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Preparation and characterization of SiO_2/PDMS/PVDF composite membrane for phenols recovery from coal gasification wastewater in pervaporation

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ABSTRACT

Silica (SiO_2)/polydimethylsiloxane (PDMS)/polyvinylidene fluoride (PVDF) composite membranes were prepared through a dynamic negative pressure method for phenols recovery from coal gasification wastewater (CGW) in pervaporation process. Multiple techniques including scanning electron microscopy (SEM), water contact angle (WCA) and fourier transform adsorption spectrum (FTIR) were used to examine the surface morphology, hydrophobic properties and functional groups of the modified PVDF hollow fiber membranes, respectively. The effects of SiO_2 concentration, coating time and coating pressure on pervaporation performance were systematically studied. The operating conditions obtained are as follows: 12 wt.% SiO_2, coating time 60 min, coating pressure 50 kPa. Under the optimum conditions, the phenols flux and separation factor were obtained as 6.55 g m^{-2} h^{-1} and 2.59, respectively. Results show that separation factor in pervaporation process based on 12 wt.% SiO_2 filled PDMS/PVDF composite membranes was about 2.5 times higher than that of the PDMS/PVDF membrane.

1. Introduction

In past several decades, energy consumption experienced a dramatically growth with the rapid industrialization, and corresponding environmental crisis has become a serious challenge. Coal still plays an important role in meeting the rising global energy demand, especially in China where coal is used to produce 79% of electricity (Ji et al., 2016). Direct coal combustion lead to serious environmental problems and low energy efficiency. These problems can be potentially resolved by coal gasification (Liang et al., 2017a). However, a large amount of non-biodegradable organic wastewater from coal gasification contains mainly phenolic compounds, alkane, aromatic hydrocarbons, heterocyclic compounds, ammonia nitrogen, cyanide, etc. (Gai et al., 2008; Ramakrishnan and Surampalli, 2013), which are hard to be treated by the traditional biological treatment (Zhang et al., 2010; Zhao and Liu, 2016; Zhuang et al., 2016). Therefore, the removal of phenols becomes a key step before the biological treatment process. It is urgent to seek an effective method to remove phenols from CGW.

The treatment methods for organic wastewater include membrane distillation (Lu et al., 2017; Mohammadi and Kazemi, 2014), adsorption (Liang et al., 2017c), imprinting (Razali et al., 2015), photocatalysis (Deng et al., 2017) and supported liquid membrane technology (Sun et al., 2017). These methods have some shortcomings and limitations. Membrane distillation is limited to the low flux and higher cost compared to other commonly used technology (Eykens et al., 2017). Adsorption is economic only at low volatile organic compounds (VOC) levels due to

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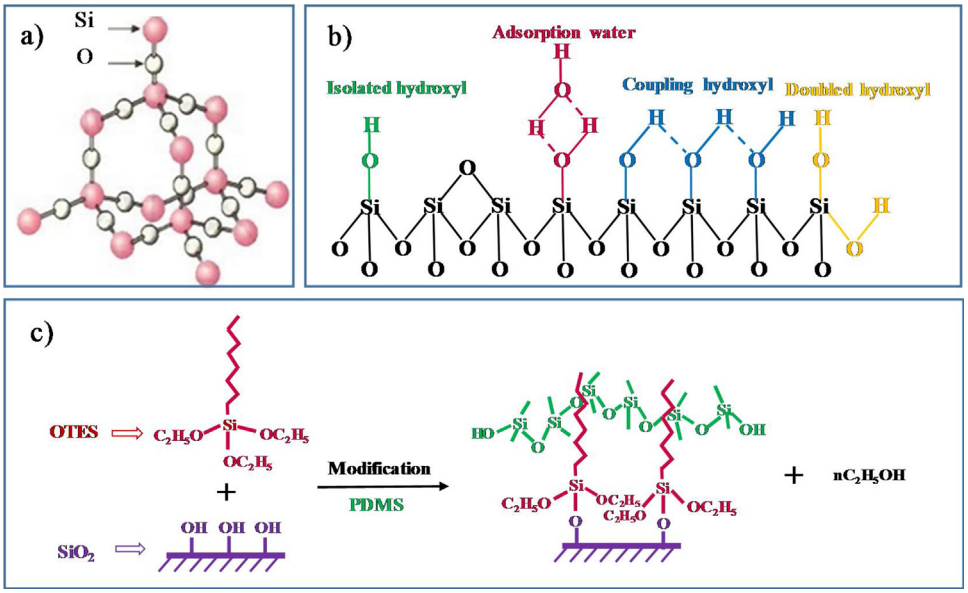

Fig. 1 – (a) Structure of SiO_2; (b) The surface character of silica; (c) The crosslinking mechanism of PDMS with SiO_2.

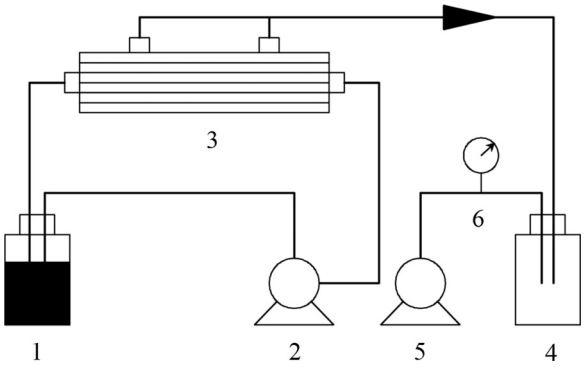

Fig. 2 – Coating experimental device. (1) Coating solution, (2) peristaltic pump, (3) hollow fiber membrane module, (4) buffer tank, (5) vacuum pump, (6) vacuum gauge.

the high cost of the adsorbents and the need for its frequent regeneration (Nikolajsen et al., 2006). Although molecular imprinting technique is a green technique, the recognition sites of the imprinted polymer are mostly inside the polymer microspheres, resulting in difficult to bind molecules to be imprinted and identification sites, with a low binding rate (Liu et al., 2011b). Photocatalysis is a method with strong oxidation ability, but quantum efficiency is low (Liang et al., 2017b). Supported liquid membrane technology is efficient for specific compound but liquid membrane phase easily lost (Jaber et al., 2005).

Pervaporation is an energy-saving and cost-effective membrane separation technique, especially suitable for separating azeotrope, isomers with same boiling point and thermo-sensitive substance (Feng and Huang, 1997; Yoshida and Cohen, 2003). As a method of preliminary treatment, pervaporation technique has gained considerable attention because of its efficiency in recycling phenolic compounds (Gupta et al., 2002; Hao et al., 2009; Hoshi et al., 2000). In pervaporation, separation of the membrane depends on solution-diffusion coefficients of the feed liquids in the dense homogeneous asymmetric polymer membrane. For the solubility and diffusivity of mixture components, surface properties and structure of the polymer membrane are vital factors. Therefore, to enhance separation efficiency physical and chemical properties of the membrane must be carefully designed (Ramaiah et al., 2013; Zhou et al., 2014).

There are different pathways to improve membrane separations performance, such as membrane surface modification (Kujawski et al., 2007), solvent treatment (Razali et al., 2017). It is well known that surface modification is a method of altering surface properties of polymeric membranes (Lu et al., 2016). As known, the hydrophobic surface is decided by two aspects: One is the low-free-energy of the hydrophobic coating; the other is the roughness morphology of the surface (Lin et al., 2015; Zhang et al., 2013). The PVDF is widely considered to be an attractive membrane support due to its good chemical stability, while the PDMS is chosen as coating layer for its low surface energy (Gholabroodi Basharzad et al., 2016; Wu et al., 2001). Yeow et al. (2002) have reported that selectively separating of xylene from nitrogen by the prepared divinyl-PDMS/PVDF composite hollow fiber membranes is clearly demonstrated with recovery greater than 95%. SiO_2 nanoparticles is widely used as a filler to increases the surface roughness in polymeric matrix (Cai et al., 2007). SiO_2 particles with a three-dimensional network structure can improve the surface property of membrane and broaden the applications of membrane technologies in water treatment (Cui et al., 2010) and other fields (Li et al., 2014). Although several studies show that organic or ceramic composite membrane have great potential to remove VOC from aqueous solutions (Gupta et al., 2003; Liu et al., 2011a; Ramaiah et al., 2013), reports regarding phenols recovery from CGW through SiO_2/PDMS/PVDF hollow fiber composite membrane have not been published as far as we know. A homogeneous dispersion of SiO_2 fillers in polymer matrix is a primary challenge for prepared composite membranes. So far, immersion/coating approach is used for the hydrophobic modification of membranes, however, it is extremely difficult to modify hollow fiber membranes. Existing methods would block the membrane channels thus decrease the permeability of membranes in the hydrophobization process.

In this study, SiO_2 particles were first grafted by *n*-octyltriethoxysilane (OTES) and then mixed with PDMS solution immediately to disperse SiO_2 particles in PDMS matrix. SiO_2/PDMS/PVDF composite pervaporation membranes were prepared by coating a layer of SiO_2/PDMS solution on surface of PVDF hollow fiber membranes through dynamic negative pressure method. Then, the characterization of modified PVDF membranes were assessed by various analytical methods: SEM-EDS, FTIR, CA. Pervaporation experiments were carried out to separate phenols from CGW. The influence of SiO_2 concentration, coating time, coating pressure and feed temperature on the resulting pervaporation performance of prepared composite membranes were studied systematically.

2. Experimental

2.1. Materials

The PVDF hollow fiber membrane module (pore size 0.16 μm, hollow fiber inner diameter 0.8 mm, external diameter