

Boiler-Feed and Process Water Reclamation from Biotreated Palm Oil Mill Effluent (BPOME): A Developmental Review

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Increased water shortages and new environmental policies and regulations have stimulated significant development in reuse programs in the past 20 years.¹ Reclaimed water has been recognized as a vital and drought-proof water source to ensure economic and agricultural activities. According to the conclusions of various water reuse surveys, the best water reuse projects, in terms of economic viability and public acceptance, are those that substitute reclaimed water in lieu of potable water for use in industrial, irrigation, environmental restoration, cleaning and toilet flushing. The main benefits of using reclaimed water in these situations are conservation of water resources and pollution reduction.¹ Low Pressure Membranes (LPMs) such as Microfiltration (MF) and Ultrafiltration (UF) integrated with adsorption system could be a viable option for separation of contaminants in wastewater for reuse as boiler-feed or process water in industry. This article technically discusses the main constituents of concern in boiler-feed and process water requirements and finally suggests potentially efficient and low-energy-low-cost hybridized LPM /adsorption treatment facilities to achieve this paradigm shift towards new water sources.

Key words:

Boiler-feed/process water, water/wastewater, reclamation and reuse, adsorption, membrane separation

Introduction

Population growth, urbanization, and industrialization contribute to water shortages by perpetually pushing up demand. Interestingly, these same factors increase water pollution, lead to higher costs in potable water treatment, and pose adverse health effects. It has been projected that by 2020, more than half the total population of Asia, Africa, and Latin America will be living in cities, and all of these cities will require additional water sources.¹ Another projection further stresses that by 2025, 35 % of the world's population at large will live in countries affected by water stress/scarcity.² With this worldwide depletion of conventional water, the need for non-conventional sources for water production is increasing. Wastewater is of course one of the best-known non-conventional sources. Industrial reuse has increased tremendously since the early '90s for most of the same reasons urban reuse has gained popularity, including water shortages and increased populations, particularly in drought

areas, and legislation regarding water conservation and environmental compliance. To meet this increased demand, some countries have increased the availability of reclaimed water to industries, and have thus alleviated the demand stress on fresh water supplies.

The palm oil industry is the leading agro-industry in Malaysia and it requires a large quantity of water for its operation, leading to the discharge of considerable amounts of wastewater called palm oil mill effluent (POME) after a few steps but insufficient biological treatments. This creates a severe threat to the environment and conventional sources of fresh water. Besides, many humid regions are becoming arid or semi-arid regions and water has become a limiting factor forcing water resource planners to look continually for additional sources of water to supplement the limited resources available to their region. In such situations, source substitution appears to be the most suitable alternative to satisfy less restrictive uses, thus allowing high quality waters to be used for domestic supply based on the United Nations Economic and Social Council policy that says "*no higher quality water, unless there is a surplus of it, should be used for a purpose*

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that can tolerate a lower grade".³ Water scarcity problems have been increasingly severe around the world and so great attention is being paid to the reclamation and reuse of wastewater from municipalities and industrial plants. The fact remains that the stringency placed on drinking water regulations is becoming higher than that of industrial or agricultural use, hence low quality waters such as wastewaters should be considered as alternative sources for less restrictive uses. This measure will prevent those wastewaters from being discharged into water environments, as well as reduce the demand stress on fresh water resources. It is therefore pertinent to efficiently define the target use of reclaimed water.

The membrane separation process is a technology that has become increasingly popular for wastewater reuse applications, since it could play a key role in removing the complex components of dissolved and particulate matter contaminants in wastewater. A wide range of membrane processes from porous MF to dense reverse osmosis (RO) filtration has been employed for advanced wastewater treatment. MF and UF have always been considered as pre-treatment steps to nanofiltration (NF) and/or RO in effective wastewater reclamation processes for sustainable high water quality. Due to this exceptional efficiency of membrane technology, many water-intensive industrial sectors such as the textile, food, pulp and paper industries are always interested in using membranes for wastewater reclamation for reuse. However, the industries are somewhat reluctant to adopt the highly energy-intensive RO and nanofiltration (NF) processes. Furthermore, NF/RO membranes have a lot more serious issues related to membrane fouling caused by colloids deposition, inorganic precipitation, and biological growth leading mostly to irreversible fouling. To overcome these drawbacks, complicated pre-treatment and operational techniques are needed.

From the foregoing, single or hybrid microfiltration (MF) and ultrafiltration (UF) processes appear to be more attractive for wastewater treatment because they promise high fluxes at relatively low pressures. Although, membrane fouling problems are still being researched, UF and MF alone or in combination with coagulation, adsorption, micelle formation, and complexation were used for the recovery of valuable materials through selective separation of colloidal particles, macromolecules, or metals besides wastewater reclamation.^{4–11} Nevertheless, extensive attempts to find more MF/UF applications for the purification of various wastewater effluents are still needed.

Being motivated by the above-mentioned treatment technologies for the potential abatement of freshwater shortages, especially from the huge con-

sumption of fresh water by the industry, this paper discusses the benefits/potentials of Biotreated Palm Oil Mill Effluent (BPOME) in terms of industrial water requirements, wastewater production and the significance of main constituents of concern in boiler-feed and process water for low pressure boilers, as well as suggests a viable process design of hybrid adsorption-membrane system for the reclamation of BPOME as a low-cost and effective method of producing boiler-feed and process water for the industry.

Industrial wastewater reclamation and reuse

Amongst others, industrial activities worldwide account for about a quarter of all water consumption and there is hardly any industry that does not use large amounts of water for its processes. During the early days of water reclamation for industrial reuse, there were no regulatory policies governing water quality; all the existing regulations then were focused on the reuse for potable purpose. However, as water reuse spread across the industries, the regulations that began to spring up for specific industrial reuse are now becoming more and more stringent.¹

Water standards related to industrial activities may vary in a wide range of parameters and limit values. Appropriate combination/integration of advanced technologies allows the production of customized reclaimed water according to the standards of the potential industrial reuse activities.

Reuse as boiler-feed water

A boiler is an equipment for steam generation and it consists of two principal parts namely the furnace, which usually provides heat through the burning of a fuel, and the boiler itself which is a device responsible for the heat changes of water into steam. The steam is then recirculated out of the boiler for use in various processes in heating applications. Proper treatment of boiler feed water is an important part of operating and maintaining a boiler system and any contaminant of concern should be controlled or removed through external or internal treatments in order to protect the boiler from corrosion or other unwanted adverse effects.

While many works have been reported on water reclamation especially from POME,^{12–16} there are very few and scope-limiting reports on BPOME polishing for reuse. Those few works only reported the membrane separation of BPOME without adsorption integration, and there are little or no reports on how to specifically tailor its treatment towards a specific industrial reuse using the recom-

mended water quality standards as benchmarks for target reuse purposes. It is technically obvious that if this has to be done efficiently, the specific parameters important to each reuse purpose have to be keenly considered and monitored during the treatment processes. Recommended values for those specific parameters have been issued by a number of authorities (Table 1), such as American Water Works Association (AWWA), British Standards Institution (BSI), American Society of Mechanical Engineers (ASME), Electric Power Research Institute (EPRI), Central Electricity Generating Board (CEGB), US Environmental Protection Agency (USEPA), etc. The chemistry of the wastewater as well as prime parameters necessary for the intended reuse purpose dictates the treatment process design.

Feed-water purity is a matter concerning both impurity quantity and nature, and this requirements vary widely. Some impurities such as hardness, iron and silica are of more concern, for example, than sodium salts. The chemistry of any wastewater to be treated for boiler-feed water reuse has to be tai-

lored towards that which has no corrosion propensity. The sought quality/purity will however depend on the pressure at which the boiler is operated. The general principle is that the higher the pressure, the higher the quality of water required. A low-pressure fire-tube boiler can usually tolerate high feed-water hardness with proper treatment while virtually all impurities must be removed from water used in some modern, high-pressure boilers.

In boiler water practice, the three main aims that must always be borne in mind are to minimize corrosion, scale deposition, and carryover of boiler water solutes in steam. The first two aims should be considered right from the boiler-feed treatment before the boiler operations starts, so that their effects will be minimal during the operation. The third aim is out of this paper's scope since it could only be effectively achieved after a period of boiler operation. Although with increasing pressure, a high degree of purity becomes more essential for the feed-water to lessen the risks of carryover and scaling, and to provide a basis for effective anti-corrosion measures. Industrial low-pressure boilers, particularly the steam generating type, such as those utilized in the palm oil industries, some food processing industries, etc., will perform more satisfactorily with softened water.

Table 1 – Boiler-feed water standards for low – moderate pressure boilers

	STANDARDS			
	ASME	BSS	AWWA	USEPA
Total Hardness (mg L ⁻¹)	0.3	10 (80*)	0 – 10	350
Ambient pH	7.5/10.0	8.5/9.5 (8*)	9.5	7.0 – 10.0
Total Alkalinity (mg L ⁻¹)	–	700	700	350
Silica as SiO ₂ (mg L ⁻¹)	< 0.05	(40*)	100 – 133	30
Total Iron as Fe (mg L ⁻¹)	< 0.10	NA	–	1.0
TDS (mg L ⁻¹)	–	3000	3000 – 5000	700
Turbidity (NTU)	–	5 – 10 (20*)	–	–
Mn (mg L ⁻¹)	–	–	–	0.3
H ₂ S (mg L ⁻¹)	–	0 (5*)	–	As Received
TSS (mg L ⁻¹)	–	1500 – 100	300 – 600	10
COD (mg L ⁻¹)	–	–	–	5

ASME refers to American Society of Mechanical Engineers Industrial Boiler Sub-Committee; 1986. – Adapted by Shreir et al (1994)

BSS refers to British Standard Specification 2468; 1978 – Adapted by Shreir et al (1994); Corbitt (1999)

AWWA refers to American Water Works Association; 1971 – Adapted by Corbitt (1999)

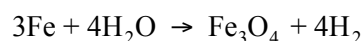
USEPA refers to U.S. Environmental Protection Agency; 1980b – Adapted by USEPA (1992), and Metcalf & Eddy et al (2007)

NA: Not Applicable; ND: Not Detectable

(*) refers to tolerance levels based on BSS recommended values (Corbitt, 1999)

Conceptualizing boiler corrosion

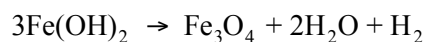
The prime reaction in boiler corrosion is the formation of magnetite and hydrogen from iron and water:¹⁷



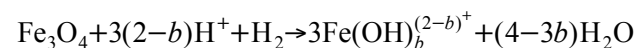
This is considered to proceed in two stages, i.e. the initial production of ferrous hydroxide:



and then it is subjected to subsequent decomposition to magnetite and hydrogen (the Schikorr reaction):



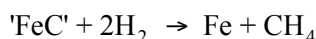
This can be generalized into the reaction:



This is an indication that, given an adequate concentration of hydrogen, magnetite can be re-dissolved. In the absence of sufficient hydrogen, the solubility of magnetite is markedly temperature dependent, which provides an explanation for some of the problems in high-temperature circuits.¹⁷

For high-pressure boilers, there is usually a relationship between corrosion rates and iron solubility and pH. pH ranges around the neutral point usu-

ally corresponds to the target ranges for *good boiler-water* practice, indicating modest corrosion rates, and deviations from neutrality in either direction lead to increasingly severe attack, though the rates are relatively faster in acidic than in alkaline conditions. Specifically, in approximately neutral solutions, solid state diffusion is dominant, while at higher or lower pH values, iron becomes increasingly soluble and the corrosion rate increases with the kinetics approaching linearity, ultimately being limited by the rate of diffusion of iron species through the pores in the oxide layer. In more concentrated solutions, e.g. pH values below 3 or above 12, the oxide becomes detached from the metal and therefore un-protective.¹⁷ By this mechanism, hydrogen generated by the corrosion process attacks iron carbide in the steel:



By this, the material's strength becomes low and at high corrosion rates, the methane produced cannot diffuse out of the steel and high internal stresses develop which blow the steel apart.¹⁷ Besides, the intercrystalline cracking of boiler metal, called *caustic embrittlement*, is associated with (a) localized stresses that have strained the metal beyond its elastic limit, and (b) a high concentration of caustic soda in the absence of an adequate concentration of sulphate in the feed water. Failure generally occurs at riveted seams and similar places of confined extent that have been subjected to stresses of high intensity.¹⁸

To mitigate potential corrosion problems, the principle is to make known the significance of some very important parameters along with their recommended standards before expanding into the overall parameters that contribute to corrosion. It is generally recommended that boilers in the range 13 – 40 bar be operated with softened water. For boilers operating at 2, 20 and 40 bar, it is usually recommended that sodium phosphate content be maintained within 50 – 100 mg L⁻¹ range and sodium sulphite within the range of 30 – 70 mg L⁻¹ depending on the constituents of the water/wastewater being treated. Total alkalinity content of 1200 mg L⁻¹ is deemed acceptable for boilers operating at 2 bar while boilers at 20 and 40 bar should be supplied with feed as lower as 700 mg L⁻¹ in alkalinity. However, the corresponding caustic alkalinity of 350, 300 and 200 mg L⁻¹ for 2, 20 and 40 bar must be maintained. Experts in boilers and boiler-feed operations usually find a correlation between the caustic alkalinity and silica contents of boiler-feed water, but the rule of thumb is that the silica content should be 40 % of the caustic alkalinity.¹⁷

Total hardness should also be as low as undetectable when it comes to the boiler issue, though

the principle may be compromised in process water reuse (as discussed in subsequent sub-section) based on the products from the industry process. However, a balanced position must be reached when those typical compromises are inevitable in order to safeguard the metals involved in the process from being attacked by corrosion or embrittlement and eventually failing. If there is no imposing compromise on hardness, then it is usually recommended that total hardness be as low as possible, if not totally undetectable.¹⁷ The maximum allowable dissolved solids content for boilers operating at 2, 20 and 40 bar should be maintained at 3500, 3000 and 2000 mg L⁻¹ respectively.¹⁷ The stringency intensifies as the boiler pressure builds up.

In the palm oil industry, as well as most food processing industries that need to generate steam, boilers are normally operated at typically low pressures of around 3 bar¹⁹ and temperatures as high as 130 °C, hence an appropriate boiler-feed water assay is required. Prior to the treatment, however, the constituents of BPOME need to be known. Table 2 shows the typical constituents of BPOME.

However, it must be noted that the level of these constituents may slightly vary from one palm oil industry to another. Seasonal changes may also affect the constituents' level.

Table 2 – Characterization of Biotreated Palm Oil Mill Effluent (BPOME)

Constituents	As-Collected Sample
Turbidity (NTU)	1050
Total Dissolved Solids (TDS) (mg L ⁻¹)	1207
Conductivity (mS cm ⁻¹)	2.04
Salinity (‰)	1.0
Chemical Oxygen Demand (COD) (mg L ⁻¹)	1730
Suspended Solids (SS) (mg L ⁻¹)	761
Ca Hardness (mg L ⁻¹ CaCO ₃)	240
Mg Hardness (mg L ⁻¹ CaCO ₃)	1800
Silica as SiO ₂ (mg L ⁻¹)	73
H ₂ S (mg L ⁻¹)	0.6
Iron as Fe (mg L ⁻¹)	< 0.02
Manganese as Mn (mg L ⁻¹)	2.14
P. Alkalinity (mg L ⁻¹ CaCO ₃)	180
T. Alkalinity (mg L ⁻¹ CaCO ₃)	2000
Hydroxide Alkalinity (mg L ⁻¹ CaCO ₃)	0
Carbonate Alkalinity (mg L ⁻¹ CaCO ₃)	380
Bicarbonate Alkalinity (mg L ⁻¹ CaCO ₃)	1770
pH	8.65

Main constituents of concern for boiler-feed water

Boiler experts affirm that problems ranging from scale deposition to overheating to corrosion are commonly experienced by boilers, especially the steam-generating types. It is recommended that the boiler-feed water be of suitable quality before being fed into the boiler and the quality required is dependent on boiler operating pressure, design, heat transfer rates, and steam use. Although, heating boilers in which almost 100 percent of the steam returns as condensate generally require protection only from corrosion, but regular checking is necessary to ensure against development of excessive accumulation of dissolved solids, which might lead to scale formation.¹⁸

The primary reaction in the corrosion of boiler steel is the formation of ferrous hydroxide and its subsequent decomposition to magnetite and hydrogen – the Schikorr reaction. This is demonstrated by the products of corrosion encountered throughout the whole range of boiler operating pressures, but the details are influenced by other factors, i.e. water quality, heat flux, and boiler operating conditions.¹⁷ Therefore, the main constituents/contaminants of concern to be controlled and monitored in boiler-feed water in order to alleviate corrosion, scale deposition and carryovers are highlighted below.^{1,20–22}

pH

pH is the basic measure of acidity or hydrogen ion concentration defined as $\text{pH} = \log [1/\text{H}^+]$. Pure water has a pH of 7.0. It is used to determine both the deposition and corrosion tendency of water. Too low or high pH can cause damage to metal directly. Calcium carbonate scale formation is affected greatly by the pH. Any system with a high dissolved solids and pH above 8.2 has a potential for calcium carbonate scaling. In many applications, pH is maintained above 7.0 to prevent corrosion problems. However, if pH control is not closely maintained, system pH can approach the range where calcium carbonate scaling occurs. A pH in the range of 6.0–7.0 can reduce corrosion to acceptable levels and eliminate any potential for calcium carbonate scaling. pH is also a controlling factor in many chemical reactions that occur in boiler water and some of these processes require specific pH levels for the most efficient chemical reaction or adsorption.^{17,18}

On the other hand, high pH does not always indicate the possibility of a high grade of scale deposit. Factually, calcium carbonate (CaCO_3) scale deposition rapidly decreases at pH above approximately 10.2, as there exists the formation of calcium hydroxide (Ca(OH)_2) which ultimately becomes

the predominant of the calcium species. The Ca(OH)_2 is much more soluble than the CaCO_3 and consequently not likely to be responsible for scale depositing. In some plants, acid is fed for decreasing the pH, based on the assumption that high pH is always undesirable. This acid addition usually lowers the pH into the 7.5–10 range, and this can consequently result in the deposition of CaCO_3 . Therefore, a critical compromise must always be made during pH control.^{17,18,20,21}

Total hardness

Source: In most water, nearly all hardness is due to calcium and magnesium. All the metallic cations besides the alkaline earths also cause hardness.

Significance: As the temperature and concentrations of the scale-forming salts (e.g. carbonates, bicarbonates, sulphates of calcium, magnesium and sodium – predominantly magnesium and calcium) in water increases, their solubility decreases and thus precipitates, leading to formation of scales.²² The bicarbonates of calcium and magnesium which break down to carbonates when the water is boiled results in what is known as the temporary hardness, while permanent hardness is due to calcium and magnesium sulphates, chlorides and nitrates, and these salts cannot be removed by boiling. These make hardness one of the chief sources of scale in heat exchange equipment such as boilers. Waters with hardness of 60 mg L^{-1} are termed soft; 61 to 120 mg/L moderately hard; 121 to 180 mg L^{-1} hard; and above 180 mg L^{-1} very hard.²¹

Silica (SiO_2)

Source: Dissolved from almost all rocks and soils, usually in small amounts (5 to 30 mg L^{-1}), but often more from acidic volcanic rocks.²¹

Significance:

1. Hard scales, similar to those usually caused by permanent hardness, resulting from silica (such as amorphous silica and magnesium silicate) are primarily found in lower pressure boilers and pipes. Silica-based deposits become more serious as silica increases and hydrate alkalinity decreases. Silica scales in high pressure must be totally avoided due to its removal difficulty.

2. Silica, in addition to forming boiler deposits, can vaporize from the boiler and be carried with the saturated steam as silicic acid, the silica further precipitates on the metal surfaces causing deposits. Silica vaporization can cause insoluble deposits on critical parts of equipment such as the turbine blades.

Iron

Sources:

Iron enters the boiler originally from two main sources:

1. Naturally occurring iron present in the raw water (usually dissolved from all rocks and soils).²¹
2. Corrosion of the mild steel components making up the boiler system, including pre-boiler and post-boiler.

Significance:

Both soluble and insoluble iron (particulate and colloidal) can be present in boiler-feed water and boiler water. Iron combines with phosphates and hydroxides to form scale. Boiler water iron will deposit on the steam-generating surfaces of the boiler and cause under-deposit corrosion and overheating problems, this insulating property of the deposit impairs heat transfer and causes the temperature of the boiler metal to increase.

Manganese (Mn)

Source: Dissolved from some rocks and soils. Not as common as iron. Large quantities often associated with high iron content and acid waters.

Significance: Same objectionable features as iron. Manganese causes dark-brown or black stain. Iron and manganese should not exceed 0.3 mg L⁻¹ for taste and aesthetic reasons. Larger quantities cause unpleasant taste and favour growth of iron bacteria.²¹

Calcium (Ca) and magnesium (Mg)

Source: Dissolved from almost all soils and rocks but especially from limestone, dolomite, and gypsiferous sediments. Mg is present in large quantities in seawater.

Significance: Cause most of the hardness and scale-forming properties of water.²¹

Dissolved solids

Source: It includes all material dissolved in the water and chiefly originates from mineral constituents dissolved from rocks and soils.²¹

Significance: This is a measure of total amount of dissolved matter. In water, the conductivity, or ability to carry an electric current, is directly related to the quantity and mobility of the dissolved solids. Conductivity is widely used to monitor cooling system blowdown and for strong fouling conditions (found in some industrial cooling towers, boilers, waste treatment plants, etc.), and where an electrode conductivity probe must be used. Dissolved solids can remain safely dissolved in the water and do not

deposit on the steel surfaces as long as they are kept within the limits that are appropriate for the boiler conditions.²⁰ Very high ranges of dissolved solids can cause process interference and foaming in boilers.

Alkalinity

Source: For most water systems, it is also important to recognize the sources of alkalinity and maintain its proper control. Alkalinity is formed in the presence of certain anions in solution. Some organic materials may also produce alkalinity.

Significance: Alkalinity is an indicator of the relative amounts of carbonate (CO₃²⁻), bicarbonate (HCO₃⁻), and hydroxide (OH⁻) ions and some anions (acid ligands). These can cause foaming, carry-over of solids with steam and boiler steel embrittlement. They can result in strong scale formations (such as magnesium carbonate, magnesium hydroxide, calcium carbonate, etc.) thereby leading to tube overheating and structural failure. A high methyl orange alkalinity (Total alkalinity) in the boiler-feed usually result in carbon dioxide content of the steam. Under the influence of heat in the boiler, bicarbonate will break down producing carbonate and liberating free carbon dioxide with the steam. The carbonate formed undergoes further decomposition, producing hydroxide and liberating additional carbon dioxide with the steam with a direct proportionality to the feedwater alkalinity.^{48,49} Carbon dioxide is usually responsible for the corrosion of the water, steam and condensate/return lines in boilers.⁴⁹

Although, it is desirable to obtain a boiler-feed that is sufficiently low in alkalinity to prevent carry-over conditions, the alkalinity should also be sufficiently high to protect the boiler metal against acidic corrosion.^{48,49} This presents the necessity of maintaining a balance between too high and too low alkalinity while simultaneously taking into consideration other factors involved in a specific boiler operation.

Hydrogen sulfide (H₂S)

Source: Natural or thermal degradation/decomposition of organic materials and/or sulphate reduction by sulphate reducing bacteria (SRB) known as *desulfovibrio*.²³

Significance: Causes objectionable odour when in concentration above 1 mg L⁻¹ and taste when in excess of 0.05 mg L⁻¹. Presence may limit water usefulness in the food and beverage industry.²¹

As mentioned earlier, many regulatory bodies have recommended water quality standards for low, moderate, high and super-critical pressure boiler-feed. The scope of this discussion is focused on low-pressure boilers, hence the summary for the required standards from ASME, AWWA, BSS and USEPA are shown in Table 1.

Reuse as process water

In order to be able to conserve our fresh water resources, appropriate quality and quantity as well as point-of-use availability need to be balanced. Reuse of water in some industries, such as food industries, electronic industries etc., has been limited for many years due to strict regulations. We now have a situation whereby current guidelines and regulations regarding use and reuse of water in those fanatically water-stringent industries, especially the food industry, has acknowledged the use of other water qualities than that of potable water.^{26,27} Despite this, it is unfortunate that research and development have been somewhat hampered in this area due to the fear of lowering hygienic standards.

However, when looking into the use of alternative water qualities for a specific process, it is essential to know the basic requirements of the water quality in a specific process, which may be used without affecting the product in its finished form. This indicates that there is no generalized industrial water quality standard. For this, a number of regulatory bodies such as USEPA, AWWA, ASME, FAO, WHO, etc. have established water quality standards for different industrial scopes ranging from water-stringent industries like the food, chemical or electronic to low-prolific water tolerant industries like the pulp and paper, tanneries and oil refineries. These regulations are being reviewed continuously based on each industry's needs in the midst of emerging water shortage. In 2007, the Spanish authorities instituted new regulation of regenerated wastewater that introduced specific standards for industrial reuse of regenerated wastewaters.²⁸

Industrial use of water encompasses quantity and quality requirements that range from the use of large volume of low-quality water for cleaning applications to the use of high-quality process water for manufacturing or boiler-feed water (when required) as previously highlighted.

More importantly, any industrial reuse feasibility of reclaimed water must include an early stage on the definition of the needs of the potential users in order to determine the specific utility, parameters of concern, and suitable treatment process design. Depending on the industry under consideration, water quality differs as products coming out from different industries differ. Water qualities may be stringent as well as low-graded, and this depends on the main water constituents of concern in each industry. Therefore, the reuse purpose must be defined so as to be aware of the important parameters to be controlled during the water treatment. For this, some of the regulatory bodies have recommended water quality standards for every industry. As for the food

industry, the principal water quality parameters are of sensory, chemical and microbiological nature.

The quality tolerances for process waters vary with the manufacturing process and with the quality of the goods to be produced.¹⁸ While some food industries, such as bakeries, may require relatively hard water for their processes, many opt for clear, colourless, tasteless, relatively soft, iron-, manganese-, organic- and hydrogen sulphide-free water with approved bacteriological quality. Examples are fine chemical industries, some food industries such as bottled beverages, canned goods, process milk, ice, packed meat and edible oils. Pulp and paper mills, tanneries, oil refineries, and steel mills do not commonly need water of high grade or drinking water quality, but they certainly have other paramount requirements necessary for their processes.

The New England Water Works Association as adapted by,¹⁸ BSS stringent parameters to assess the quality of process waters generally for food industries such as palm oil mill industry and others are necessary. The parameters and their maximum allowable concentrations are; Turbidity (10 NTU), Iron as Fe (0.2 mg L⁻¹) and Manganese as Mn (0.2 mg L⁻¹). Other parameters such as colour, taste/ odour, H₂S, Hardness as CaCO₃, Alkalinity as CaCO₃, and total solids should be maintained as low as possible/required depending on the tolerance of the industry's processes and products.

The constituents are all very significant and their recommended values should be known in order to be able to efficiently design appropriate treatment process and tailor the final effluent towards a specific reuse. Beside the effects on the industrial products, they can also aggravate corrosion of vessels and reactors if required monitoring is not done before reuse. For instance, reduction in hardness, silica, and alumina alleviate scale formation. Also, maintenance of a high ratio of sulphate to carbonate controls caustic embrittlement, while the elimination of oxygen, reduction of bicarbonate ions, and relatively increased pH can suppress corrosion.

In the industry, various purification processes are used for the preparation of process water, starting from the utilization of simple water filtration devices to complex coagulation, adsorption and precipitation systems, even including ion exchangers. Increasing attention has been focused on the application of membrane processes in numerous water treatment procedures.

With the type and levels of pollutants in the BPOME as characterized in our laboratory, a degree of its purification through hybridizing membrane processes with adsorption or coagulation processes is a viable method of producing a process water grade suitable for reuse in any food processing industry using the recommended standards as benchmarks.

Capability of integrated adsorption-membrane process for BPOME treatment

Different combinations of technologies are being utilized in wastewater reclamation and they must be selected based on wastewater chemistry and effluent quality to be achieved. Stringent control of water quality and operational reliability and sustainability are the drivers for choice in technology. Wastewaters are commonly treated by activated sludge (AS) systems that use suspended microorganisms to remove organics and nutrients, and large sedimentation tanks to separate the solid and liquid fractions. This level of treatment could only efficiently produce effluent of low profile water, such as that which fulfils the requirement of cooling water in the industry, or irrigation water where the food crops are consumed after cooking.

A type of membrane technology called membrane bioreactor (MBR) is now replacing the AS system based on the combination of a suspended biomass reactor and separation step on porous membrane filtration (Fig. 1).

Membrane technology has been proved to stand up to scrutiny in terms of sustainable development criteria. Water and wastewater treatment membranes

are typically classified in order of decreasing pore size as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Low Pressure Membrane (LPM) processes of microfiltration (MF) and ultrafiltration (UF) have found favorite use in the removal of turbidity, bacteria, parasites, pathogenic microorganisms, suspended solids, particles, and organic matter. MF and UF are used mostly as pre-treatments for wastewater desalination using High Pressure Membrane (HPM) processes of nanofiltration (NF) and reverse osmosis (RO) when targeting very high quality effluent. As a general rule, MF is suitable for the efficient removal of turbidity and suspended solids, including larger micro-organisms like protozoa and bacteria. Although, MF's effluent does not present standard characteristics for reuse in most industrial applications, it is usually utilized as a pre-treatment stage for UF process in most industrial reuse. UF is required for the removal of viruses and organic macromolecules down to a size of around 20 nm.²⁹ Furthermore, UF is increasingly used as a complete or intermediate water purification technique depending on the level of quality required for a particular reuse program. UF is very efficient in removing different parameters, e.g., a noticeable elimination of suspended solids and turbidity has been achieved; metals like Fe, Zn, Al, Cr, Cu and Mn, and microbial contamination have reportedly been eliminated significantly or totally; Fecal coliforms, total coliforms, fecal streptococcus, protozoan cysts (*Giardia* and *Cryptosporidium*), and even viruses are totally removed by UF; reduction in the concentration of organic matter occurs when the organic fraction is mostly in the suspended form. No clear effect is produced on inorganic salts abatement, and consequently conductivity values are not affected by UF.²⁸ UF produces permeate of uniform and higher quality despite any changes in the influent/raw water quality. MF and UF are usually considered for the design of membrane bioreactor (MBR). MBRs are systems in which biological degradation of wastewater has been integrated with membrane system. MBR can be designed to be side-stream or submerged. Air will be passed from beneath the tank to serve as source of mixing (in case of chemical additions for adsorption or coagulation), aeration or membrane scouring. Fig. 1 depicts MBR configurations.

The configuration could also be made with just simple integration of membrane (MF or UF) with adsorption/coagulation unit without the need for aeration, especially when considering wastewaters already treated biologically (biotreated). However, mechanical mixers must be provided for efficient mixing of adsorbents, coagulants or flocculants being applied as pre-treatment prior to the membrane

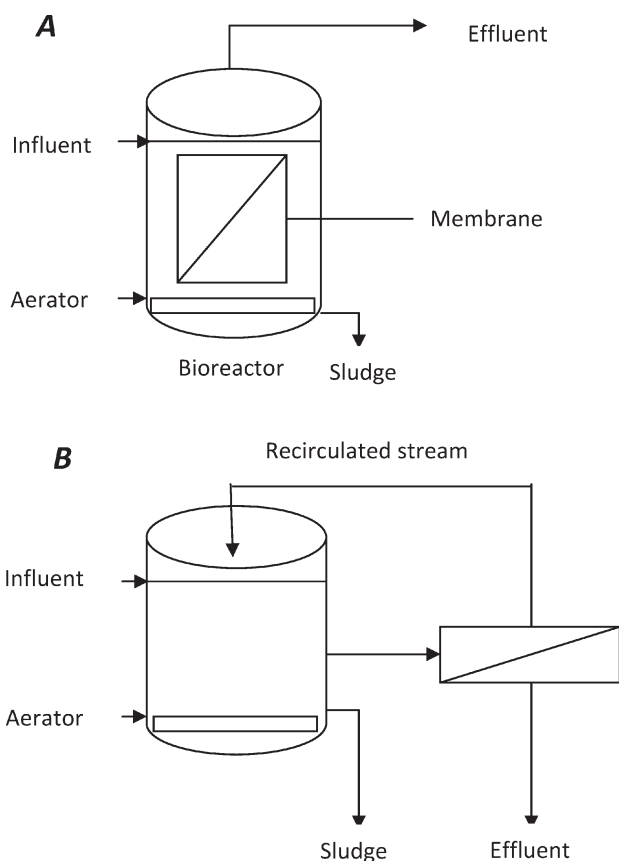


Fig. 1 – Configurations of an MBR: (A) Submerged; (B) Side-stream

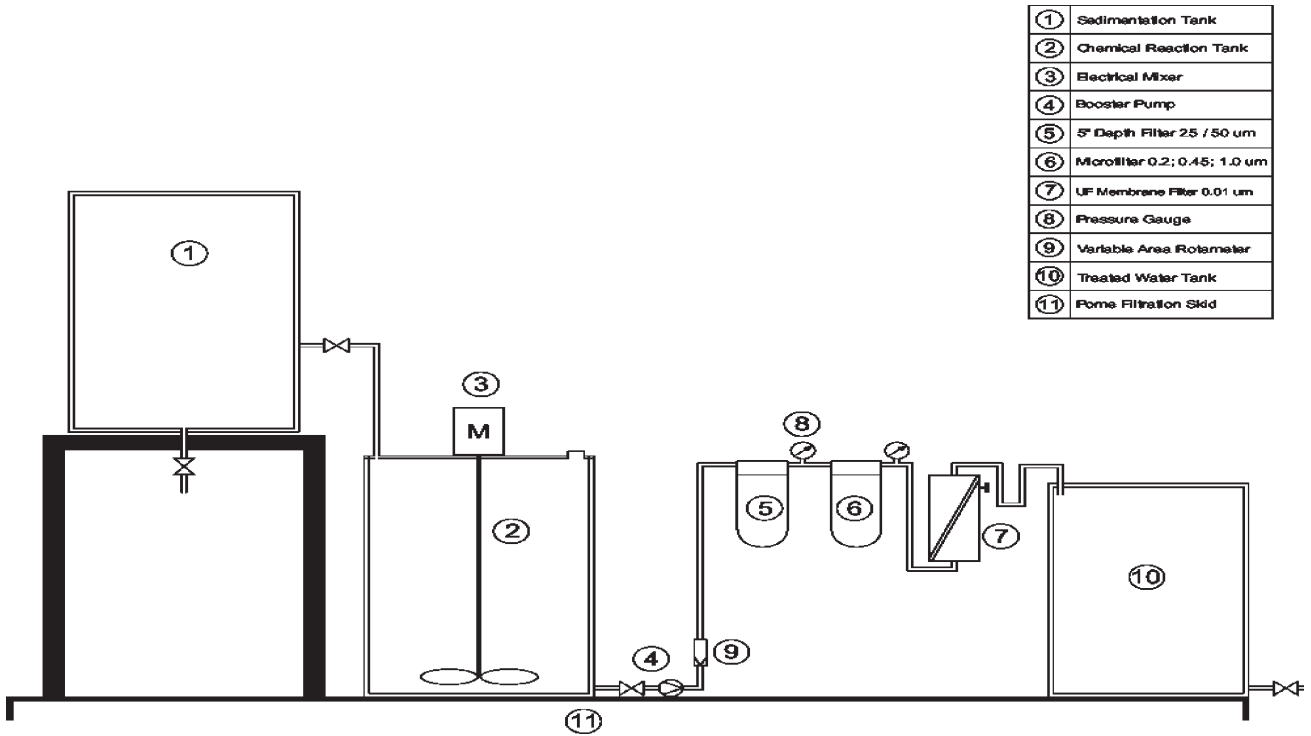


Fig. 2 – Schematics of a newly developed hybrid Adsorption-Membrane System

filtration. Fig. 2 depicts an example of such configurations with specific designs depending on the influent chemistry and target effluent. As for this particular configuration in Fig. 2, unit (5) indicates a water filter with pore size of 25 μm to serve as screen for the incoming feed from the chemical reaction (adsorption or coagulation) tank and reduces much of the membrane fouling that would have occurred due to the activated carbon particles. This will remove larger particles before the feed proceeds to unit (6) which is microfiltration membrane with pore sizes of 0.1, 0.2, 0.45 or 1 μm, and unit (7) indicates an ultrafiltration membrane with a molecular weight cut-off (MWCO) of 10,000, 20,000 or 50,000.

For water reuse, contaminants requiring treatment over and above what is provided solely by conventional biological treatment include suspended solids, microbial contaminants, nutrients, trace dissolved contaminants (e.g. endocrine disruptors), and in certain cases, dissolved salts. UF membranes, especially when combined with biological or chemical treatment for the removal of dissolved contaminants, can easily handle all the contaminants mentioned above.⁸ The presence of pathogenic microorganisms in wastewater has been the main barrier to its reuse acceptance. However, with membrane filtration, all micro-organic contents of the wastewater could be efficiently controlled since the sizes of bacteria are within 0.2 – 10 μm, parasite spores, cysts, oocysts, and eggs are larger than bacteria and range in size from 1 μm to above 60 μm.

The eggs and larvae, which range in size from about 10 μm to above 100 μm, are resistant to environmental stresses and may survive usual wastewater disinfection procedures.¹ Viruses occur in various shapes and range in size from 0.01 to 0.3 μm. Protozoan pathogens such as cryptosporidium oocysts are 4 to 6 μm in diameter, while Giardia cysts range between 8 to 16 μm in diameter. Also, commonly used disinfectants such as chlorine are not as effective for inactivating the protozoa as compared to bacteria and viruses. In light of this, membrane filtration appears to be the best measure in removing these microorganisms. UF and MF membranes have a minimum solute rejection size of 0.01 and 0.1 μm respectively.³⁰ MF is a partial removal barrier for pathogenic microorganisms, while UF is an absolute barrier to microorganisms, including viruses.³¹ Thus, water filtered through these membranes is pathogenically and microbiologically safe.³² The driving factors (increasing demand, decreasing quality water source, and more stringent regulatory standards) influence membrane use in treating wastewaters prior to reuse. Improvements in the technology which uses size exclusion principle in separating suspended solids, colloidal particles,³⁰ dissolved compounds, and pathogens from reclaimed water have recently inspired greater confidence in the use of reclaimed water for purposes which include both direct and indirect human contact.¹ Fig. 3 illustrates the size exclusion criteria of all the pressure driven membranes.

Cut-offs of different liquid filtration techniques								
Micrometer logarithmic scaled	0,001	0,01	0,1	1	10	100	1000	
Angstroms logarithmic scaled	1	10	100	1000	10 ⁴	10 ⁵	10 ⁶	10 ⁷
Molecular weight (Dextran in kD)	0,5	50	7.000					
Size ratio of substances to be separated	Solved salts		Viruses		Bacteria		Yeast	
	Atomic radius		Pyrogens		Red blood cells		Pollen	
	Sugar		Albumin (66 kD)		Human hair		Sand	
Separating process	Reverse osmosis		Ultra filtration		Micro filtration		Particle filtration	
	Nano filtration							

Fig. 3 – Pressure-driven membranes and the size exclusion criteria³⁰

Nonetheless, some soluble matters such as natural or synthetic dissolved organics, taste and odour, trihalomethanes, etc. cannot be fully controlled by MF and UF systems only. Adsorption using adsorbents such as powdered activated carbons (PAC), zeolites, activated alumina, chitosan etc. could therefore be used as a pre-treatment step for membrane process. Membrane filtration could therefore be a polishing step for an adsorption stage in wastewater treatment. The adsorption stage will cause a decrease in the load of organic matter against the membrane,³³ thus reducing fouling with improved sustainable flux. Adsorption process is a promising approach for the removal of organics in water and wastewater. Previous studies show that adsorption is efficient for the removal of a wide range of organic compounds, and different types of adsorbents have been produced to remove organic contents from water and industrial effluent. Although there has been no report on the use of adsorbents on complete BPOME, we have done related works, such as the use of commercial adsorbent (granular activated carbon) to remove COD, colour and turbidity with combination of other treatment processes with efficiency of 89 %, 97.9 % and 98.9 %, respectively

from BPOME.³⁴ Aber and Sheydaei³⁵ removed COD from dying factory with efficiency 75 % using activated carbon fibre. Kutty *et al.*³⁶ used microwave incinerated rice husk ash (MIRHA) to adsorb anaerobically treated POME and found 41 % of COD removal.

There have been many reports^{29, 33, 37–43} on the successful removal of dissolved organics such as phenol, as well as dissolved inorganics such as metallic salts like zinc, copper, etc. from wastewaters other than BPOME with the use of various adsorbents based on the selection of proper operating conditions of pH, contact time, adsorbent dose, mixing strength, and probably the reaction temperature.⁴⁴

Many researchers^{4–11} have investigated the wastewater purification and reclamation potentials of the low-pressure membranes (LPM) and have concluded that the LPMs can efficiently reclaim water from wastewaters, especially when adsorption systems are integrated, depending on the target use of the reclaimed water. Moreover, research continues in our research centre towards establishing optimized operating conditions for wastewater reclamation (from BPOME and other industrial waste-

waters with similar or lower characteristics) for several industrial reuse purposes, and besides our preliminary findings on BPOME adsorption treatment³⁴ based on pH control, colour, turbidity, COD, TSS and TDS removal efficacies using granular activated carbon, adsorption using powdered activated carbons from coconut shells in the removal of TSS, TDS and COD show optimistic headway for further researches. However, our current focus is mainly on the exploitation of the empty fruit bunches (a waste from the palm oil industry) for the production of powdered activated carbon (PAC). This PAC could be used as sorbent in place of the commercial types thereby bringing about a cost-effective operation.

The benefit of this proposed concept of membrane-adsorption process being a part of POME treatment cannot be over-emphasized considering the case study of Malaysia, which is one of the top palm oil producers in the world. Malaysia has a total number of 434 active palm oil mills and each of these mills utilizes a huge amount of water for the production of Crude palm oil (CPO). For instance, each of these active palm oil mills produced 16.99 million tons of CPO from a precursor of 88.74 million tons of Fresh Fruit Bunch (FFB), thereby generating 49.85 million tons of Palm Oil Mill Effluent (POME). Likewise in the year 2012, 55.22 million tons of POME was generated.^{45, 46} The usual requirement for the production of 1 ton of CPO is 5 – 7.5 tons of water and more than 50 % of the water input is generated as POME,^{12, 37} indicating that in the year 2012 alone, the production of 18,785,030 tons of CPO could have utilized up to 140.93 million tons of fresh water.

According to its current water tariff, the Malaysian Ministry of Energy, Green Technology and Water imposes a charge of RM 1.32 (0.43 USD) per cubic meter (or per ton) of water for industrial supplies.⁴⁷ This implies that an average of RM 190 million (60.4 million USD) would have been spent on water supply by the Malaysian palm oil industry in the year 2012. From the reports showing that 55.22 million tons of POME was generated this year as wastewater, it is philosophized that even only 80 % water reclamation from POME could return at least 44.18 million tons of water for reuse. This will reduce fresh water consumption by 32%, and waterways pollution and demand stress on fresh water sources will be reduced.

From the foregoing, 44.18 million tons of water is a considerable volume, which will go a long way in reducing the demand stress on fresh water resources besides the profits amounting to millions of USD which the palm oil mill industries could save and/or derive from such a recycle and reuse program.

Membrane fouling aspects

The fouling abatement concern is the main membrane problem being considered in water reclamation and reuse. Commonly used approaches are feed pre-treatment to remove/reduce the components with high fouling propensities. The most usual forms of pre-treatment used are sedimentation, pre-filtration, chemical coagulation, adsorption and anion exchange resins. Chemical coagulation has been widely applied as a simple and effective means for the removal of particulates, colloids and high molecular weight organic materials from water/wastewater. However, there are cases where coagulation has had adverse effects on the membrane performance.²⁸ Coagulation may also compromise the permeate constituents in terms of the addition of more chemicals, which may be unwanted in permeate. Anion exchange resin has been used as a means of improving membrane performance in a few reports through the removal of a significant fraction of organic matter from wastewaters.

Several cleaning methods are used to remove the densified gel layer of retained material from the membrane surface. Alkaline solutions followed by hot detergent solutions are indicated for organic polymer colloids and gelatinous materials fouling. Ferrous deposits, typical in water treatments, are usually removed with a citric or hydrochloric wash.

Backflushing is another way of cleaning heavily fouled membranes. During backflushing, a slight overpressure is applied to the permeate side of the membrane forcing from the permeate side to the feed side of the membrane. The flow of solution lifts deposited materials from the surface. Typical backflush pressure is 5 – 15 psi.²⁸ Transmembrane pressure (TMP) adjustment and influent flow rate adjustment can also assist in the mitigation of membrane fouling.

Conclusions and recommendations

1. *No higher quality water, unless there is a surplus of it, should be used for a purpose that can tolerate a lower grade.*³
2. Boiler-feed and process water for industrial reuse appear to be one of the best water reuse projects that could substitute reclaimed water in lieu of potable reuse, in terms of economic viability and public acceptance.
3. The feasibility of recycling BPOME for beneficial reuse such as boiler-feed and process water using hybrid adsorption-membrane system is supported in various previous works on adsorption and membrane filtration concepts.

4. Possible options from which optimum reuse scheme is chosen are review of the technical, public health, environmental, financial and economic criteria associated with wastewater reuse.

5. Recommended water quality standards, such as APHA, USEPA, ASME, AWWA, BSS etc. should be strictly considered as benchmarks during the wastewater treatment for any industrial reuse as boiler-feed or process water. This will assist in effectively defining the target reuse of a wastewater before any reclamation project.

6. The use of LPMs and adsorption processes has proven to be practically efficient and fits into low-cost budgets, which will make it affordable to industries with wastewater discharges to adapt for reclamation purposes.

7. All schemes resulting in effluent discharges should be revisited at the pre-investment study stage with respect to potential reuse of the wastewater. In countries where there is no established national policy on wastewater reclamation and reuse (i.e. no legislation to enforce such policy), a preliminary assessment should be made of the potential for reuse, and a decision obtained on whether the proposed reuse is acceptable to the producers, the users and society at large. By this, the reuse potential would be established through a feasibility study, and detailed studies carried out to determine the least cost solution to collect, treat, and distribute the wastewater (and the sludge from the wastewater treatment process).

8. Researchers should concentrate more on wastewater reclamation and reuse for some other industrial reuse purposes such as boiler-feed for high or supercritical pressure boilers and process water specific and suitable for several productions such as petroleum and petrochemical processing, mining, pulp and paper, chemical, textile industries, etc.

9. The capability of advanced technologies in water reclamation for industrial reuse has been illustrated in this review, and it has been proved to be a potentially effective tool for fresh water conservation and sustainable industrial development under water scarcity conditions.

10. In addition, the selection of the most suitable combination of advanced technologies should be addressed taking into account the final reuse targets.

11. Consumer perception should be changed in making them aware of the true value of water as well as the environmental impacts related to high consumption of fresh water. Restoring confidence in science can only take place by improving communication between the different parties, i.e., scientists, risk managers, media, industry and consumers.²⁷

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