Use of membrane hybrid processes for phenol recovery/separation from industrial wastewater

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Uso de procesos híbridos de membrana para la recuperación / separación de fenol de aguas residuales industriales
Ús de processos híbrids de membrana per a la recuperació / separació de fenol d'aigües residuals industrials

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SUMMARY

Phenol is a raw material that is used for the manufacture of several products of industrial origin; consequently, an excessive amount of phenolic effluents is obtained, giving rise to a marked problem of pollution, since phenol causes toxic effects in the environment. Therefore, the development of feasible treatment methods has been a key challenge to reduce pollution related to this substance.

Today, hybrid membrane systems contain new and several alternatives that have been developed for the recovery, elimination and degradation of phenol. The objective of this short communication is to provide an overview of the scope of these hybrid systems for their application in the treatment of phenolic effluents.

Keywords: Phenol; membrane; hybrid systems; phenolic wastewater.

RESUMEN

El fenol es una materia prima que se utiliza para fabricar varios productos de origen industrial; en consecuencia, se obtiene una cantidad excesiva de efluentes fenólicos, dando origen a un marcado problema de contaminación, ya que el fenol causa efectos tóxicos en el medio ambiente. Por lo tanto, el desarrollo de métodos factibles de tratamiento ha sido un desafío clave para reducir la contaminación relacionada con esta sustancia.

Hoy en día, los sistemas híbridos de membrana contienen nuevas y varias alternativas que se han desarrollado para la recuperación, eliminación y degradación de fenol. El objetivo de este documento es proporcionar una visión general del alcance que tienen estos sistemas híbridos para su aplicación en el tratamiento de efluentes fenólicos.

Palabras clave: Fenol; recuperación; membranas; efluentes fenólicos; procesos híbridos.

RESUM

El fenol és una matèria primera que s'utilitza per fabricar diversos productes d'origen industrial; en conseqüència, s'obté una quantitat excessiva d'efluents fenòlics, donant origen a un marcat problema de contaminació, ja que el fenol causa efectes tòxics en el medi ambient. Per tant, el desenvolupament de mètodes factibles de tractament ha estat un desafiament clau per reduir la contaminació relacionada amb aquesta substància.

Avui dia, els sistemes híbrids de membrana contenen noves i diverses alternatives que s'han desenvolupat per a la recuperació, eliminació i degradació de fenol. L'objectiu d'aquest document és proporcionar una visió general de l'abast que tenen aquests sistemes híbrids per a la seva aplicació en el tractament d'efluents fenòlics.

Paraules clau: Fenol; recuperació; membranes; efluents fenòlics; processos híbrids.

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INTRODUCTION

For a long time, the pollution by phenol has been a topic of interest into the chemical engineering, health sciences and environment research. Nowadays, it continues to be a matter of concern, since the phenol is utilized in the manufacture of several chemical products. Consequently, a considerable pollution by waste of this substance is localized in an important number of industries and several toxicity problems in water are related to discharge of contaminated effluents.

Because phenol is a benzene derivative, it is a dangerous pollutant, highly toxic, and of difficult degradation. According to the Environmental Protection Agency[1], phenol is considered among chemical substances that have direct effect on the ecosystems and on human health. Due to endocrine disrupting that their exposure or contact produces in the organism, phenol is also found among some of Hazardous Substances of Agency for Toxic Substances and Disease Registry[2].

The phenolic wastewater is originated from manufacturing and refining processes such as production of phenolic resins, pharmaceutical products, herbicides, fiberglass, petrochemicals, coke ovens and coal conversion systems[3]. The phenol concentration range depends on the industrialized products; nonetheless, it generally falls between 100 to 90,000 mg/L[4], which suggests that it is feasible to recover the phenol when it is found in high concentrations, or its degradation or separation when it is required. The decision of recovery or separation depend of various factors. The complexity of the industrial effluents is crucial, because they contain often other substances associated to phenol; thus, a high cost must be paid to recover it. These pollution conditions make also very difficult their treatment to achieve maximum permissible levels (MPL) in water discharge.

Currently, there are several phenol treatment studies which contain degradation techniques and separation operations; among them, it can be found distillation, extraction, adsorption, chemical oxidation, UV oxidation and biological treatment. However, a single operation is not enough to respond to the industrial problem of contamination of water with phenol. Furthermore, some of these methods present low efficiency, high cost, inferior selection and rigorous running conditions which restrict their widespread application[5]. Likewise, a considerable number of these studies have been applied on simple water containing low concentrations of phenol as a single component, while others studies have been utilized to phenol as model molecule to prove treatment methods. Thus, these environments are far removed from the complexity of real industrial effluents and from the standards required for treated water discharges. As a result, research regarding this topic continues increasing in order to achieve the treatment's purpose.

In this research line, membrane technology for phenol treatment has proved to be an innovative, future oriented, economically meaningful, and an environmental protecting technology. Membrane processes, mainly in the range of ultrafiltration (UF), nanolfiltration (NF) and reverse osmosis (RO) are increasingly used as an excellent option to solve phenol removal problems by recovering phenol from water[6-8], which is attributable to their selective recapture capacity to remove high phenol concentrations from industrial effluents. However, membrane fouling has long been known to be the main obstacle to achieve high performance in membrane operations. Thus, currently ongoing studies are focused on membrane hybrid processes (MHP). These systems can be defined as technologies where one or more membrane processes are coupled with a conventional unit process (MHP-CUP). CUP are considered pretreatment procedures, for instance coagulation-UF, distillation-NF, or extraction-UF.

HMP are also considered as a sequential membrane processes (MHP-SMP) as UF-NF or NF-RO; as well as, incorporated processes in membrane operations (MHP-IP) by grouping without of different membrane contactors, or a combination of membranes with some kind of aggregation. Some of these methods are assisted UF by micellar agents (MEUF), Emulsion Liquid Membrane (ELM), immobilized liquid membranes (ILM), membrane pervaporation (PV), vapor permeation (VP), membrane biological reactors (MBR), membrane catalytic reactors (CMR) and membrane distillation (MD).

The main purposes of MHP are to achieve better performance than any of the component parts, to reduce fouling, costs, pressure, and to lower energy requirements; in general, to improve separation (cheaper, easier, enhanced) [9]. The selection of these MHP system depends of water pollution and phenol concentration. The most reported MHP include SMP and IP, because these HMP may be integrated into a single system to carry out specific task.

This review focuses on the recent studies on phenol treatment by MHP-SMP and MHP-IP, in order to provide a comprehensive overview on feasible alternatives for phenolic industrial wastewater depuration and phenol recovery.

MHP-SMP

The use of membrane technology to remove phenol from wastewater is nowadays well known. NF and RO membranes have been widely tested as efficient methods for recovery of this pollutant from aqueous streams. However, recent research suggests the application of MHP-SMP to enhance the efficiency and lifetime of the membrane during the operation of the phenolic wastewater depuration. According to their pore size, combined processes SMP, UF/NF or RO are utilized for the treatment of industrial effluents with good results, because phenol is rejected by membrane surface and remain on the feed or concentrate side, while the water pass through the membrane to the filtrate side. So, the phenol is concentrated for its reuse and clean water can be discharged or also disposed for its reuse. In addition to efficient reducing of phenol concentration into the water, these systems are utilized because they can significantly reduce the membrane fouling potential over the conventional pretreatment processes. Figure 1 presents samples of concentrated phenol and permeated water by MHP-SMP. The sample correspond to industrial wastewater with high phenol content.

Figure 1. *Samples of concentrated phenol and permeated water by MHP-SMP.*

Sun et al.[10] found that UF/RO membranes exhibited the best performance with almost complete removal of suspended solids and removal of phenol (56.4% as COD), and highest phenol rejection of 94.9% and relatively high permeate flux of 26.4 L/m^{2}h at 30 bar. Compared with other membrane processes, the system UF/RO had a higher phenol rejection and less energy consumption.

Currently, MHP-SMP are studied under various aspects, such as, phenol rejection, water flux, membrane materials, membrane structure, modes of operation, and feed solution chemistry, process scaling and reducing the energy requirements, because all these aspects affect membrane fouling and flux. Particularly, today are studied new materials to improve membrane performance. The materials are based in composite polymers, improving fouling problem in a system UF/RO[11].

MHP-IP

The most recent research show MHP-IP are also promising systems for phenol separation. This technology is distinguished because they are membrane contactors, where one operation and membrane separation are carried out to remove or recovery the phenol.

Specifically, MEUF separation, involves the addition of a micellar agent (surfactant or polymer) into the aqueous phenolic stream above its critical micelle concentration (CMC), which causes the formation of aggregates (micelles) containing solubilized phenol. Thus, wastewater depuration and micelles rejection occur because their diameter size is larger than the UF membrane pore size[12].

Due to micellization, these processes have been developed to replace NF and RO membranes. Therefore, the micellization process is the low cost and its efficiency depends on the micellar agent characteristics (anionic, nonionic or amphoteric surfactant), the CMC, phenol solubility, micelles formation and stability.

Fig. 2 presents a schematic diagram of MEUF displaying process steps. Micellization is produced by a combination of phenol contained in wastewater, and the micellar agent. First, the micellar solution is passed through a membrane to obtain two resulting streams, the treated effluent (permeate) and phenol entrapped in micelles. At this point a demicellization process is required as means to recover both the micellar agent and the phenol.

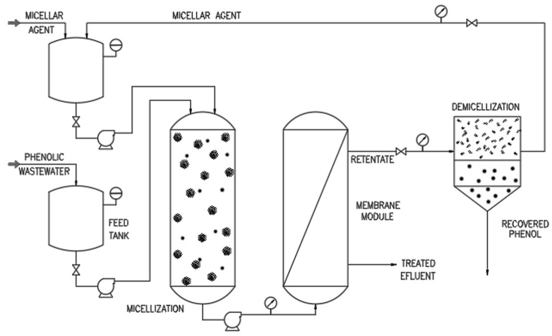

Figure 2. *MEUF diagram process for phenol recovery from phenolic wastewater.*

A MEUF striking advantage is its high phenol recovery efficiency; however, this process is applied for removing only low phenol concentration, since it is solubilized into micelle. In addition, membrane fouling caused by micelles is a significant problem restricting its industrial application in complex effluents and high concentration of phenol.

Residual micellar agent and phenol content in the retentate (fraction containing the components that have not been transported through the membrane) may also be increments the process costs by the required additional polishing step to separate both the phenol and the micellar agent.

Actually, the works on the use of MEUF for phenol removing are based in the study of new surfactants, flux behavior and membrane fouling[13,14].

Other MHP-IP systems are based in membrane extraction and separation operations. These processes are described as ELM and ILM which are performed on a liquid membrane or film (emulsion). The general system consists in four steps: emulsification, extraction, settling, and demulsification. The liquid film may be in a supported (ILM) or unsupported form (ELM) [15]. The supported form consists of a rigid polymer with lots of microscopic pores in its structure filled out with an emulsion. In both methods, phenol is transferred to a membrane and then stripped down by the internal phase; a stripping agent may also be used to increment phenol removal efficiency. These processes are highly selective and are relatively highly efficient since liquid membranes do not present fouling problems, they have a high interfacial area for extraction, and they consume low energy[16]. The aforementioned technology offers an innovative alternative to phenol recovery from wastewater; however, studies reported in the literature show values from laboratory scale tests carried out using phenol as a pollutant molecular model, and it is worthwhile noting that up to date there is no reliable information about their large-scale application[17].

Fig. 3 shows an ELM process steps diagram. In the first step, an emulsion dispersed in globules is prepared with an emulsifier agent (might be a surfactant), after each globule is formed, a liquid membrane may be seen. In the second step, the phenolic effluent gets in contact with each globule consisting of an aqueous internal receiving phase, which selects and encapsulates phenol. A settling operation follows in order to separate the treated water from the phenol containing globules. At this point, depurated water may be treated anew or discharged. Finally, for a recovery purpose, separation of phenol from the emulsion globules must be done by demulsification. This operation is usually performed by applying an electrical field so the liquid membrane can be recycled while phenol is recovered and thus can be reused.

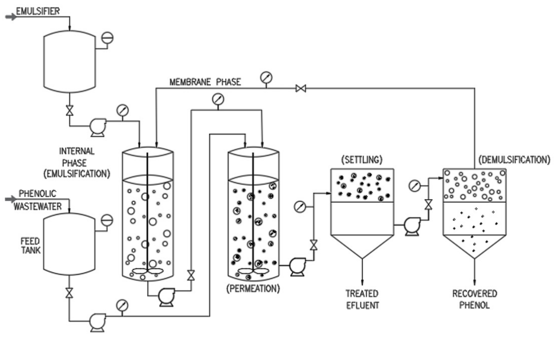

Figure 3. *ELM process diagram for phenol recovery from phenolic wastewater.*

The major restrictions of an ELM wastewater treatment system concern the stability of the emulsion, so anything affecting membrane formation must be controlled, i.e. ionic strengths, and pH, against fluid shear and osmotic swelling. These obstacles have impeded the application of the emulsion liquid membrane for use in industrial separation processes. Breakage of emulsion globules and subsequently release of the internal phase reagent into the external feed phase would nullify the extraction process[15].

Currently, various studies published on ELM and ILM systems focus on developing new membranes in ILM[18]; innovative extracting agents[19,20]; in this case, are similarly remarkable reports where some oils are utilized as extract agents and NaOH as stripping agent[21]. The addition of stabilizers such as polyisobutylene (PIB), polybutadiene (PBD), and polystyrene (PS) have also been utilized to improve the emulsification process by converting the membrane phase into a non-Newtonian form[22]. Additionally, operation conditions as pH, temperature, and agitation speed, are studied in order to increase the emulsion stability and the phenol extraction efficiency[16, 23, 24].

Nowadays, the researchers are looking at these methods as promising and advantageous alternatives among other industrial applications for phenol recovery or removal.

MHP-IP recognized as PV and VP are also utilized to separate phenol from wastewater. These processes are described as membrane separations technology involving a liquid-vapor phase change. In PV processes, the feed stream is a liquid phase which requires a partial vaporization; this condition is achieved by applying a partial pressure difference of the permeation across the membrane[25].

In a VP process, the feed side of the membrane is vapor or a gaseous component; therefore, partial vaporization should be maintained in order to carry out the separation; yet, there is no phase change during the process. In contrast, in a PV process no heat of vaporization (enthalpy) is required in the membrane unit, and there is no temperature drop along the membrane[26].

Fig. 4 shows a VP process diagram applied to recover phenol from phenolic wastewater. Initially, the effluent is fed into a distillation tower to obtain a mixture of vapors, being phenol the main component. Then the stream is fed into the membrane system to separate phenol. Permeate is collected in a vapor state at the opposite side of the membrane feed by applying vacuum either as a result of reducing the total pressure on the permeate side of the membrane using a vacuum pump system or via sweeping an inert gas on the permeate side of the membrane and finally condensing the removed phenol.

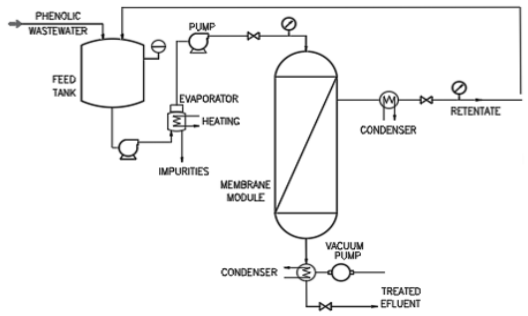

Figure 4. *Process diagram of VP for phenol recovery from phenolic wastewater.*

In addition to high phenol recovery, VP and PV devices have the advantage of performing with a minimal membrane cleaning maintenance because the vapor flow eliminates the concentration polarization effect prevalent in liquid phase separations (fouling) making these processes potentially attractive in phenol separation. However, in these systems is considered a low flux in comparison con other MHP.

Presently, new membrane materials and operational conditions are being developed to increase the selectivity and permeability necessary to make PV and VP economically more attractive for phenol removal[27-29].

MBR systems are membrane contactors. They are biological reactors consisting of activated sludge for pollutant biological oxidation, combined with a membrane batch system. The membrane can be localized into the bioreactor (submerged) or as an external device. In both cases, the membranes are utilized to remove biomass and biochemical components from cells, as well as, dissolved or suspended solids [30]. An additional membrane system may also be integrated to the process so as to improve water quality for reuse. Fig. 5, presents a diagram of process showing an aerated bioreactor coupled with an external membrane system. In the first step, phenolic wastewater is placed in contact with aerobe microorganisms, and subsequently treated water is filtered working with an UF membrane.

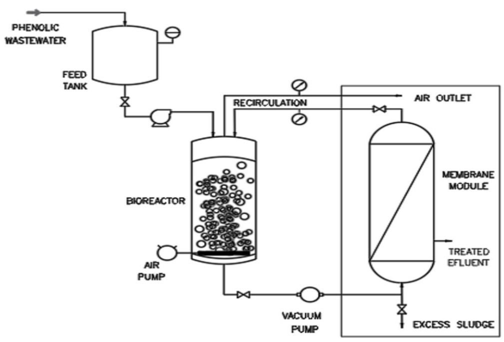

Figure 5. *Process diagram of MBR to degrade phenol from phenolic wastewater.*

Two key advantages of MBR processes are: the capacity to mineralize pollutants, and the ability to effectively separate residues. Submerged membranes may also present advantages including small footprint, better control of oxygen demand, and 28% reduction of the cost of operation and liquid pumping. However, the main disadvantages of MBRs are related to the fouling problem, high aeration cost and the complex biological degradation conditions required, since the use of microorganisms is limitative for high phenol concentration treatment[31].

Currently, MBR processes have been implemented in full scale for industrial and municipal applications[32-34]; nevertheless, up to date there are few studies for phenol treatment using this type of process. The results show efficiencies up to 80% for phenol concentrations under 300 mg/L, indicating that further research on this topic is necessary to impulse the use of this technology since the MBR represents a feasible alternative method on account of the fact of its fast construction and easy implementation for phenolic wastewater depuration even as a tertiary process.

Today, new device technology from MBR has also been studied for this purpose. In this case are utilized compact hybrid unit that uses several processes: biodegradation by activated sludge, membrane filtration, and degradation by electrokinetic phenomena. These units are known as electrobioreactor (MEBR); in this case, catalytic electrodes are utilized to cause a previous electrocoagulation. Then these systems can reduce the fouling problem by applying direct current (DC) in a medium current density (15 to 25 A/m^2) into the bioreactor[35].

Investigating the influence factors such as initial concentration, voltage, pH value, temperature and mixed liquor suspended solids (MLSS) toward phenol degradation process, can be seen in[35]. The authors found that MEBR increased the quality of the treated wastewater than conventional MBR. Qualitative analysis looks at the degradation products of phenol generated in MEBR, through which 2,6-di-tert-butyl-p-benzoquinone was confirmed as the main degradation product.

Recently, additional coupled methods of treatment MHP as MCR have also reported to carry out the separation of phenol. MCR are systems that include degradation by chemical oxidation as photocatalysis and the use of a membrane for retention of the particles or photocatalytic compounds and products derivative of phenol degradation. This technology consists of a hybrid reactor in which photocatalysis is coupled with a membrane process. These systems are designed to solve problems concerning separation of the photocatalyst as well as products and by-products of photodecomposition from the reaction mixture. The membrane utilized (generally, MF, UF or NF) may be applied as a simple barrier for the photocatalyst, or as a selective barrier for the molecules to be degraded. The catalyst might also be immobilized in a membrane (photocatalytic membrane) or suspended in the reaction mixture.

The high efficiency and phenol removal obtained are related to the synergistic effect of the electrochemical oxidation and separation in the reactor. However these processes are limited by efficacy of photocatalysis and membrane fouling.

Other alternative that shows the efficacy of MHP, involve conventional separation methods as distillation, adsorption on synthetic resins and coupled membrane separation techniques as PV and/or ELM. This MHP process can be seen in[25], which was designed for phenol removal from solutions modeling wastewater from phenol production with cumene oxidation.

Accordingly the above review, here was found that the study of MHP processes is actually an important research subject in membrane applications for phenol separation. MHP contains new and several alternatives that have been develop in order to improve existing membrane method designs to phenol recovery, removal, and phenol degradation.

New studies on UF/RO, NF/RO, PV or VP systems, show that they are already being used to recover phenol and they are industrially efficient. While, MBR systems have great perspectives for implementation at the industrial level on account of the fact that they possess a great capacity for phenol biodegradation and water depuration. MHP can be considered for industrial scaling, and some other systems are being developed combining or integrating membrane processes to improve the performance in phenol separation. Therefore, MHP can be applied under industry requirements; they can be customized according to the specific phenolic wastewater, environmental aspects, the cost of the process, and they might replace conventional methods for phenol separation, offering sustainability and high performance.

CONCLUSIONS

The contamination of wastewater by phenol is recognized as an issue of growing importance in recent years. In this topic, the development of feasible phenol separation methods has been a key challenge to reduce pollution related to this dangerous contaminant from industrial manufacturing.

Current ongoing studies have shown that membrane technologies, forming combined or integrated systems as MHP are suitable for separate the phenol, improving the efficiency of existing processes.

In detail, MHP as NUF/RO and NF/RO are already implemented at industrial level to phenol recovery. Other systems as PV, VP and ELM or ILM have also been considered for this purpose with great advantages on the existing technologies.

Another research are focusing on developing biological and chemical phenol degradation processes coupled with MHP, where MBR systems have much capacity for phenol biodegradation and water depuration.

At present, MHP systems constitute an open field for research in relevant membrane areas for phenol recovery, separation, and degradation.

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