/min, according to the standard method [37].

The microbial growth was analyzed by both the optical density (OD) measurement obtained from a spectrophotometer Eppendorf at 600 nm and the colony count analysis (CFU). Furthermore, the genetic characterization of the isolated bacteria was carried out using polymerase chain reaction.

The CO_2 produced from the bacteria during their respiration was calculated using a solution containing $Ba(OH)_2$ and measuring the $BaCO_3$ produced from the following reaction:

$$Ba(OH)_2 + CO_2 \Rightarrow BaCO_3 \downarrow + H_2O$$

3. Results and discussion

3.1. Adsorption kinetics and isotherms

Results from the adsorption kinetics experiments carried out with the synthetic water have shown that

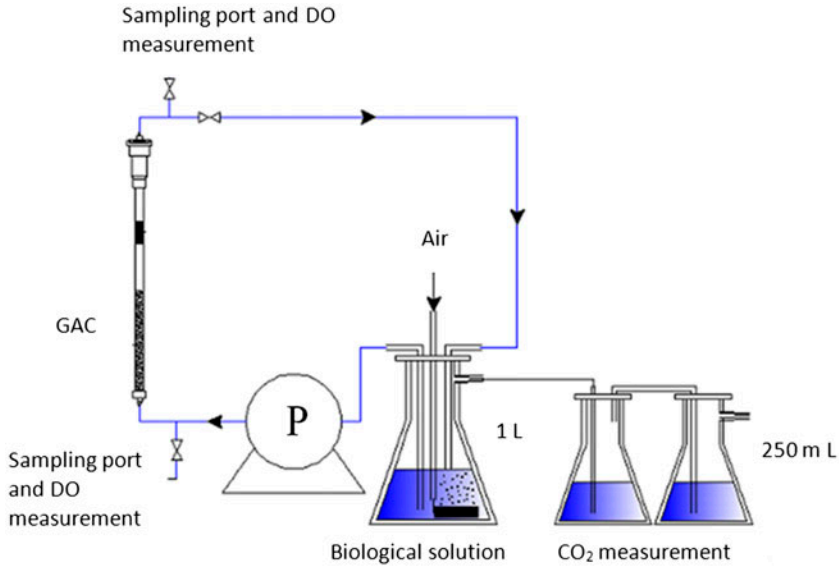

Fig. 2. Experimental setup used for the OBR.

the maximum removal of both benzene and toluene was reached within 2 h for all the types and doses of GAC used. Therefore, two hours of reaction time was sufficient to reach the equilibrium in all the kinetic experiments conducted. As a result, adsorption isotherms were determined using different doses of GAC in batch reactors with reaction time of two hours. The obtained experimental data is well fitted by the Freundlich isotherm and shows a similar performance of the employed GAC types, with the exception of the PICABIOL which is less effective for the removal of benzene and toluene, as shown in Fig. 3. It is noteworthy that the adsorption capacity for toluene was higher than that for benzene for all the investigated GAC types, according to prior research [38–40].

3.2. Breakthrough curves for benzene and toluene in hypersaline water and Produced Water

Fig. 4 shows the breakthrough curves for benzene and toluene obtained using the synthetic water with different GAC types and employing the RSSCT. Obtained results from the dynamic adsorption experiments have confirmed that PICACARB and NORIT PK1-3 have a much higher adsorption performance for both benzene and toluene than of NORIT ROW 0.8 SUPRA. Indeed, the breakthrough of both benzene and toluene occurs faster in the case of NORIT ROW 0.8 SUPRA GAC.

Furthermore, it is notable the better adsorption of toluene onto the investigated GAC types, in agreement with the obtained isotherms and also according to prior research [41,42].

Continuous flow adsorption experiments were also performed using the Produced Water. Obtained results (Fig. 5) show a faster breakthrough of both benzene and toluene in Produced Water than that observed in synthetic water. This result is expected due to the fact that the EBCT was 5 min in the case of Produced Water and 10 min in the case of synthetic water. Furthermore, Produced Water is a much more complex solution containing other organic and inorganic constituents which compete with the target compounds for the GAC adsorption sites. Dynamic adsorption tests conducted with Produced Water demonstrated a better performance of the PICACARB GAC, which was, therefore, used for the GAC saturation, and the following OBR experiments were carried out with the Produced Water.

3.3. OBR of GAC loaded with synthetic hypersaline water

Fig. 6 shows the barium carbonate produced over time for each OBR experimental setup. In setup A, the production of barium carbonate is due to the respiration of micro-organisms in the presence of substrate (benzene and toluene). The $BaCO_3$ concentration has increased reaching the maximum value at a reaction time of 17.5 h and then has decreased due to the substrate consumption. The results obtained from the control setup B show a very low production of barium carbonate practically constant throughout the course of the experiment. For the control setup C, the biological activity has decreased steadily due to a lack of substrate resulting in a final endogenous phase.

The trend of carbon dioxide concentration during the OBR experiment obtained by the stoichiometric calculation matches very well with the OD values found in the biological solution during the bioregeneration of setup A as shown in Fig. 7. Indeed, the maximum values of CO_2 (61.37 mg), OD600 (0.138), and colony count (2.5×10^{10} CFU/mL) were observed simultaneously at a reaction time of 17.5 h. At the same reaction time, also the maximum concentration of both benzene and toluene was measured in the biological solution of the control setup (setup B), highlighting that the maximum bioavailability of benzene and toluene has occurred together with the highest biomass production. The latter result demonstrates that benzene and toluene were the carbon source for the biomass growth.

The genetic characterization of the isolated bacteria has shown the presence of *Pseudomonas*, *Sphingomonas*, *Alcaligenes*, *Arthrobacter*, and *Mycobacterium* which are well known for the degradation of hydrocarbons. Indeed, the *Pseudomonas* often occurs in water contaminated by aromatic hydrocarbons [43–46], the *Sphingomonas* species are effective in the degradation of aromatic compounds, such as Toluene, xylene, naphthalene, fluorene [47,48], and the *Alcaligenes* and *Mycobacterium* are also well known for aromatic contaminants degradation [49–51].

Overall, obtained results from the OBR experiments using GAC pre-loaded with synthetic water confirms that the biological degradation of benzene and toluene was achieved and that the estimated CO_2 production can be used together with or alternatively to the biomass concentration measurements (OD and colony count) to investigate the effectiveness of the OBR.

3.4. Adsorption of benzene and toluene in Produced Water on GAC and OBR of spent carbon

Fig. 8 shows the benzene and toluene breakthrough from dynamic adsorption experiments carried out using Produced Water throughout the PICACARB adsorption column before (Run 1) and after (Run 2) the OBR. Both Run 1 and Run 2 experiments were conducted in duplicate by employing two experimental setups (column A and B).

According with the results obtained by the dynamic adsorption experiments using both the synthetic and real Produced Water (Figs. (3)–(5)) and in agreement with prior research [41,42], the adsorption effectiveness of toluene was much higher than that of benzene and only a slight breakthrough was observed (Run 1). The breakthrough curve obtained during the Run 1 shows a decrease in concentration of benzene,

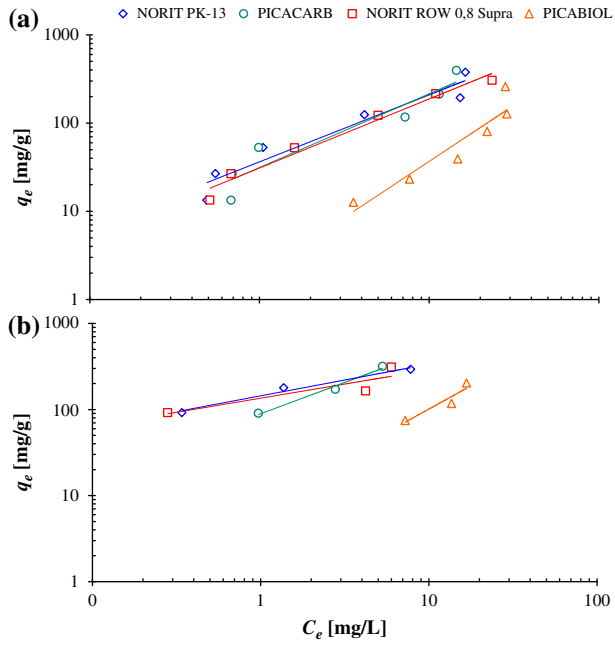

Fig. 3. Freundlich isotherms for benzene (a) and toluene (b) in synthetic hypersaline water.

and to some extent also of toluene, in the effluent at the time of influent change (BV = 660). Indeed, in order to minimize the amount of Produced Water used, the effluent from the adsorption column was analyzed for benzene and toluene and then was spiked with the requisite amount of both the target compounds up to 50 mg/L and used as the influent of the GAC columns. The decrease in benzene and toluene concentration in the effluent at the time of the change of the influent can be explained as either the improvement of the influent quality (most organic matter already removed before the change of the influent by adsorption was absent in the subsequent adsorption step) or the slow diffusion phenomena due to the stop of the run for about 12 h. However, considering the less evident effect of the subsequent influent change (BV = 1,350), it can be concluded that the improvement in water quality was the main factor affecting the adsorption mechanism. Indeed, the breakthrough curve after the second influent change did not undergo a significant variation in slope compared with the curve obtained before the influent change. This indicates that the mechanism of adsorption of the target compounds is not significantly affected by the influent water quality.

The results obtained during the Run 2, shown only for column A (Fig. 8), demonstrate the partial regeneration of the carbon adsorption capacity due to the biological degradation of hydrocarbons. The amount of

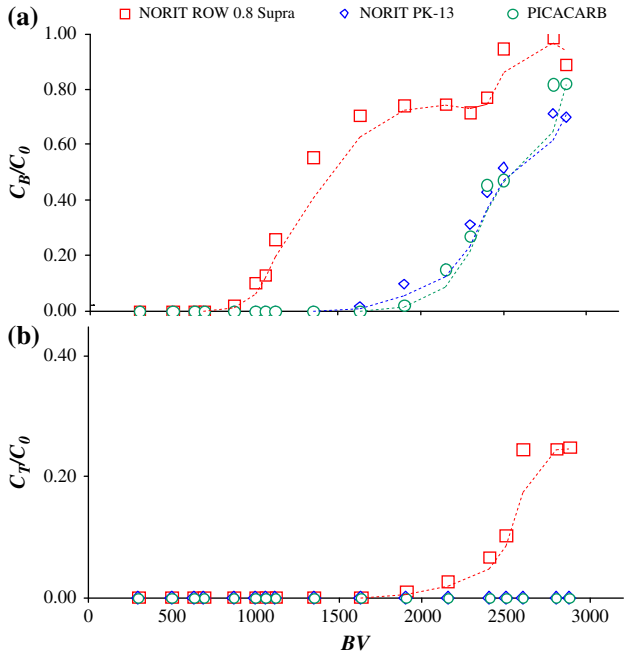

Fig. 4. Benzene (a) and toluene (b) breakthrough for different GAC types. RSSCT carried out using synthetic water. BV = Bed Volumes treated.

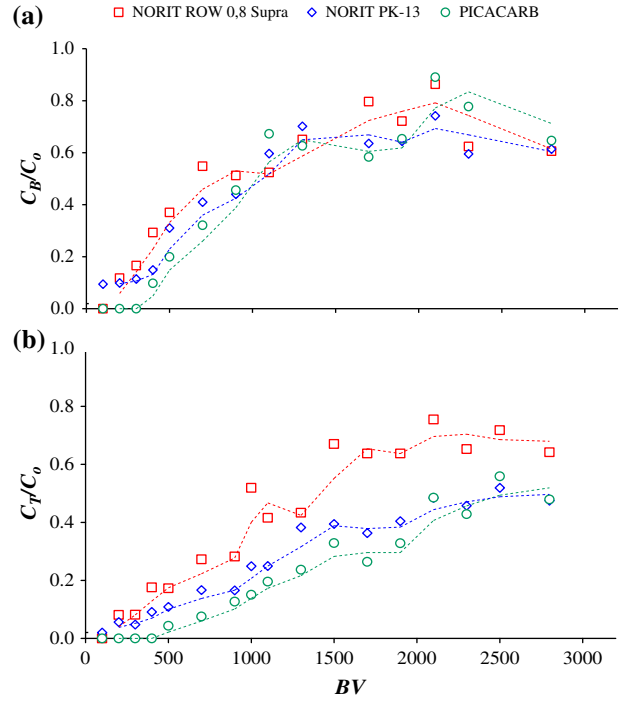

Fig. 5. Benzene (a) and toluene (b) breakthrough for different GAC types. RSSCT carried out using Produced Water. BV = Bed Volumes treated.

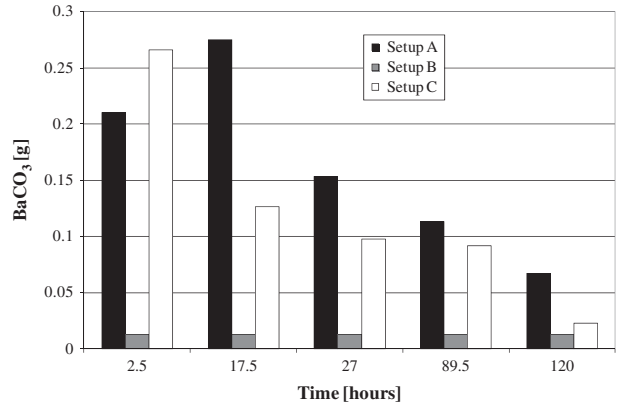

Fig. 6. Barium carbonate production during OBR of GAC saturated with synthetic water in different experimental setups.

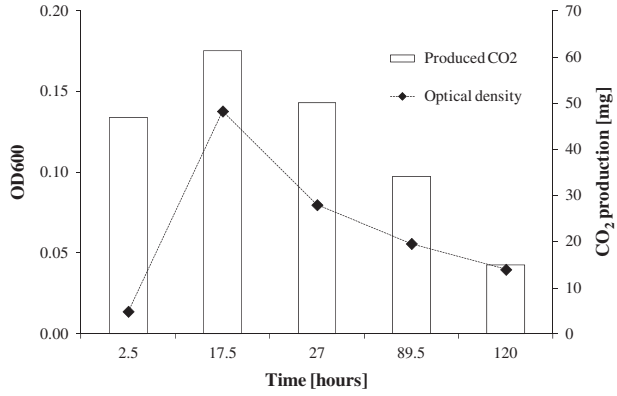

Fig. 7. OD and carbon dioxide production values at different bioregeneration times due to microbial growth in setup A experiment.

benzene removed in Run 1 was 2.74 g, while in Run 2 was 1.55 g. As a result, it can be estimated that about 57% of the benzene adsorption capacity was recovered. Similarly, it was calculated that about 50% of the Toluene adsorption capacity was restored. The higher regeneration capacity for benzene than that for toluene is possibly due to the higher adsorption affinity and, therefore, lower desorption efficiency of toluene with the employed GAC (Fig. (3)–(5)). This results corroborate prior research supporting the hypothesis that adsorbent bioregeneration occurs by the desorption of sorbate [33,52]. The partial regeneration of the GAC can be interpreted as the result of a biological fouling of GAC [53] or as a structural modification of carbon due to the microbial action [54]. However, this behavior was different for the two target molecules. Indeed, the slope of the breakthrough curve obtained for benzene after the OBR is slower than that found before

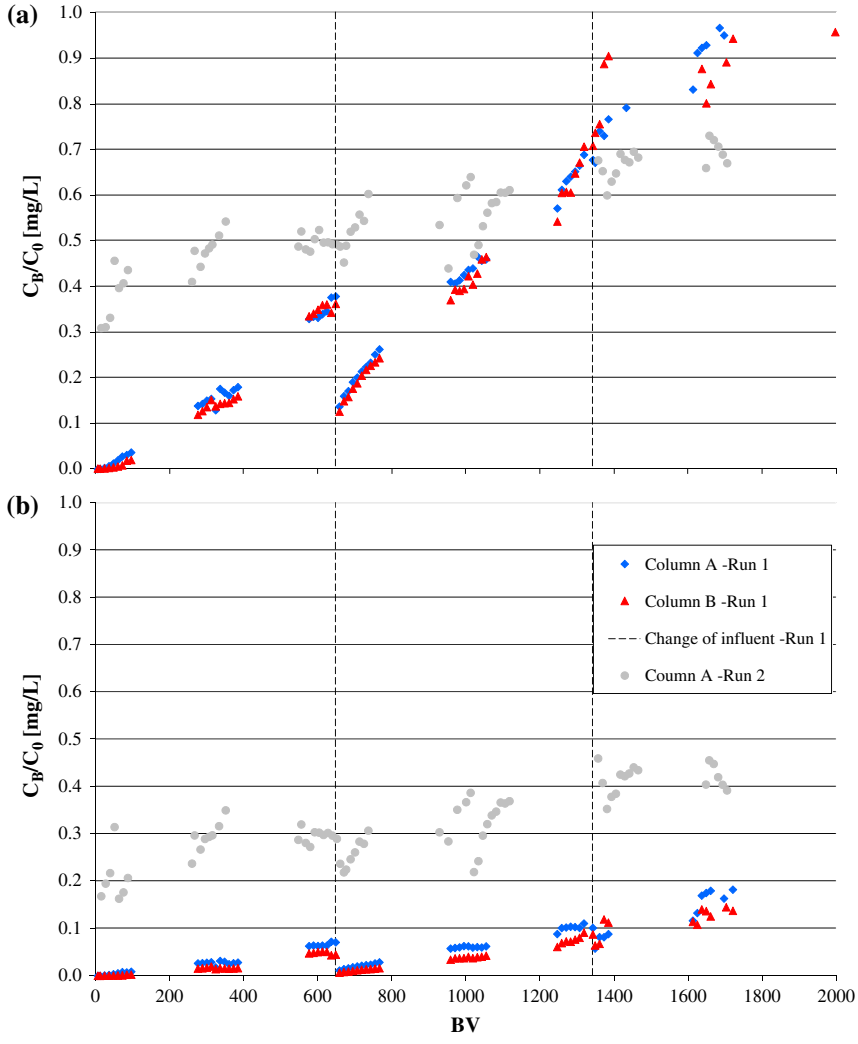

Fig. 8. Benzene (a) and toluene (b) breakthrough before (Run 1) and after (Run 2—showed only for column A) OBR. BV = Bed Volumes treated.

the OBR. On the other hand, the slopes obtained for toluene are similar regardless of the OBR. This result can be interpreted as a relevant competition for GAC adsorption sites between benzene and other organic molecules present in the Produced Water which were adsorbed preferentially especially during the Run 1. On the other hand, this competition was much less prominent for toluene which was adsorbed preferentially. Furthermore, it seems that OBR improves the adsorption affinity with benzene.

Fig. 9 shows carbon dioxide production calculated by the barium carbonate formed over time for each OBR experimental setup. In this case, two columns, namely column A and column B, were employed with the same setup A in order to duplicate the OBR experiment. The setup C was also employed as an experimental control while the setup B was not used, also considering the results obtained by the OBR experiments carried out with synthetic water (Fig. 6).

Obtained results show that also in the case of GAC loaded with Produced Water, the production of barium carbonate can be explained as the respiration of micro-organisms in the presence of substrate (benzene and toluene). Indeed, the CO_2 concentration has increased reaching the maximum value at a reaction time of two days and then has decreased due to the substrate consumption. The results obtained from the control setup C has shown that the biological activity has decreased steadily due to a lack of substrate resulting in an endogenous phase.

The genetic characterization of the isolated bacteria from the regeneration solution has shown the presence of bacteria well known for the degradation of hydrocarbons such as *Pseudomonas sp.* [55], *Mycobacterium* sp.

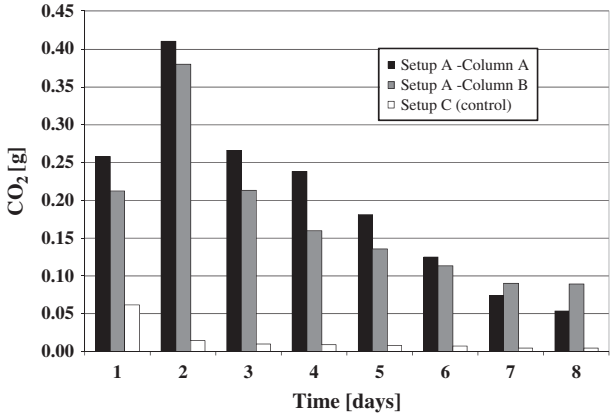

Fig. 9. Carbon dioxide production during OBR of GAC saturated with Produced Water in different experimental setups.

[56,57], *Microbacterium* sp. *ITRC1* [58], *Sphingomonas* sp. [47,48], *Alcaligenes* sp. [51,59,60], *Microbacterium* sp. RI48 [53], *Nocardioides* sp. MSL16 [53], and *Mycobacterium peregrinum* [61].

Overall, the obtained results show that hydrocarbons are selectively removed by GAC which is not fully regenerated by OBR even though a significant part of the adsorption capacity can be recovered.

4. Conclusions

GAC adsorption has been found very effective to remove target compounds (benzene and toluene) from both synthetic hypersaline water and real Produced Water. The adsorption effectiveness is compound specific, showing a much higher removal of toluene. The relatively fast saturation of the GAC stresses the need for an economic regeneration process in order to make the adsorption process feasible.

The OBR seems a promising solution for the regeneration of the saturated GAC. The recovery of the adsorption capacity was 50% and 57% for toluene and benzene, respectively. The genetic characterization of the isolated bacteria has shown the presence of species which are well known for the degradation of hydrocarbons. The maximum values of OD, CFU, and CO_2, indicating the highest biomass growth, have been found simultaneously with the maximum bioavailability of benzene and toluene.

Overall, obtained results demonstrate that preloaded GAC with either synthetic or real Produced Water can be regenerated by OBR. The developed methodology can be used further in full-scale experiments to better understand the feasibility of the OBR.

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