

Two phase partitioning bioreactor applied to produced water treatment

Vincenzo Piemonte, Luisa Di Paola and Marina Prisciandaro

ABSTRACT

Produced waters are the largest waste associated with the production of oil and gas; they contain dissolved salts, oil (dissolved and scattered organic compounds), chemicals and additives involved in the oil well operations, suspended particles, sand and other compounds, making their treatment very complex. In this paper, we propose the use of a TPPB (two phase partitioning bioreactor) for the biological treatment of produced waters. We model the application of the TPPB on the stream after classical pre-treatment stages: the reactor behaviour is based on the controlled release of substrate by means of an organic solvent. This study aims at developing a mathematical model for a TPPB adopting oleic alcohol (Adol 85 NF) as a solvent: we test model reliability by means of a sensitivity analysis in order to evaluate the reactor efficiency for chemical oxygen demand (COD) removal in a produced water stream, aimed at water reuse.

Key words | bioreactor, mathematical modelling, produced water treatment, TPPB

Vincenzo Piemonte (corresponding author)

Luisa Di Paola

Faculty of Engineering,
University Campus Biomedico of Rome,
Via Alvaro del Portillo 21,
00128 Rome,
Italy
E-mail: v.piemonte@unicampus.it

Marina Prisciandaro

Department of Industrial and Information
Engineering and of Economics,
University of L'Aquila,
Viale Giovanni Gronchi 18,
67100 L'Aquila,
Italy

INTRODUCTION

Produced water (PW) is the water that, being trapped in underground formations, is brought to the surface with the oil during the extraction process. It is the largest by-product, or waste, associated with the production of oil and gas. Currently, it is treated and disposed of in deep wells on onshore platforms or directly discharged into the sea. Specifically, about 65% of this water is re-injected to the well for pressure maintenance, 30% of total PW is injected to a deep well for final disposal in the case of proper aquifer conditions, whereas the remaining part is discharged directly to surface water (Çakmakci *et al.* 2008).

Extraction technology and reservoir characteristics affect the quality and the quantity of PW (Pendashteh *et al.* 2010). Generally, the PW amount accounts for around 70% of total oil production wastewaters volume. Salinity, dissolved oil and aromatic content represent the most important players in PW quality determination. Furthermore, salinity also affects the PW toxicity assessment since current regulatory test organisms are salt intolerant. Therefore, there is a great need to develop cost effective

technology for desalination and to consider more salt tolerant toxicity test species. Typically, PW contains high concentrations of aromatic hydrocarbons, e.g. BTEX (benzene, toluene, ethylbenzene, xylene), NPD (naphthalene, phenanthrene and dibenzothiophene, see Table 1) and PAH (polycyclic aromatic compounds) (Utvik 1999; OGP 2002), minerals, radioactive substances, dissolved gases, scale products, waxes, microorganisms and dissolved oxygen (Igunnu & Chen 2012). The salt concentration may range from a few to 300,000 mg L⁻¹; the total organic carbon (TOC) concentrations lies between 0 and 1,500 mg L⁻¹, while oil and gas (O&G) concentrations are comprised between 2 and 565 mg L⁻¹ (Pendashteh *et al.* 2010).

Nowadays, as water demand increases day by day, it is essential to recover and reuse water (Barba *et al.* 2006). As fresh water supply becomes increasingly scarce, PW can become an important water source after suitable treatment. In addition, it is crucial to find new technologies aimed not only at the environmental sustainability but also at complying with the more stringent rules and regulations of the field.

Table 1 | BTEX composition

Component	Lower value (mg L ⁻¹)	Upper value (mg L ⁻¹)
Benzene	0.032	15.00
Toluene	0.055	5.85
Ethylbenzene	0.086	0.56
m-Xylene	0.258	1.30
p-Xylene	0.074	0.33
o-Xylene	0.221	1.66
Total BTEX	0.730	24.10

The permit limits of O&G for treated produced water according to the United States Environmental Protection Agency regulatory limits are 29 mg L⁻¹ for a monthly average and 42 mg L⁻¹ for a daily maximum (USEPA 1996).

Biological, physical and chemical methods are available to specifically remove hydrocarbons from produced water. In offshore extraction facilities, due to space constraints, compact physical and chemical treatment technologies mostly apply (photo-electrocatalytic processes, hydrocyclones, coagulation and flocculation; Ahmadun *et al.* 2009). Most of these techniques are only suitable for pretreatment of wastewater for *in situ* reuse, for example for reinjection to enhance oil recovery yield (Pendashteh *et al.* 2010).

Biological treatments (secondary treatments) are based on the microbial degradation in aerobic conditions and have proved to be a good and efficient method to remove dissolved hydrocarbons (BTEX) in produced water. The most commonly used biological treatments in wastewater issues include activated sludges, the sequencing batch reactor (SBR) and the biological aerated filter (BAF). Among these systems, the SBR has proved to be the most effective method for water purification from dissolved hydrocarbon compounds (Pendashteh *et al.* 2010): however, this applies only for concentrations of substrate (chemical oxygen demand, COD) below a given threshold since the efficiency drops down for larger concentrations, due to a marked substrate inhibition.

To exceed this limitation, in this paper we explore the feasibility of a two phase partitioning bioreactor (TPPB) based on the 'controlled release' of substrate by means of the liquid-liquid equilibrium. Working as an SBR, it contains two phases: an aqueous phase, containing the biomass, and a second organic partitioning phase

(an organic solvent or polymer beads). Organic compounds are partitioned in the organic phase and gradually released into the aqueous phase; this way they do not inhibit the biomass growth and activity (digestion of organic compounds).

This study aims at modelling the TPPB, in order to evaluate its performance and efficiency in terms of COD removal applied to produced water: the requirements are that the COD concentrations upon treatment must be lower than those given by laws for water reuse for irrigation purposes.

MATERIAL AND METHODS

Process analysis

We adopted as reference for the inlet stream a produced water whose properties are reported in the first column of Table 2.

Analogously to a previous work of our group (Piemonte *et al.* 2015), the high BTEX concentration value complies with literature: the technical study of the International Association of Oil & Gas Producers (OGP 2002), based on the analysis of data from twenty oilfields, sets the total BTEX content in the range of 0.73–24.1 mg L⁻¹.

Figure 1 reports the proposed process block scheme for produced water treatment: a pre-treatment of the produced water is followed by the biological treatment in the TPPB. The properties of the stream out of the pre-treatment stage have been computed elsewhere (Piemonte *et al.* 2015) and reported in Table 2 (second column). This stream is then directly fed to the TPPB.

Table 2 | Produced water composition

Component	Influent stream (mg L ⁻¹)	TPPB inlet (mg L ⁻¹)
Oil and grease	565	<10
Total suspended solids (TSS)	1,000	<0.1
Chemical oxygen demand (COD)	3,000	2,300
Biochemical oxygen demand (BOD)	1,500	1,100
Total organic carbon (TOC)	1,500	1,500
BTEX	20	20
Total dissolved solids (TDS)	37,500	35,000

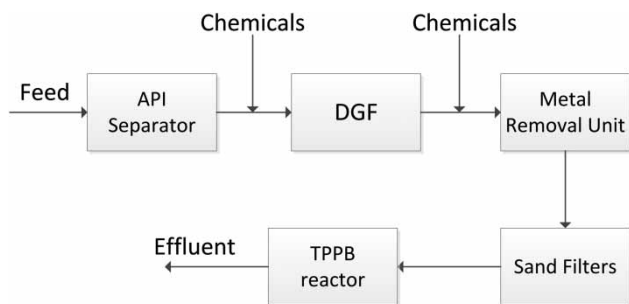


Figure 1 | Block scheme of the produced water (PW) treatment.

Each bioreactor in the scheme is a TPPB. **Figure 2** shows a schematic representation of the two reactors (SBR and TPPB) during the reaction phase.

As pointed out above, TPPB is based on the ‘controlled release’ of substrate, such as it works as a two phase SBR: an aqueous phase containing the biomass, and an organic partitioning phase. Organic compounds are partitioned into the organic phase and then gradually released into the aqueous phase in order to limit inhibitory effects on the biological reactions. This way, even in the case of high organic loads, microorganisms are exposed to low substrate concentrations, optimal for the reaction rate.

Reactors modelling

In the following, we briefly sketch a modelling description of the SBR and TPPB reactors. A more detailed analysis can be found elsewhere (Tomei *et al.* 2010; Annesini *et al.* 2014; Piemonte *et al.* 2015).

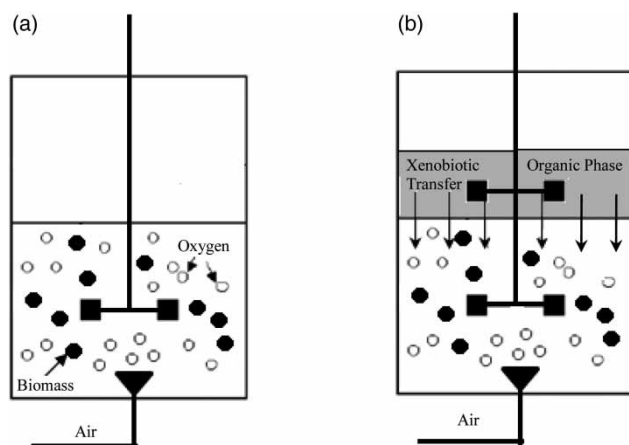


Figure 2 | Schematic representation of the SBR (a) and TPPB (b) reactors during the reaction phase.

The xenobiotic degradation rate was modelled by the Haldane equation to describe the substrate inhibited kinetics:

$$r_S = v_{\max} \frac{C}{C + K_s + \frac{C^2}{K_I}} = k_{\max} \cdot X \frac{C}{C + K_s + \frac{C^2}{K_I}} \quad (1)$$

where X and C are the biomass and substrate concentration, respectively, K_s is the saturation constant and K_I the inhibition constant, k_{\max} stands for the maximum removal rate.

The Haldane equation has been recast to reveal parameters more descriptive of the process kinetics (Tomei & Annesini 2008):

$$r_S = k_{\max} \cdot X(2 + \beta) \frac{C/C^*}{1 + \beta(C/C^*) + (C/C^*)^2} \quad (2)$$

$C^* = \sqrt{K_s \cdot K_I}$ is the substrate concentration at which the maximum removal rate occurs and $\beta = \sqrt{K_I/K_s}$ accounts for the substrate inhibition.

To model the two phase system, we accounted for substrate mass balance in both phases, the kinetic equation (reported above) and the substrate transfer (see **Figure 2**). **Table 3** reports the model equations for both SBR and TPPB reactors.

We assumed a uniform, mean substrate concentration in the organic phase of the TPPB and the corresponding transfer rate is described in terms of an overall mass transfer coefficient.

Model parameters

Table 4 reports the partition coefficients and costs for several organic solvents with respect to BTX compounds. As suggested by Collins & Daugulis (1999), Adol 85 NF solvent realizes a good trade-off between cost, biocompatibility and selectivity, therefore we adopted it in the process simulation as partitioning phase in the TPPB reactor.

Finally, **Table 5** shows the model parameters used in the process simulation. We identified benzene as the key component to evaluate the reactor performance, since it is the most soluble (in water) xenobiotic component present in the produced water and it has a higher inhibition influence

Table 3 | Balance equations for single phase and two phase reactors

Substrate mass balance	Reactor type
$\frac{dC_w}{dt} = aK_{ws} \left(\frac{C_{org}}{P} - C_w \right) - r_S$	TPPB (water phase)
$\frac{dC_{org}}{dt} = -\frac{V_w}{V_{org}} aK_{ws} \left(\frac{C_{org}}{P} - C_w \right)$	TPPB (organic phase)
$\frac{dC_w}{dt} = -r_S$	SBR
Biomass mass balance	Reactor type
$\frac{dX}{dt} = r_X$ with $r_X = Yr_S - bX$	TPPB, SBR
Oxygen mass balance	Reactor type
$\frac{dC_{O_2}}{dt} = aK_{O_2}(C_{O_2}^* - C_{O_2}) - r_{O_2}$ with $r_{O_2} = (1 - Y)r_S + bX$	TPPB, SBR

V_w = aqueous phase volume; V_{org} = organic phase volume; C = substrate concentration; C_{O_2} = oxygen concentration in the aqueous phase; $C_{O_2}^*$ = oxygen concentration in equilibrium with gas bulk phase; K_{ws} = substrate mass transfer coefficient; a = specific surface area referring to the aqueous phase; P = partition coefficient; r_S = substrate degradation rate; r_{O_2} = oxygen uptake rate; r_X = biomass growth rate; Y = biomass yield coefficient; b = endogenous respiration constant; K_{O_2} = oxygen mass transfer coefficient. Subscripts: w = aqueous phase; org = organic phase.

Table 4 | Organic solvent for TPPB reactor (Collins & Daugulis 1999)

Solvent type	P (Benzene)	P (Toluene)	P (Xilene)	Cost (\$/L)
Adol 85 NF	161	405	524	33
Dipentyl ether	365	473	781	781
Ethyl heptanoate	743	2,874	3,463	88
1-Decyne	427	1,587	NA	1,776
Jasmone	306	1,240	1,770	1,474
2-Decanol	94	745	NA	1,896
2-Decanone	210	1,384	1,896	990
2-Undecanone	205	1,304	1,883	61

on biomass. We chose *Pseudomonas putida* as biomass, since it is tolerant to salt concentrations tested in this work.

RESULTS AND DISCUSSION

In order to test the model reliability, we performed a sensitivity analysis on key model parameters affecting the reactor performance. Figure 3 reports the kinetics of xenobiotic removal in the aqueous phase at different initial

Table 5 | Model parameters (Tomei et al. 2010; Annesini et al. 2014)

Parameter	Value
K_{max} (h^{-1})	0.05
aK_{ws} (h^{-1})	2.5
aK_{O_2} (h^{-1})	20
Y	0.67
P	161
b (h^{-1})	0.0001
X_0 (mg/L)	1,000
$C_{O_2}^*$ (mg/L)	1.5
K_I (mg/L)	100
K_S (mg/L)	30
V_w (L)	10
V_{org} (L)	2

concentrations of the key component: an increase of the xenobiotic initial concentration does not seem to affect the reactor removal efficiency in terms of xenobiotic amount removed from liquid phase, in fact, the figure shows the biomass digests almost all the xenobiotic in the aqueous phase in 1 hour. This is due to the high capacity of the organic phase being able to balance the xenobiotic transfer to biomass by reducing the inhibitory effects.

To better understand the reactor behaviour, it is important to point out that the xenobiotic concentration in the aqueous phase is not a clear index of reactor removal capacity: from Figure 4 it is evident that after 1 hour almost all the xenobiotic loaded in the reactor is still stored in the organic phase, which slowly releases the compound in the aqueous phase. In other words, in the conditions tested, the characteristic time related to xenobiotic transfer between the two phases ($1/aK_{ws}$) is much higher than the reaction characteristic time in the liquid phase ($1/K_{max}$). Therefore the reactor removal capacity is strongly affected by the overall xenobiotic transfer coefficient. Figure 5 shows the effect on an increase of aK_{ws} on the xenobiotic removal in the aqueous phase: low values of aK_{ws} determine a non-reliable course of the TPPB reactor.

The developed mathematical model has been used to evaluate the process reliability to treat produced water

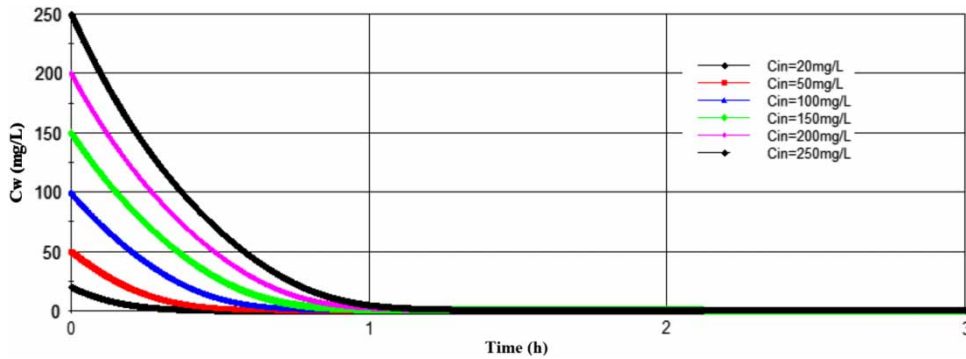


Figure 3 | Influence of initial xenobiotic concentration in the water phase (C_{in}) on reactor removal performance.

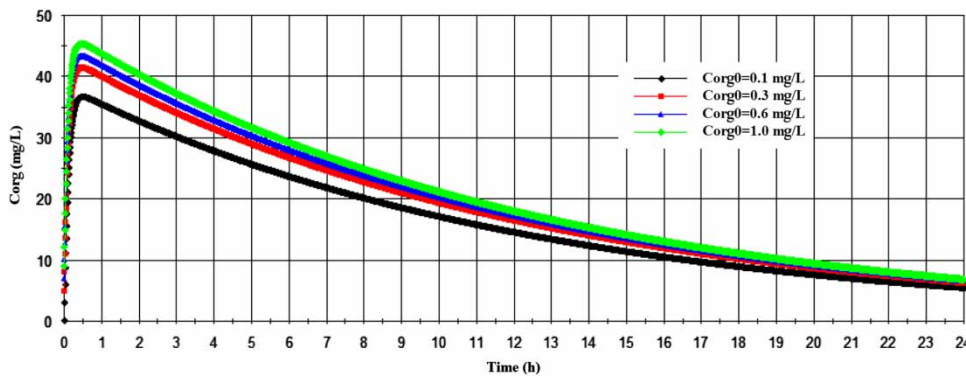


Figure 4 | Influence of initial xenobiotic concentration in the organic phase (C_{Org0}) on reactor removal performance.

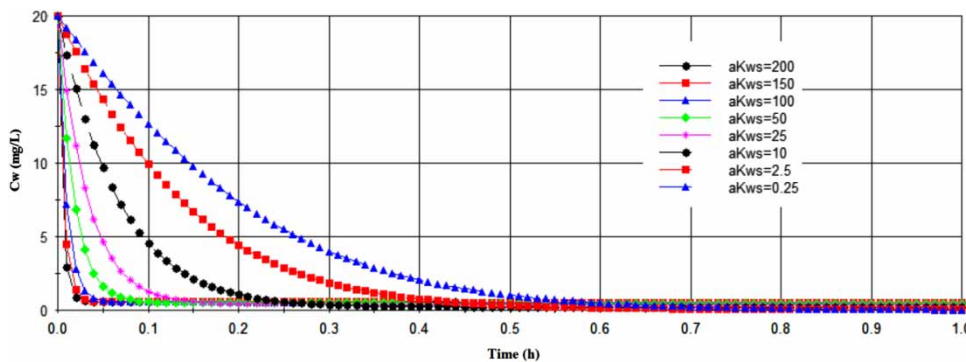


Figure 5 | Influence of xenobiotic mass transfer coefficient between organic and water phases on reactor removal performance.

for agricultural purpose. With reference to benzene as the key component, [Figure 6](#) highlights how the proposed process is able to meet the law requirement

(0.001 mg L^{-1}) but only when benzene concentrations in the inlet stream to bioreactor are low (up to about 4 mg L^{-1}).

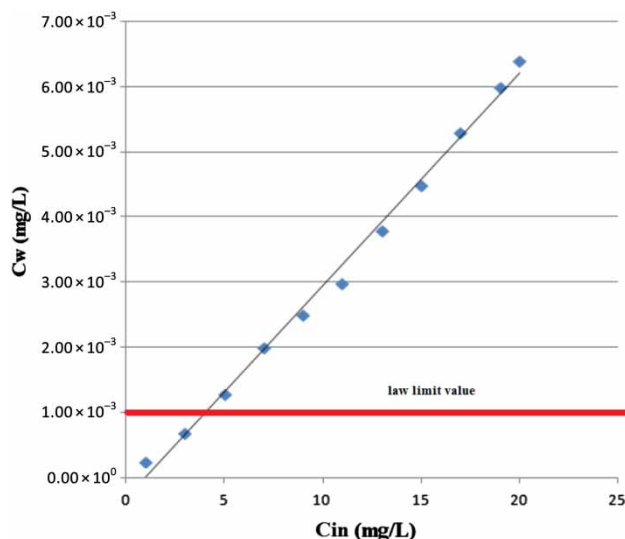


Figure 6 | Benzene concentration in the water phase in the outlet reactor stream for different initial benzene concentration in the reactor. Comparison with law limit concentration (0.001 mg/L) of benzene for agricultural water purpose.

CONCLUSIONS

In this work we present a model to compute the efficiency in terms of COD removal of a two phase partitioning bioreactor when applied to a produced water treatment.

This work demonstrates the great potentiality of this biotechnological solution for the reuse of wastewater, with a specific application for produced waters.

Biotechnology processes promise to have a great impact in the future for wastewater treatment, since they rely on devices operating at mild conditions. On the other hand, they require great care in control, which must rely on correct modelling, providing the mathematical framework for a successful control strategy.

In the future, we plan to cross experimental data with modelling to validate model hypotheses and provide a more reliable base for systems scale-up in the perspective of industrial applications.

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