



Produced water desalination: An exploratory study

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HIGHLIGHTS

- A novel hybrid adsorption/ion exchange (IEX)/reverse osmosis (RO) process is proposed for produced water desalination.
- Water in liquid phase at high pressure and temperature is utilized to regenerate the adsorber. This has multiple advantages for strongly adsorbed components including better desorption with less regeneration fluid, lower energy requirements because there is no phase change, and lower costs.
- IEX regeneration with RO retentate eliminates added chemicals.
- Optimized process to minimize costs at three different brine disposal costs.
- Hybrid process water recovery up to 86% is feasible and economical for the produced water considered in this work.
- This work is based on computer modeling for process synthesis, design, and optimization. Experimental studies are needed to verify the assumptions made in this analysis.

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ABSTRACT

Produced water is the largest volume byproduct stream in oil and gas production, and has an adverse environmental impact due to its complex composition and high disposal costs. Membrane fouling due to hydrocarbons limits purification of produced water by reverse osmosis (RO). A novel hybrid adsorption/ion exchange (IEX)/RO process is developed in which the adsorber removes dissolved hydrocarbons, IEX removes scale causing precursors, and RO desalinates the water. A part of the hydrocarbon free liquid from the adsorber is pressurized to 6.2 bar, heated to 160 °C and used to regenerate the adsorber, which resulted in an improvement in water recovery (to 86%), and translated into a predicted 22.8% decrease in costs amounting to US\$ 27 million annual savings. The new high water recovery processes delineated in this work provide an array of novel options for removing hydrocarbons and desalination under different conditions. Experimental studies are needed to verify the assumptions made in this analysis.

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1. Introduction

The term “Produced Water” is used to describe the water from oil and gas (O&G) extraction processes. Water is frequently injected into wells to increase oil recovery. Steam is injected to decrease the viscosity of oil resulting in improved flowability. Liquid water containing surfactants is used to help release oil adhering to the rock matrix, and high pressure water containing additives and particulates is used in fracking to increase the rock porosity. The O&G industry in USA produces about 18 billion bbls of produced water (≈ 7 bbl of water per bbl of oil). It is the largest volume byproduct

stream associated with O&G production (75 billion bbls of produced water) worldwide annually. Note: 1 bbl = 42 US gal) [1,2].

Management of produced water presents environmental challenges and costs (\$0.30/bbl–\$105.00/bbl depending on the disposal method [3]). The major hydrocarbon groups present in produced water include alkanes, aromatics, polynuclear aromatics, hydrocarbon compounds containing oxygen, nitrogen and sulfur and unknown hydrocarbons (oil & grease). Produced water also contains high amounts of dissolved salts with predominant cations such as Na^+ , K^+ , Ca^{2+} and Mg^{2+} ; anions such as Cl^- and SO_4^{2-} , and silica (SiO_2) [4].

A clarification step is used to remove particulates and induced gas flotation (IGF) is used to remove free oil. The most common method to remove emulsified oil is by pH adjustment and coagulation. A key disadvantage of this method is the problem of additives affecting the downstream operations. When large volumes of produced water

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are treated, chemical addition may increase the cost significantly [5]. Other methods such as electro-coagulation and hydrocyclones are also used. Electrocoagulation involves the use of extremely high voltages, and can become expensive as scale of operation increases. Hydrocyclones are efficient for some emulsions but are capital intensive and expensive to run and maintain [1,2,6].

Membrane processes have emerged as an alternative. The key advantages of membrane based processes are low operating cost, the absence of chemical addition and subsequent generation of oily sludge. However, mineral scale deposition and fouling on the membrane surface (membrane fouling) is a critical issue which limits the water recovery. The hydrocarbons present in produced water adsorb on the membrane surface and form a foulant layer that causes permeate flux decline. In addition, aromatic hydrocarbons are potentially damaging to the polysulfone support layer of the membrane. Antiscalants have been used to avoid scaling on the membrane and increase the water recovery to a certain extent. However antiscalant addition promotes biofouling because antiscalants have been designed to be biodegradable to make concentrate disposal environmentally friendly [7–9].

Hodgkiess et al. [9] studied the impact of hydrocarbons on RO membranes. Their studies involved crude oil/water, diesel/water mixtures and hexane/water emulsified/single phase mixtures. They found that exposure to diesel/water emulsified mixtures was extremely damaging to the membranes. After just 30 min of exposure to dilute diesel water mixtures of 1/50 or 1/100 ratios, they observed greater than 50% reduction in permeate flux and greater than 100% increase in salt passage. Hexane also caused serious deterioration of the performance of RO membranes when in contact in pure or emulsified form. However, no changes in flux or salt passage were observed in single phase oil/hexane/water solutions. From the experimental studies of Hodgkiess et al. [9], and for the hydrocarbons studied, it can be inferred that hydrocarbons retained in aqueous solution do not have damaging impact on performance of RO membranes while hydrocarbons in pure or emulsified form or concentrated hydrocarbon mixtures have a deleterious impact on the membranes. Due to this incompatibility between the raw produced water and the RO membrane, pretreatment is essential to eliminate the problematic hydrocarbons, hardness, metals, oil and grease.

RO desalination processes with an adsorption pretreatment and an ion exchange (IEX) water softening treatment after the IGF unit are proposed in this paper. Adsorption processes are capable of removing iron, manganese, total organic carbon, hydrocarbons, heavy metals (>80% removal efficiency) and oil from produced water thereby alleviating the problem of fouling [3]. Activated carbon has been used extensively for municipal water treatment as a process for removal of organics from drinking water. Based on tonnage used and market value, activated carbon is one of the most widely used porous adsorbents. Organoclay materials such as bentonite can also be used, however they do not have the same adsorption capability as activated carbon [10]. Although activated carbon is the market standard for water treatment, synthetic polymeric adsorbents such as DOWEX OPTIPORE L/V 493 offer advantages in specific cases. Synthetic polymeric adsorbents can be used for recovery of organics from water for identification and quantification purposes [11]. IEX treatment will remove the scale causing precursors in water such as Ca^{2+} and Mg^{2+} , thereby alleviating the problem of mineral scaling on the surface of RO membranes. The concentrate from the RO unit will be used to

regenerate the IEX column which would then eliminate the need for external regeneration chemicals. If the water to be treated does not have any scale causing precursors, then an IEX pretreatment might not be required. The water from the IGF and the adsorbents, would directly be sent to the RO.

Modeling of IEX and RO, and development of RO/IEX hybrid systems for desalination of concentrated brackish waters at municipal plant scale and desalination of the Colorado River water at the YUMA plant scale were done by Venkatesan and Wankat [12–15]. As the modeling of IEX and RO cascades has been done extensively, the main focus of this paper will be the modeling of the adsorption unit and its integration with the RO/IEX system. The hydrocarbons considered in this paper were aromatic compounds and, classified as mono- and polycyclic depending on number of equivalent benzene rings. These compounds are described in Table 1. Toluene was used to represent BTEX as it is close to the average molecular weight for this class of compounds. Naphthalene (for NPD class of compounds) and anthracene (for Polycyclic Aromatic Hydrocarbons, PAH) were selected because data was available.

After describing the process, the modeling of the adsorber and adsorber results are presented followed by an evaluation of different heating methodologies. As the modeling of RO/IEX has been covered extensively previously [12–15], the focus of the current modeling efforts are on the adsorber and the different heating methodologies employed. Finally, the different operations are integrated into one process and the overall results are presented. The evaluations of RO/IEX models are presented along with the overall results.

2. Process description

In this section, a brief description about the proposed process is given. The composition of a particular raw produced water (Texas, USA) is listed in Table 2. After pretreatment to remove suspended solids, the incoming water ($\geq 80^\circ\text{C}$) is sent to an IGF unit. In IGF, the water is de-oiled and almost all of the oil droplets and, the straight and branched chain hydrocarbons are removed at this stage (>98% removal efficiency). The injection of gas bubbles into the water phase increases the buoyant force on the oil droplets. The oil droplets are removed when they rise to the water surface. The water composition after clarification and IGF is also shown in Table 2. This pretreatment does not remove the emulsified and dissolved hydrocarbons, especially lighter aromatics as their solubility is higher than that of straight/branched chain hydrocarbons.

Dow FILMTEC SW30XLE-400i RO membranes were used in this study. These are typically used for two-pass seawater designs and high TDS brackish water applications. These membranes have a higher maximum operating pressure (83 bar) than FT-SW30HR (≈ 70 bar) and FT-BW30HR (≈ 40 bar) membranes. As the membranes, SW30XLE, SW30HR, and BW30HR are spiral-wound elements made of polyamide thin-film composites, they are all susceptible to the problem of membrane fouling due to hydrocarbons [11]. Therefore, before sending the water from IGF to RO for desalination, a check for hydrocarbon solubility and mineral salt precipitation is done by PHREEQC [16]. This check determines the maximum possible recovery at which the RO can be operated without mineral scale formation or hydrocarbon fouling on the membrane surface. Presence of emulsified hydrocarbons quickly fouls the membrane and prevents

Table 1
Aromatic compounds in produced water.

Class	Definition	Examples	Representative compound
BTEX	Monocyclic aromatics	Benzene, toluene, ethylbenzene, xylene	Toluene
NPD	2–3 ring aromatics	Naphthalene, phenanthrene, dibenzothiophene	Naphthalene
PAH	3–6 ring aromatics	Anthracene, pyrene, chrysene	Anthracene

Table 2
Composition of raw produced water [18].

Analyte	Water quality (raw)	Water quality (after clarification and IGF pretreatment)
Total dissolved solids (TDS) (ppm)	5500–7500	5500–7500
Calcium (ppm)	80	80
Magnesium (ppm)	10	10
Sodium (ppm)	2300	2300
Potassium (ppm)	39	39
Strontium (mg/L)	1.0	1.0
Sulfate (ppm)	133	133
Chloride (ppm)	3400	3400
Bicarbonate (ppm)	696	696
Carbonate (ppm)	2.0	2.0
Silica (ppm)	160	90
BTEX ($\mu\text{g/L}$)	1500	1500
NPD ($\mu\text{g/L}$)	720	720
PAH ($\mu\text{g/L}$)	85	85
Total oil & grease (ppm)	53	38
Free oil (ppm)	17	1.0
pH	7.5	7.5
T ($^{\circ}\text{C}$)	80	80

operation of RO. As a pretreatment, the de-oiled water is cooled ($\approx 45^{\circ}\text{C}$) and then sent to an adsorber packed with granular activated carbon (TOG 20 \times 50). Alternatively, the de-oiled water from IGF can be sent to the adsorber without cooling. However, the discharge from the adsorber must then be cooled before sending to RO since operating at temperatures greater than 45°C will void the membrane manufacturer's warranty [11].

The single adsorber column shown in Fig. 1 represents a number of columns in parallel. The adsorbers are in parallel to handle the large flowrate and allow for operation in a cyclic fashion involving a

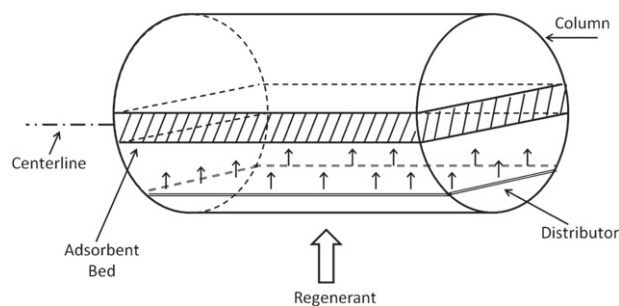


Fig. 2. Schematic of a horizontal column with regeneration countercurrent to feed.

feed step, a regeneration step and a cooling step. In all the figures, only the important heat exchangers are shown. Each adsorber consists of a horizontal column with vertical flow through a relatively shallow packed bed of granular activated carbon (Fig. 2). Horizontal columns are commonly used for solvent recovery from gases using activated carbon as adsorbent [17]. During the feed step, hydrocarbons (BTEX, NPD and PAH) are adsorbed on the highly porous activated carbon and the discharge from the adsorber is stripped of hydrocarbons. The discharge from the adsorber is split into four streams as shown in Fig. 1. An alternative that will be discussed later is to have adsorbers in series in addition to parallel.

2.1. Stream 1 (regenerant)

This stream is heated to 160°C and its pressure elevated to 6.2 bar before it is sent to the adsorber as regenerant. Temperature is elevated in order to desorb the hydrocarbons from the activated carbon

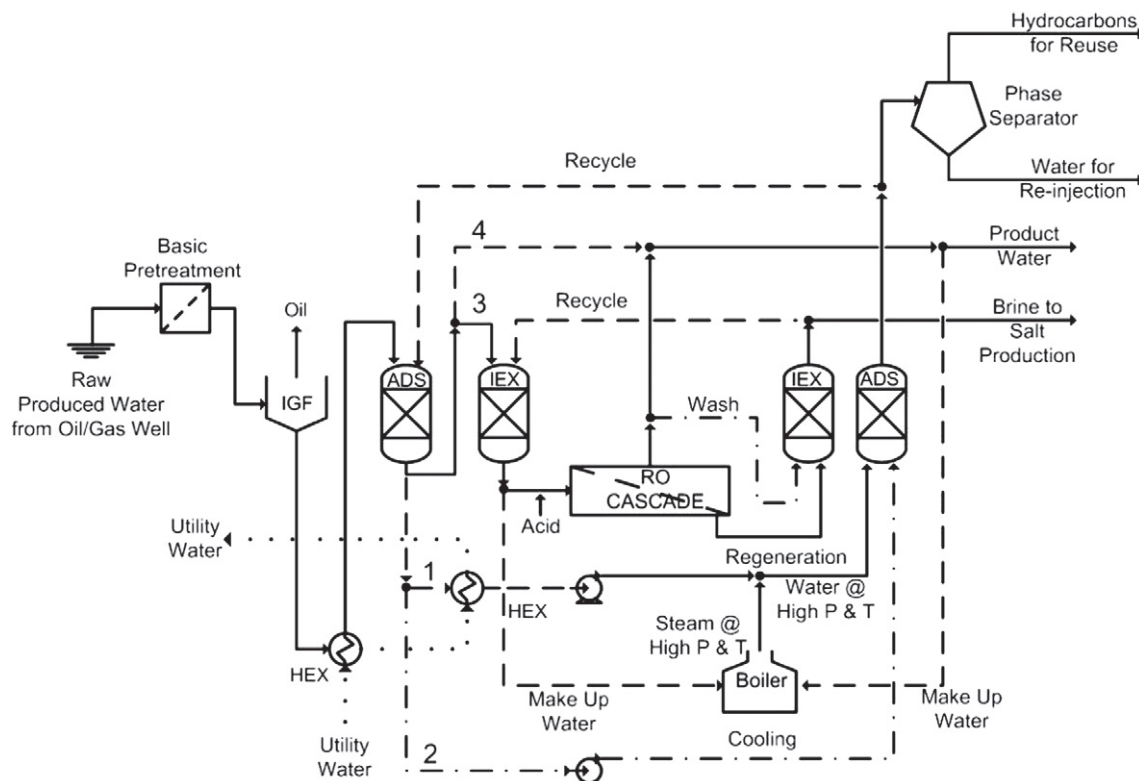


Fig. 1. Proposed process scheme with single column adsorber and IEX pretreatment for RO.

(adsorbent) while pressure is increased to prevent boiling. Heating and pressurization is done either by direct injection of steam from a pressurized boiler or by heat exchangers (HEX) and pumps. During the regeneration step the hot, high pressure water shifts the isotherms such that the hydrocarbons present on the bed are desorbed. Depending on their solubilities at 160 °C, a supersaturated solution may be formed during regeneration when the hydrocarbons (BTEX, NPD and PAH) are released from the adsorbent and enter the water. A supersaturated solution may result in formation of droplets of hydrocarbons which would interfere with fixed bed operation. Thus, regeneration is done counterflow to the feed in an expanded bed at an upward velocity such that the hydrocarbon droplets formed are carried out of the column through overflow (as they follow a streamline), while the much larger adsorbent particles remain in the column with negligible carryover. If experimental data show that droplets are not formed, then a packed bed can be used with upward flow during feed and downward flow during regeneration and cooling.

When the hot, high pressure regenerant is pumped in the column counter flow to the feed, the liquid exiting the column remains at the feed concentration and temperature until temperature breakthrough occurs. This effluent is depressurized and recycled to the adsorber column as feed for the next cycle.

2.2. Stream 2 (cooling)

Before the next feed cycle begins, the column is depressurized as the feed is at low pressure. However, since the column is at 160 °C and 6.2 bar at the end of regeneration, a reduction in pressure will cause flashing of water inside the column, unless the column is cooled before the pressure is reduced. The amount of regenerant and Stream 2 is such that the maximum temperature in the column, after it is depressurized (to 1 bar), does not exceed the boiling point of water at 1 bar, i.e., 99.6 °C. When Stream 2 is pumped into the column, the effluent is the spent regenerant. To partially offset pumping costs, a pressure exchanger is used to depressurize the entire effluent from regeneration and cooling steps, and, the energy recovered is used to partially pressurize the regenerant stream.

2.3. Stream 3 (feed to RO/IEX system)

This stream is cooled to 45 °C and sent to a system of RO cascades with IEX water softening pretreatment as shown in Fig. 1. The IEX exchanges the scale causing precursors such as Ca^{2+} , Mg^{2+} , Ba^{2+} and Sr^{2+} with Na^+ thereby alleviating the problem of mineral scaling on the membrane. This system is very similar to the previous work [12,13]. Alternatively, Stream 3 can be sent to a system of RO cascades with intermediate IEX water softening as shown in Fig. 1. For the regeneration of IEX column, the concentrate from the RO cascade is used. The product water from different cascades is mixed in order to achieve a water stream of desired purity.

2.4. Stream 4 (optional bypass)

This stream is cooled to 45 °C and mixed with the product water coming from the RO cascades. Depending on the purity of product water desired, the amount of bypass stream is adjusted.

The different alternatives evaluated are as follows:

- Adsorber column configuration, i.e., single or two columns in series.
- Heating methodology, i.e., direct steam injection or indirect heating with heat exchangers.
- RO/IEX system configuration, i.e., intermediate IEX or IEX pretreatment.

3. Adsorber modeling & results

3.1. Single column

The adsorber is operated as a packed column in the feed step and as an expanded bed in desorption step. The simplified governing mass and energy balance equations, shown in Eqs. (1a) and (1b), are solved using Aspen Chromatography 2006. In order to describe the adsorption equilibrium of a single solute, the Langmuir isotherm is used.

$$\epsilon \frac{\partial c}{\partial t} + u_0 \frac{\partial c}{\partial z} - E_b \epsilon \frac{\partial^2 c}{\partial z^2} + \rho_s (1 - \epsilon)(1 - \epsilon_p) \frac{\partial \bar{q}}{\partial t} + K(1 - \epsilon) \epsilon_p \frac{\partial \bar{c}_p}{\partial t} = 0 \quad (1a)$$

$$C_{pf} \epsilon \frac{\partial T}{\partial t} + u_0 C_{pf} \frac{\partial T}{\partial z} - C_{pf} \epsilon D_{axial}^{thermal} \frac{\partial^2 T}{\partial z^2} + \rho_s C_{ps} (1 - \epsilon)(1 - \epsilon_p) \frac{\partial \bar{T}_s}{\partial t} + C_{pf} (1 - \epsilon) \epsilon_p \frac{\partial \bar{T}^*}{\partial t} = 0 \quad (1b)$$

where ϵ is bed void fraction, c is concentration of solute in bulk liquid, u_0 is the superficial velocity, E_b is axial dispersion coefficient, ϵ_p is the particle porosity and ρ_s is the adsorbent density. \bar{q} and \bar{c}_p are the volume average solid loading and fluid concentration inside the adsorbent respectively.

The Chung and Wen correlation [19] is used to estimate the axial dispersion in packed beds and the correlation by Kikuchi et al. [20] is used for expanded beds. The mass transfer between phases is accounted for by film diffusion. The correlation by Wilson and Geankoplis [21] is used to estimate film mass transfer coefficients in packed beds (Eq. (1c)) and the correlation by Rowe [22] (Eq. (1d)) is used for expanded beds.

$$k_f = \frac{2D_0}{d_p} + 0.31 \left(\frac{\mu}{\rho D_0} \right)^{-2/3} \left(\frac{(\rho_s - \rho) \mu g}{\rho^2} \right)^{1/3} \quad (1c)$$

$$Sh = \frac{\frac{2\xi}{\epsilon} + \frac{2\xi^2(1-\epsilon)^{1/3}}{(1-(1-\epsilon)^{1/3})^2 \epsilon^2} \tanh(\xi/\epsilon)}{\frac{\xi}{\epsilon(1-(1-\epsilon)^{1/3})} - \tanh(\xi/\epsilon)} (0.001 < Re < 10,000) \quad (1d)$$

where

$$\xi = 0.35 Re^{1/2} Sc^{1/3} \left[\frac{1}{(1 - \epsilon)^{1/3}} - 1 \right] \quad (1e)$$

$$D_p = \frac{\epsilon_p D_0}{\tau} \quad (1f)$$

A linear driving force with a lumped resistance is used to describe mass transfer. As linear lumped resistance is used, the effective mass transfer resistance is given by a sum of resistances model. For film and pore diffusion.

$$k_m a_p = \left[\frac{1}{k_f a_p} + \frac{1}{(k a_p)_{pore}} \right]^{-1} = \left[\frac{1}{k_f a_p} + \frac{d_p^2}{60 D_{mp} K (1 - \epsilon) \rho_p} \right]^{-1} \quad (2a)$$

where k_f is film diffusion coefficient and K is the linear equilibrium constant. For non-linear systems

$$K = \left(\frac{\partial q}{\partial c} \right)_{avg} \quad (2b)$$

For Δq driving force, if film diffusion is neglected, Eq. (2a) becomes,

$$k_m a_p = \frac{60 D_{mp} (1 - \epsilon) \rho_p}{d_p^2} \quad (2c)$$

Table 3
Parameters used for adsorption simulation.

Parameter	Value
Number of nodes	200
P.D.E discretization method	UDS1
Integration method	Gear 5th order
Fixed step size	0.001
Viscosity of water (20 °C)	0.001 kg/ms [25]
Density of water (20 °C)	1019 kg/m ³ [25]
Particle diameter	620 μm [26]
Density of activated carbon	850 kg/m ³ [26]
Activated carbon saturation capacity (q_m)	215.71 mg/g [24]
Activated carbon heat capacity ($C_{p,s}$)	850 J/kg-K [27]
Heat of adsorption (ΔH_{ads})	10.2 KCal/mol [26]
Mass transfer coefficient @ 30 °C ($k_m a_p$) _{Benzene}	8.1 min ⁻¹ [24]
Mass transfer coefficient @ 30 °C ($k_m a_p$) _{Toluene}	6.8 min ⁻¹ [27]
Mass transfer coefficient @ 30 °C ($k_m a_p$) _{Naphthalene}	5.64 min ⁻¹ [28]
Mass transfer coefficient @ 30 °C ($k_m a_p$) _{Anthracene}	4.73 min ⁻¹ [29]
Isotherm parameter ($K_{\infty, Benzene}$)	7.5×10^{-5} L/mg [24]
Isotherm parameter ($K_{\infty, Toluene}$)	6.2×10^{-5} L/mg [27]
Isotherm parameter ($K_{\infty, Naphthalene}$)	3.8×10^{-5} L/mg [28]
Isotherm parameter ($K_{\infty, Anthracene}$)	7.6×10^{-6} L/mg [29]
Arrhenius parameter ($A_{Benzene}$)	2237.1 K [24]
Arrhenius parameter ($A_{Toluene}$)	2441.5 K [27]
Arrhenius parameter ($A_{Naphthalene}$)	2747.1 K [28]
Arrhenius parameter ($A_{Anthracene}$)	3671.4 K [29]

As the adsorber is operated under non-isothermal conditions, the effect of variation in temperature has been considered, but the tortuosity factor has been assumed constant. Molecular diffusivity was correlated by the equation of King et al. [23].

To benchmark the proposed model, simplistic cases of single and binary component adsorption on activated carbon were analyzed [15]. For the single component benchmarking, the adsorption of benzene from aqueous solution onto activated carbon was used. The physical properties and references for the activated carbon parameters used for simulation are listed in Table 3. The heats of adsorption of all compounds on activated carbon are assumed to be equal and the maximum saturation capacities of all compounds on activated carbon are assumed to be equal. A mixture of benzene and toluene using the multicomponent Langmuir isotherm was the model system for the case of binary multicomponent adsorption [24].

$$q_i^* = q_m \frac{K_i c_i}{1 + \sum_{j=1}^n K_j c_j} \quad (3a)$$

where q_i^* is the equilibrium adsorbed concentration, c_i is the equilibrium liquid phase concentration, q_m is the saturation capacity and K_i is the isotherm parameter. The variation of the isotherm parameter is given by Eq. (3b) where A_i is the Arrhenius parameter.

$$K_i = K_{\infty, i} e^{A_i/T} \quad (3b)$$

Since isotherm data for liquids at high temperatures and pressures are not available, Eq. (3b) was used to extrapolate to 160 °C.

As the scale of the process is huge, 250 million gallons (US) per day (Mgpd), multiple adsorption columns in parallel are required

Table 4
Fixed bed and expanded bed parameters.

Parameter	Fixed bed value	Expanded bed value
Average linear velocity	0.0027 m/s	0.00475 m/s
Depth of adsorption bed	1 m	1.43 m
Void fraction	0.4 [30]	0.58
Input stream temperature	30 °C	110 °C
Input stream pressure	1 bar	3 bar
Input stream duration	100 min	3 min
Constant dispersion coefficient	5.5 cm ² /min [19]	23.28 cm ² /min [31]

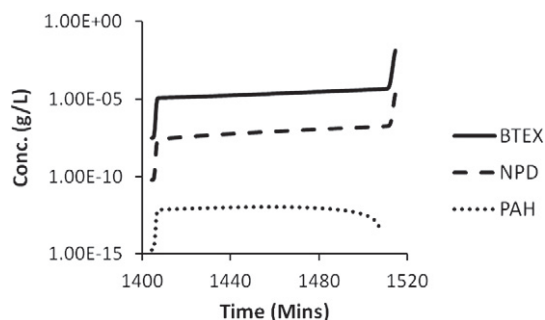


Fig. 3. Breakthrough curves of BTEX, NPD and PAH at cyclic steady state, feed temperature: 80 °C.

during the feed step. All the feed columns are operated with the same linear velocity as listed in Table 4. At the start we have one column feeding. Once breakthrough occurs, a new column starts feeding and the saturated column starts regenerating. Since the regeneration time is less than feed time, with two columns the regenerated column would sit idle until the feeding column is saturated. The number of columns should be large enough that at any given time we do not have idle columns. The feasible number of columns such that no column is idle is found from Eq. (4). For example, at cyclic steady state, we might have 14 columns feeding and two columns regenerating simultaneously. When one column becomes saturated, it immediately starts regenerating and a regenerated column starts feeding.

$$\text{Feasible Column} = \left\lceil \frac{\text{Feed Time}}{\text{Regeneration Time} + \text{Cool Time}} \right\rceil \quad (4)$$

3.2. Results for single adsorption columns in parallel

Although the adsorber was retrofitted to the RO/IEX network, for presentation purposes the adsorber design and results are decoupled from those of RO/IEX.

The produced water from IGF has a TDS of 7500 ppm. The primary hydrocarbons present are; BTEX (1500 μg/L), NPD (720 μg/L) and PAH (85 μg/L). Using a solubility check [15], it was determined that the produced water from IGF unit requires pretreatment before being sent to the RO. Hence, the produced water from IGF is sent to the adsorber packed with activated carbon. The breakthrough curves at the end of the feed step at cyclic steady state are shown in Fig. 3. Note, the ordinate in Fig. 3 is in logarithmic scale. The x-coordinate represents time at cyclic steady state. As BTEX compounds are less adsorbed than PAH, BTEX breakthrough occurs earlier than PAH breakthrough. The NPD compounds are intermediate between BTEX and PAH, and hence their breakthrough occurs before PAH but after BTEX. Operating times are listed in Table 5. The BTEX, NPD, and PAH removal efficiencies were close to 99.95%.

Table 5
Adsorption column (ADS) specifications.

Parameter	Single column		Multiple columns	
Feed temperature	45 °C	80 °C	45 °C	80 °C
Number of feed columns	14	16	28	32
Number of regenerating columns	2	2	4	4
Column length (m)	16.6	15.1	16.6	15.1
Column shell thickness (mm)	10	10	7	7
Column diameter (m)	3.5	3.5	2	2
Bed depth (m)	1	1	0.3	0.3
Expanded depth (m)	1.43	1.43	0.429	0.429
Feed time (min)	220	175	90	70
Regeneration time (min)	13	9.5	7.5	5.5
Cool time (min)	2.5	2.5	1.5	1.5

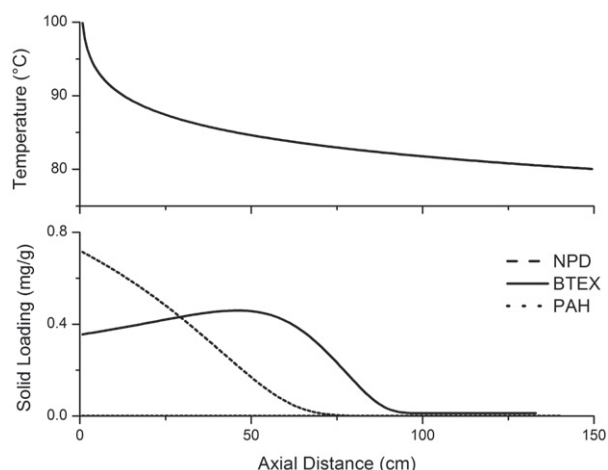


Fig. 4. Solid loading of BTEX, NPD and PAH at the end of regeneration/cooling step at cyclic steady state, feed temperature = cooling temperature: 80 °C.

The exit concentration of PAH slightly increases and then decreases (small hump as noticed in Fig. 3). The maximum concentration of this hump is much less than the feed concentration of PAH. Because the concentrations of BTEX and NPD are much higher than the concentration of PAH (the ratio of BTEX and NPD concentration to PAH concentration is $\mathcal{O}(10^2)$) and the isotherms are competitive, some of the PAH is desorbed by BTEX and NPD. But as the Langmuir isotherm parameter $[K_{PAH} = K_{\infty,PAH} \times \exp(\frac{A_{PAH}}{RT})]$ of PAH (0.036 L/mg) is higher than that of BTEX (0.013 L/mg) and NPD (0.022 L/mg), the desorption of PAH by BTEX and NPD is minimal.

If the produced water at 80 °C from the IGF is cooled and then sent to the adsorber, the adsorption behavior changes. The breakthrough of BTEX, NPD and PAH occurs later since at lower temperatures, adsorption is higher. However, there is a decrease in mass transfer coefficient at lower temperatures which slightly alters the breakthrough curves.

The regenerant to the adsorber is at 160 °C and 6 bar. When the regenerant is pumped in the column counterflow to the feed, the effluent is at feed concentration until the thermal wave breaks through. This effluent is depressurized and recycled back to the column as feed for the next cycle [13]. The column is not completely regenerated, and a heel of BTEX and NPD is left. A cooling step (Stream 2) is included to prevent flashing of water in the column when the column is depressurized. When Stream 2 is pumped counterflow to the feed, the temperature in the column drops. In order to minimize the use of Stream 2, a temperature heel is left such that the maximum temperature in the column is less than the boiling temperature of water at 1 bar (99.6 °C). The temperature profile and the concentration of different hydrocarbons (in the bed) at the end of regeneration and cooling step at cyclic steady state is illustrated in

Fig. 4. Feed enters at the top of the bed (Axial distance $z=0$) and exits at the bottom (Axial distance $z=150$) while the regenerant and cooling fluid enter at $z=150$ and exit at $z=0$. At the end of regeneration and cooling, the column is not completely regenerated and a heel of concentrated BTEX and NPD is left at the top of the bed. This helps minimize the use of regenerant and cooling water. The heel shown in Fig. 4 might be expected to cause BTEX and NPD to exit during the feed step. However, after the low temperature feed enters the column, the equilibrium shifts and both BTEX and NPD are adsorbed on the activated carbon.

3.3. Two columns in series

Use of multiple columns in series has several advantages which necessitates its evaluation as an alternative to adsorption in single column. With two columns in series, the biggest advantages are reduction in total adsorbent compared to a single column and producing a more concentrated waste [17]. The reduction in total adsorbent and the amount of waste leads to potential economic benefits, especially when the waste disposal costs are high. The potential drawbacks are as follows [17]:

- Increase in total number of columns and a potential increase in capital cost.
- May be more difficult in operation and control as switching times are faster due to shorter duration of operation in each cycle.

With downward flow during feed, two columns feeding in series were operated such that the top column is near saturation while making sure that breakthrough of hydrocarbons has not happened in the bottom column. The bed depths were adjusted so that these conditions were met and the waste was concentrated.

At low bed depths (<0.3 m), the top column is saturated but breakthrough of hydrocarbons occurs in the bottom column because the length of the mass transfer zone is greater than bed depth and breakthrough time is less than feed time. At higher bed depths (>0.3 m), the breakthrough of hydrocarbons does not occur from the bottom bed, but the top bed is not saturated. A bed depth of 0.3 m is found to be optimum since breakthrough of hydrocarbons does not occur from the bottom bed and the top bed is near saturation [15].

The operation at two consecutive cycles for two columns feeding in series is shown in Fig. 5. The first cycle ends when Bed 1 is almost saturated; breakthrough hasn't happened in Bed 2 and Bed 3 is regenerated (Fig. 5 (a)). In the next cycle, feed is sent to Bed 2 and the effluent from Bed 2 goes to Bed 3. Bed 1 is regenerated by the time Bed 2 is almost saturated and breakthrough has not happened in Bed 3 (Fig. 5 (b)). The adsorption column specifications are listed in Table 5.

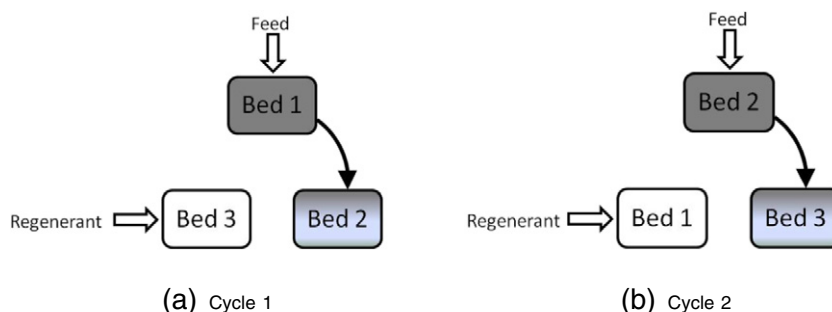


Fig. 5. Cyclic operation for two beds feeding in series.

3.4. Results for two columns in series

The breakthrough curves at the end of the feed step at cyclic steady state for a bed depth of 0.3 m are shown in Fig. 6. Note, the ordinate in Fig. 6 is in logarithmic scale. The abscissa is the time at cyclic steady state. BTEX breakthrough occurs before NPD and PAH. The column concentration and temperature profile at the end of regeneration and cooling step at cyclic steady state are illustrated in Fig. 7. Similar to Fig. 4, a temperature heel is left in Fig. 7, such that the maximum temperature in the column is less than the boiling temperature of water at 1 bar (99.6 °C) in order to minimize the use of coolant.

The effluent profile from the regenerated adsorber column is shown in Fig. 8. The first part of the effluent is at the feed concentration and after cooling is recycled back to the adsorber for the next feed cycle. The remaining effluent is cooled and then sent to a phase separator where the hydrocarbons are separated from water. The water is then sent for re-injection. Alternatively, it can be sent back to the IGF, with a small purge stream taken off to prevent buildup of impurities. Note: this waste stream is not mixed with the brine coming from the RO cascade since the disposal strategies are different for these streams.

4. Evaluation of heating methodologies

In order to elevate the temperature of the discharge water from the adsorber (after the feed step), two methods can be employed. Both methods; direct injection of steam from high pressure boilers and indirect heating by heat exchangers were evaluated.

4.1. Direct injection of steam

In the current process, high pressure steam (7 bar, 165 °C) from the boiler was used to elevate the temperature of a fraction of discharge from the adsorber. Prior to heating by steam injection, the discharge stream from the adsorber was pressurized to 6 bar. Steam at higher pressure is used in order to prevent any backflow. The final temperature desired is $T_{final} = 160$ °C. The amount of steam required was calculated as

$$\dot{m}_{Steam}[\lambda + c_{pw}(T_{Steam} - T_{final})] = \dot{m}_{Water,in}c_{pw}(T_{final} - T_{in}) - \dot{Q}_{Feed,Cool} \quad (5a)$$

c_{pw} is the specific heat capacity of liquid water (kJ/kg K), λ is the latent heat of vaporization (kJ/kg) while $\dot{m}_{Water,in}$ represents the mass flowrate of water leaving the adsorber that is used for regeneration and \dot{m}_{Steam} (kg/hr) is the required mass flowrate of steam. $\dot{Q}_{Feed,Cool}$ is the heat released when the water from IGF is cooled before sending it to the adsorber. This heat is used to reheat the discharge from the adsorber (feed step) before pumping it back as regenerant. If

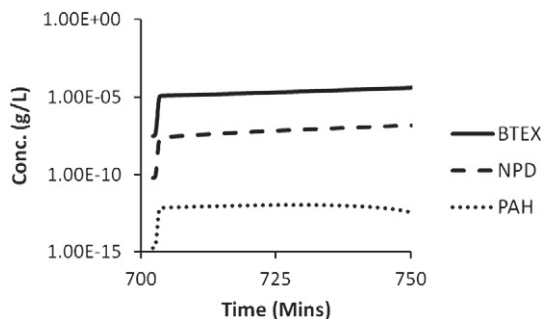


Fig. 6. Breakthrough curves of BTEX, NPD and PAH for the bottom column at cyclic steady state. Two columns in series, feed temperature: 80 °C.

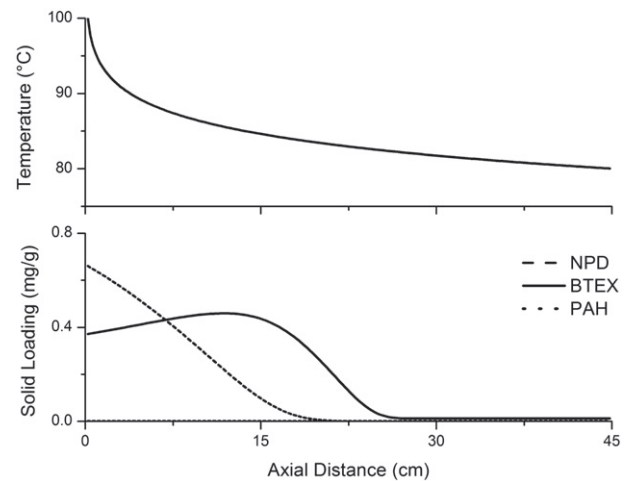


Fig. 7. Solid loading of BTEX, NPD and PAH for the bottom column at the end of regeneration/cooling step at cyclic steady state. Two columns in series, feed temperature = cooling temperature: 80 °C.

the produced water from IGF is not cooled, then $\dot{Q}_{Feed,Cool} = 0$. If x fraction of discharge from the adsorber is used for regeneration,

$$\dot{m}_{Water,in} = \dot{Q}_{Feed,ADS} \times \rho_{water} \times x \quad (5b)$$

where $\dot{Q}_{Feed,ADS}$ is the feed flowrate to the adsorber. The steam completely condenses and the total flowrate of water going as regenerant is

$$\dot{m}_{Steam} + \dot{m}_{Water,in} = \dot{Q}_{Reg} \times \rho_{water} \quad (5c)$$

If \dot{Q}_{Cool} is the volumetric flowrate of the cooling water pumped in the adsorber for a duration of t_{Cool} and if t_{Reg} is the duration of the regeneration step, then the amount of water leaving the adsorber and going to the RO/IEX system is

$$\dot{Q}_{Feed,RO/IEX} = \frac{\dot{Q}_{Feed,ADS}t_{feed} - \dot{Q}_{Reg}t_{Reg} - \dot{Q}_{Cool}t_{Cool}}{t_{Feed}} \quad (5d)$$

A drawback of heating by direct injection of steam is that make up water must be added to the boiler because water is continuously consumed. For medium pressure boilers (50 ≤ P ≤ 300 psi) the feed to boiler must have TDS ≤ 3500 ppm with maximum alkalinity of 700 ppm and with maximum hardness ≤ 15 ppm [32]. Hence, a part of the product water from the RO mixed with the discharge from IEX (from the feed step) was used as feed to the boiler. A mass balance

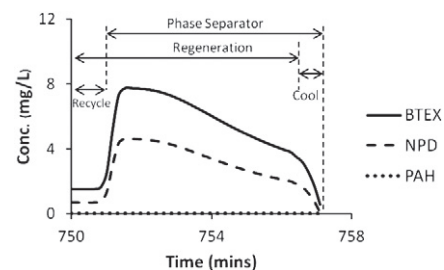


Fig. 8. Effluent profile of BTEX, NPD and PAH from the top column during regeneration/cooling step at cyclic steady state. Two columns in series

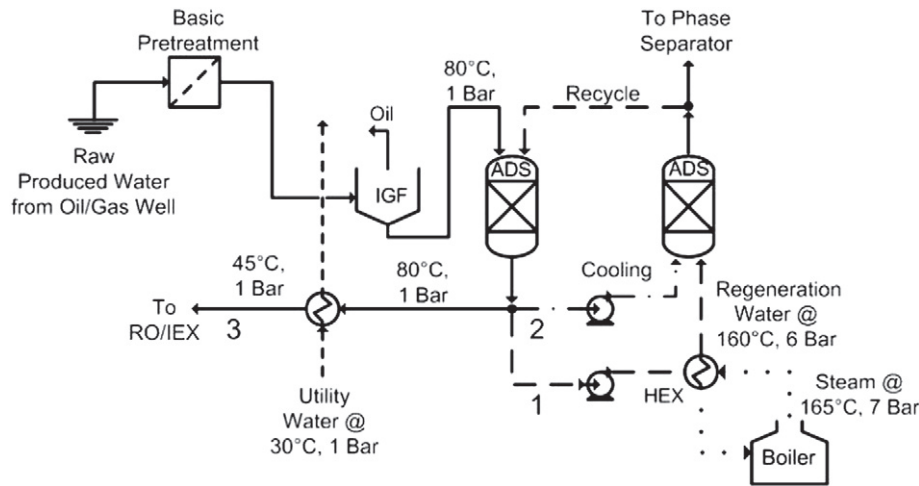


Fig. 10. Process with hot feed (80 °C) to adsorber and heating with HEX.

thickness based on the design stress and the internal diameter is used [35]. The cost of granular activated carbon ($cc_{actcarbon}$) for water treatment is US\$ 85/ft³ [36]. The column thickness is computed from Eq. (7) and found to be 10 mm. As illustrated in Fig. 11, the total cost of adsorption ($cc_{ADS} + cc_{actcarbon}$) decreases with increase in number of columns (ignoring the cost of end fittings). The costs have been updated to December 2012.

Shell and tube multipass heat exchangers with U-tubes are used in the proposed process. Most published purchase-cost data are correlated in terms of heat exchange surface area (usually based on the outside surface area of the tubes) for a base case design, with correction factors only for pressure and materials for the shell and tubes [34]. In some cases, corrections for tube length are given. However, for the purpose of this work, tube length corrections have not been taken into account. The base cost for a shell and tube exchanger is given by [34]

$$C_B = \exp\{11.147 - 0.9186[\ln(A)] + 0.0979[\ln(A)]^2\} \quad (9a)$$

where A is the surface area in square feet. The purchase cost is determined by [34]

$$cc_{HEX} = F_P F_M C_B \quad (9b)$$

where F_M is a material factor for various combinations of tube and shell materials and is given as a function of surface area A in square feet

$$F_M = a + \left(\frac{A}{100}\right)^b \quad (9c)$$

For carbon steel shell and tubes, $a = 0$ and $b = 0$. The pressure factor, F_P , is based on the shell side pressure, P , in psig and is given by [34]

$$F_P = 0.9803 + 0.018 \left(\frac{P}{100}\right) + 0.0017 \left(\frac{P}{100}\right)^2 \quad (100 < P < 2000) \quad (9d)$$

The entire process is designed to handle a total feed of 250 Mgpd. A capital recovery factor (CRF) of 15% was used in order to convert total capital cost into an annual operating cost. To account for the brine from the IEX, a high brine disposal cost (BDC) of US\$ 6.29/m³ [37], a low cost of US\$ 0.29/m³ [38] and an average of high and low costs were used. To account for the waste from the ADS, a high waste disposal cost (WDC) of US\$ 25.29/m³ [39,40], a low cost of US\$ 5.16/m³ [39,40] and an average of high and low costs were used. The brine from IEX and the waste from the adsorber columns are not mixed. The total disposal cost is calculated as

$$TDC = BDC \times Q_{Brine,IEX} + WDC \times Q_{Waste,ADS} \quad (10a)$$

where $Q_{Brine,IEX}$ and $Q_{Waste,ADS}$ represent the volume of brine from IEX and waste from adsorber sent to their respective disposal units. In order to facilitate economic analysis, an average of the brine disposal and waste disposal cost per unit volume (DC) is considered.

$$DC = \frac{BDC \times Q_{Brine,IEX} + WDC \times Q_{Waste,ADS}}{Q_{Brine,IEX} + Q_{Waste,ADS}} \quad (10b)$$

In order to find the disposal cost where change in the optimal process takes place, a quick estimate is done. The tipping points are defined as the points where the optimum shifts from two adsorbers

Table 6
Utility requirements, heat exchanger area and feed flowrates.

Heating method	Adsorber feed temperature	Columns in series	$Q_{Feed,ADS}$ (Mgpd)	Steam (Mlbs/d)	HEX area (m ²)	$Q_{Feed,RO/IEX}$ (Mgpd)	Utility water (Mgpd)
Steam	45 °C	1	250	47.4	28130	222	460.3
		2	250	31.9	28384	224	414.8
Injection	80 °C	1	250	31.9	28384	224	414.8
		2	250	16.4	28638	226	369.3
HEX	45 °C	1	250	58.0	34283	218	465.5
		2	250	37.8	34092	220	409.5
	80 °C	1	250	37.8	34092	220	409.5
		2	250	17.6	33902	222	352.5

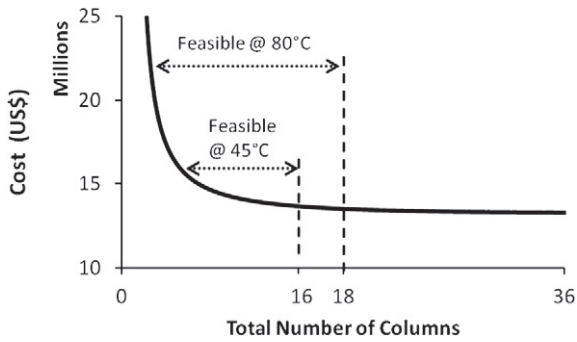


Fig. 11. Feasible number of columns to prevent idle time.

in series to a single adsorber, and, from IEX pretreatment to intermediate IEX. For a rough estimate, it was assumed that the adsorber and the RO/IEX system can be decoupled and are independent. At the tipping point for adsorber, the money saved by reduction in amount of waste from the adsorber by using columns in series equals the increase in capital cost. Similarly, at the tipping point for RO/IEX configuration, the money saved by reduction in amount of brine equals the increased capital and operating cost (excluding brine disposal). The disposal costs at the tipping points act as decision variables. If the tipping point lies in between the high and the low disposal costs ($WDC_{Low} < WDC_{Tipping} < WDC_{High}$ and $BDC_{Low} < BDC_{Tipping} < BDC_{High}$) then the optimal processes for the high and low disposal costs are different. However, if the tipping point lies either below the low disposal cost or above the high disposal cost, then the optimal process is the same for the entire range of disposal costs considered.

$$WDC_{Tipping} = CRF \times \frac{\text{Savings in ADS Column Cost}}{\text{Reduction in Waste (gal)}} \quad (10c)$$

And similarly

$$BDC_{Tipping} = \left(\frac{CRF \times \text{Savings in RO/IEX Capital Cost}}{\text{Reduction in Brine (gal)}} \right) + \left(\frac{\text{Savings in RO/IEX Operating Cost (excluding Brine Disposal)}}{\text{Reduction in Brine (gal)}} \right) \quad (10d)$$

The overall recovery of the entire process ($\theta_{Overall}$) based on fresh feed is computed as shown in the equation below, where $Q_{RO/IEX}$ and $\theta_{RO/IEX}$ are the feed and the effective recovery of the RO/IEX process (including bypass), Q_{Boiler} is the amount of pure product water sent to boiler as make up water, and, Q_{ADS} is the feed sent to the adsorber.

$$\theta_{Overall} = \frac{Q_{RO/IEX} \theta_{RO/IEX} - Q_{Boiler}}{Q_{ADS}} \quad (10e)$$

6. Integrated process results

The overall process results are presented in this section. Detailed results of the RO/IEX system have been presented elsewhere [15].

The overall recovery and the cost of product water are summarized in Tables 7 and 8 for three brine and waste disposal costs and for the same product water concentration (≈ 400 ppm).

The economic impact of the different alternatives evaluated in this work (listed in Section 2) are sequentially analyzed below.

6.1. Adsorber feed temperature

Feed temperatures of 45 °C and 80 °C were systematically evaluated (Figs. 10 and 11). At 45 °C, adsorption is stronger which makes the solute wave move slower and hence increases the amount of feed water processed. At low feed temperatures, the regenerant stream has to be heated through a greater temperature difference. At high feed temperatures (80 °C), adsorption is weaker which makes the solute wave move faster and thereby reduces the amount of feed processed. At high feed temperatures the regenerant stream has to be heated through a smaller temperature difference. The cost analyses in Tables 7 and 8 consistently show a lower cost for the 80 °C feed temperature, but all of the differences are less than 10% and most are less than 5% of the 80 °C cost. Thus, although the higher temperature feed is probably more economical, the analysis is not accurate enough to prove this.

6.2. Adsorber column configuration

A single adsorber column was compared with two adsorber columns feeding in series. A single adsorber column uses higher quantities of adsorbent but fewer columns. Two adsorber columns feeding in series reduces the amount of adsorbent but increases the number of columns. As the adsorbent is activated carbon, the cost of the adsorbent is less than the cost of the columns (Section 5). The predominant capital cost is the column.

Operation with two adsorber columns feeding in series (Fig. 12) generates a waste stream which is more concentrated and of less volume [15]. Hence at high disposal costs, it is beneficial to have a two columns in series configuration, since a reduction in the volume of waste pays for the excess capital cost. However, at low disposal costs, it is not beneficial to have a two columns in series configuration, since a reduction in the volume of waste is not sufficient to pay for the increased capital. In this scenario, it is better to use a single column configuration. The results in Tables 7 and 8 agree with the qualitative analysis, but the differences in costs are quite small (often 1% to 2%), which is less than the error in the cost comparison. If a more expensive adsorbent is used two columns in series could be less expensive than a single column at low disposal costs.

6.3. Heating methodology

Heating by direct injection of steam (Figs. 1 and 12) and by heat exchangers (HEX, Figs. 10 and 11) were evaluated in this work. Equal amount of waste is generated from the adsorber column when either direct injection of steam or HEX is used to heat the regenerant stream (Stream 1). When direct injection of steam is used, the net amount of water going to the RO/IEX system is higher (Stream 3), which results in an increased capital cost (of RO/IEX), and an increase in the amount of product water from RO. However, part of the product

Table 7
Cost summary: Single adsorber column.

Configuration		ADS-PRO-IEX-SRO				ADS-IEX-RO			
Heat input source		Direct heat		Indirect heat		Direct heat		Indirect heat	
Feed temperature (°C)		45	80	45	80	45	80	45	80
Overall recovery (%)	83.54	84.88	84.12	85.64	82.64	84.08	83.34	84.14	
Cost(\$/1000 gal)									
	High DC	4.20	4.03	4.08	3.94	5.15	4.89	4.91	4.85
	Avg. DC	4.08	3.98	3.93	3.86	4.13	4.02	3.99	3.88
	Low DC	3.16	3.15	3.10	3.08	3.65	3.61	3.61	3.56

Table 9

System configuration and RO specifications with bypass.

Configuration	Effective feed (Mgpd)	RO stages	Operating pressure (MPa)	Pressure vessels	Modules	RO/IEX recovery (%)	Product conc. (ppm)
Intermediate IEX	215	2,1	(5.6,6.0), 7.6	(4200, 1700), 750	(3,4), 3	96.5	399
	217	2,1	(5.6,6.0), 7.6	(4200, 1700), 800	(3,4), 3	96.5	399
	219	2,1	(5.6,6.0), 7.6	(4200, 1700), 850	(3,4), 4	96.5	401
	221	2,1	(5.6,6.0), 7.6	(4250, 1700), 850	(4,4), 4	96.5	402
	223	2,1	(5.8,6.2), 7.8	(4250, 1800), 850	(4,4), 4	96.5	403
IEX Pretreatment	218	2	6.0, 7.6	4250, 2645	3,4	96.0	398
	220	2	6.0, 7.8	4250, 2700	4,4	96.0	399
	222	2	6.4, 7.8	4300, 2700	4,4	96.0	401
	224	2	6.4, 7.8	4340, 2750	4,4	96.0	402
	226	2	6.4, 8.0	4400, 2800	4,4	96.1	403

- For high and average disposal costs, a process with two adsorbers in series appears to be the optimal solution while for low disposal costs the single adsorber process appears optimal. These effects are smaller than the probable error.
- The PRO-IEX-SRO configuration is the optimal RO/IEX configuration for all disposal costs. This result is definitive.

7. Discussion

Liquid water at high pressure and temperature was used to regenerate the adsorption column. This method was chosen over traditional methods such as solvent extraction or steam regeneration due to inherent drawbacks in the traditional methods. At large scales of operation, solvent extraction requires large amounts of solvent and an additional solvent recovery step which adds to the cost of the overall process. In many applications the downstream solvent recovery step (often distillation or a chemical stripping step) is more expensive than the actual extraction step. This method is only used when one wants to recover a valuable adsorbate [41].

Steam can be directly used for regeneration. The operation involves the following steps in sequential order; adsorption, drain, steam regeneration and purge (condense gas), cool, and refill. The drain step is to remove the liquid from the interparticle spaces and the intraparticle pores as this would reduce the amount of steam needed for regeneration. However, the drain step cannot completely drain the liquid in the intraparticle pores and is very difficult to model. Any liquid remaining in the pores after drainage will have to be evaporated by steam which will require more energy [17,41]. When the exiting vapor is condensed, a hydrocarbon and a contaminated water layer that needs to be reprocessed are obtained. Steam regeneration is typically practiced at 1.0 atm with a 100 °C steam temperature to avoid the decrease in latent heat at higher temperatures and pressures. If needed, higher temperatures and pressures can be employed for desorption of heavy components. The energy requirements for steam regeneration can be estimated and then be compared to regeneration with pressurized hot water [15].

Table 10

Intermediate IEX column specifications.

Parameter	Intermediate IEX				
Feed flowrate (Mgpd)	15.1	15.2	15.3	15.5	15.6
Number of feed columns	8	8	8	8	8
Number of regenerating columns	2	2	2	2	2
Column length (m)	6.5	6.5	6.5	6.5	6.5
Column shell thickness (mm)	7	7	7	7	7
Column diameter (m)	3.5	3.5	3.5	3.5	3.5
Bed depth (m)	1.0	1.0	1.0	1.0	1.0
Expanded depth (m)	1.43	1.43	1.43	1.43	1.43
Feed time (min)	65	65	65	65	65
Regeneration time (min)	4.5	4.5	4.5	4.5	4.5
Wash time (min)	1.5	1.5	1.5	1.5	1.5

When pressurized hot water is used, there is no change of phase. As latent heat is considerably larger than sensible heat, $\text{EnergyRequirement}_{\text{Water}} < \text{EnergyRequirement}_{\text{Steam}}$. In light of these disadvantages, liquid water at high pressure and temperature was chosen as regenerator.

For this exploratory research, the lack of experimental data required several assumptions to obtain results. The assumptions are analyzed and possible areas of improvement are outlined in this section.

One of the key assumptions is that during the feed and cooling cycles the hydrocarbons are in solution. The hydrocarbons could also be present as drops in certain cases. Better solubility data, particularly at high temperatures are needed. If oil occurs in drops, an extra source term must be included in the model mass balance equations.

The multicomponent Langmuir isotherm was used to describe the equilibrium adsorption behavior. Although this isotherm is commonly used for modeling, few multicomponent systems actually follow this isotherm and there are additional inherent drawbacks [42]. The ideal adsorbed solution theory (IAST) is a better equilibrium isotherm for multicomponent mixtures [43,44]. However, IAST requires extensive computing resulting in long simulation times [45].

Because data are not available, several key assumptions were made in the regeneration step. Either one assumes that at 160 °C the oil is soluble in water or the following assumptions are required:

- During regeneration oil is not trapped within the pores of activated carbon and oil droplets do not adhere to the surface of activated carbon.
- The time of droplet coalescence is much longer than the residence time in the column.

Even if not all of the oil dissolves, increased solubility makes the other assumptions more likely. Experimental verification of the adsorber regeneration step is required. In order to translate this process into an operating plant, several lab-scale and pilot plant studies must be conducted to obtain the following:

- High temperature solubility data.
- Either multicomponent equilibrium data or column adsorption runs at high temperature and pressure.
- If supersaturation occurs, data on formation/dissolution of droplets/emulsions during regeneration.
- Data on rate of carbon attrition and poisoning of the carbon (both must be very low).
- Very good chemical analysis of the waste stream from the adsorber, so that an appropriate treating system can be identified.

The possible outcomes for variations in raw produced water concentration (relative composition) and temperature are listed as follows:

1. Feed concentration: Depending on the relative amounts of hydrocarbons in the raw produced water the position of ADS in the process configuration varies. For the situation when hydrocarbons are present in negligible quantities such that the produced water can be directly sent to RO, the ADS either is not required, or can be used as an intermediate step between RO cascades, for e.g., PRO-ADS-IEX-SRO.
2. Feed temperature: The ADS can be operated at the same temperature as the discharge from the IGF unit. At higher temperatures ($> 80^{\circ}\text{C}$) it must be ensured that the breakthrough time from the ADS is long enough to process sufficient amounts of feed water in order to make the process self sustaining. The IEX too can be operated at higher temperatures such that the temperature of operation is less than the melting temperature of the polymeric sorbent. However care must be taken that the feed to the RO is never above 45°C as it can potentially irreversibly damage the RO membrane.

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