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A novel forward osmosis-nano filtration integrated system for coke-oven wastewater reclamation

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ABSTRACT

A forward osmosis–nanofiltration (FO–NF) integrated new system in flat-sheet cross-flow module was designed to separate reusable water from coke-oven wastewater with reduced concentration polarization and high flux using low energy. Investigations were carried out under different sets of operating conditions of pressure, cross-flow rate, pH of the feed solution and run time for better understanding of the phenomena of concentration polarization and reverse salt diffusion in the new system. A set of polyamide composite membranes were investigated to screen out the best performing ones (NF-2 for forward osmosis and NF-1 for draw solute recovery) for the final experiments. While investigating effects of different draw solutions (DS) on the water flux and rejection of target contaminants, 1.5 M NaCl was found to be the best for forward osmosis. Removal of about 96–98% of cyanide, phenols, NH_4^+ -N and chemical oxygen demand from real coke-oven could be achieved along with pure water flux of 46 L/(m^2h) in FO system under optimized conditions. Downstream nanofiltration module ensured continuous recovery and recycle of 99% of the draw solute while ensuring recovery of reusable water at the rate of 45 L/(m^2h).

1. Introduction

Thousands of tonnes of metallurgical coke are produced on carbonization of coal in coke ovens in the emerging economies of the east to meet the huge demand of steel industry. One of the harmful by-products from coke production process is coke oven wastewater (COWW), which contains highly hazardous contaminants including carcinogenic compounds (Pal and Kumar, 2014). Combating the environmental consequences of COWW discharges is a major challenge to the concerned industries in these countries (Chu et al., 2012). Characterized as a typical refractory industrial wastewater, coking wastewater contains cyanide, thiocyanide, high-strength ammonia, phenolic compounds, heterocyclic nitrogenous compounds and poly-nuclear aromatics compounds (Wei et al., 2012). Such a heavily loaded industrial wastewater discharged without proper treatment to any surface water body like the river or lake or agricultural land is bound to cause severe long term environmental and ecological impacts (Duan et al., 2015).

Extensive research over the last few decades encompassing the broad options of biological treatment such as anoxic-oxic, anaerobic-anoxic-oxic, sequencing batch reactor, fix-bed biofilm reactors, fluidized bed reactors, membrane bioreactor, moving bed biofilm reactors have been carried out (Zhao et al., 2009; Wang et al., 2012; Chon et al., 2013). However, because of the tremendous fluctuation of the influent as well as the inherent instability of the systems, conventional treatments hardly meet the stringent wastewater discharge standards (Kumar and Pal, 2012). Many other methods such as adsorption (Zhang et al., 2010), coagulation (Lai et al., 2007), wet oxidation (Wang et al., 2008) and advanced oxidation (Chu et al., 2012), have been investigated to treat coking wastewater. However, these

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methods are either technically complicated or economically unfavourable, which often make them difficult to be used in practice. Biological treatment plants are highly sensitive and slow and often fail because of presence of toxic contaminants. Adsorption bed gets quickly saturated and is not expected to treat such dirty and complex wastewater on long term basis without the necessity of frequent replacement of adsorbent. Necessity of frequent regeneration/replacement of adsorbent does not make such processes economically attractive. In case of wet air oxidation, salt precipitation and inhibition of ammonia destruction process in the presence of phenol and toxic contaminants often lead to process failure.

In the countries of huge population, surface water contamination from industrial or municipal sewer lines has reached serious dimension necessitating immediate intervention from policy makers for reclamation of water from the waste stream for reuse instead of discharging into the river bodies. In this context, membrane-based technology has been gaining importance because of their inherent potential of producing reusable water from wastewater streams (Jin et al., 2013). Among the pressure-driven membrane based processes, nanofiltration (NF) and reverse osmosis (RO) are capable of achieving high standard of purification. However, RO involves much higher trans-membrane pressure and hence high energy. RO membranes themselves are expensive and require high pressure vessels for housing. Fouling problem is another big hindrance in almost all pressure-driven membrane separations. FO is now an emerging technology that promises high degree of separation of contaminants from water involving low energy consumption, low fouling and high recovery in easy and simple design. The principle of FO desalination lies in transporting water through a semi-permeable membrane by natural osmotic process using a highly concentrated solution (called draw solution or DS) that draws water from the feed solution (Lutchmiah et al., 2014). As an emerging technology, FO has attracted significant interest in seawater/brackish water desalination (Zhao et al., 2012; Phuntsho et al., 2013), liquid food processing (Dova et al., 2007), complex industrial streams such as those from textile industries (Banerjee and De, 2010), oil and gas well fracturing (Fakhru'l-Razi et al., 2009), landfill leachates (Renou et al., 2008), nutrient-rich liquid streams (Holloway et al., 2007), wastewater from activated sludge plants (Cornelissen et al., 2008), wastewater from municipal sources (Kim et al., 2015; Ke et al., 2013) and even nuclear wastewater. However, removal of pollutants from COWW through FO has received very little attention in the backdrop of a major environmental concern. A FO scheme may be considered complete and sustainable when it is made continuous through provision of feed water and DS of constant composition. This can be ensured only by periodic discharge of concentrated cyanide, phenol and NH_4^+ -N rejects for subsequent treatment and addition of fresh feed COWW to feeding tank and economical separation of draw solute for recycle/reuse of permeate water in the same industry.

Attempt has been made to address the issues of concentration polarization through better designs of membranes and draw solutes. Thus Widjojo et al. (2011) used thin film composite polyamide membranes and 2.0 M NaCl DS in FO mode but obtained a flux of only 15 L/(m^2h). Wang et al. (2010) used 2.0 M NaCl DS and with FO membranes embedded with Aquaporin Z obtained a high flux of 145 L/m^2h. But the procedure is extremely complicated and scale up appears to be difficult. Issues of concentration polarization and fouling over a reasonably long operation time have also not been addressed. Use of RO in recovery of draw solute offsets the gain of low energy involvement in the forward osmosis. Thus the major problem of flux decline after a certain time of operation following concentration polarization or reverse salt diffusion (diffusion of the draw solute to the feed solution) still stands in the way of implementation of FO in wastewater purification. Diffusion of draw solute is normally accompanied with back diffusion of feed solute from the active membrane surface to the bulk feed solution. Thus reverse salt diffusion progressively increases the osmotic pressure of the feed solution thereby seriously limiting separation of the desired solute (Boo et al., 2012).

In this investigation, a novel design is made to overcome the major hurdles of FO in the context of removal of contaminants from coking wastewater. The proposed scheme is a complete system comprising a forward osmosis loop in the upstream where water is separated out from waste stream and a downstream loop of flat sheet cross-flow nano filtration membrane module for recovery of draw solute for recycling while producing reusable water. The objectives of this study are to examine whether the proposed design succeeds in reducing concentration polarization and reverse salt diffusion and in enhancing pure water flux while ensuring efficient draw solute recovery involving low energy.

2. Theoretical background

When two aqueous solutions of different concentrations are separated by a membrane permeable to the solvent but impermeable to the solute, transport of water takes place across the membrane from the dilute solution to the concentrated solution even at same temperature, electrical potential and hydrostatic pressure. Such water transport takes place because of difference in chemical potential of water on two sides of the membranes and is known as osmosis and the minimum pressure required to stop such water transport from the dilute solution side to the concentrated solution side is called osmotic pressure and is denoted by $\Delta\pi$. This osmotic pressure differential ($\Delta\pi$) is the driving force in water transport across the membrane in FO whereas hydraulic pressure differential acts as the driving force in RO. In FO, applied pressure ΔP is equal to zero, in RO process $\Delta P \gg \Delta\pi$ and in pressure retarded osmosis (PRO), $\Delta P < \Delta\pi$. Directions of water flow are the same in FO and PRO. In RO the direction of water flow is reversed by applied ΔP where it is in excess of the osmotic pressure differential. Water flux in all these processes can be in general described by as:

$$J_{\text{water}} = A(\alpha\Delta\pi - \Delta P) \quad (1)$$

where, A is water permeability constant of the membrane, α is the reflection coefficient, J_{water} is water flux.

2.1. *Flux calculation of FO process*

Considering the osmotic pressures and mass transfer coefficient on the feed side and DS side, the volumetric flux for a FO system may be computed using following equation:

$$J_{v,cw} = L_w \left[\pi_{DS} \times \exp\left(-\frac{J_{v,cw}}{k_{m,DS}}\right) - \pi_{FS} \times \exp\left(\frac{J_{v,cw}}{k_{m,FS}}\right) \right] \quad (2)$$

$J_{v,cw}$ is the volumetric flux of water, L_w is the water permeability, π_{DS} and π_{FS} are the osmotic pressure on the draw and feed side, respectively whereas $k_{m,DS}$ and $k_{m,FS}$ are denoted as