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Enhancement in copper ion removal by PPy@Al_2O_3 polymeric nanocomposite membrane

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ABSTRACT

γ-Al_2O_3 nanoparticles were coated with PPy via an in situ polymerization reaction. 0.01, 0.1 and 1.0 wt.% of PPy@Al_2O_3 nanoparticles were introduced into polyethersulfone (PES) flat sheet membrane to seek the adsorptive capability of nanocomposite membrane in removing copper ion from water. Nanocomposite membranes were prepared using phase inversion method. It was revealed that PPy@Al_2O_3 could significantly promote copper removal superiorly in membrane mixed with 1.0 wt.%PPy coated alumina nanoparticles. Showing higher water flux in comparison with pristine PES, acceptable permeation was achieved with a partial decrease compared to the neat alumina mixed membrane.

Introduction

Addition of metal oxides as adsorbents into the wastewaters has attracted a large amount of attention in water treatment processes due to their larger specific surface area and large number of active sites of adsorption [1–11]. Moreover, employment of nanoparticles in the membrane preparation (nanocomposite membranes) is an approach to employ specific features of nanoparticles for improving the morphology and performance of membranes. Accordingly, some metal oxide nanoparticles such as Fe_3O_4 [5,6], ZnO [12,13] and graphene oxide [8,14], due to the great affinity for heavy metal adsorption, were widely used in preparation of nanocomposite membranes and improvement of membrane performance in removal of heavy metals from aqueous media.

At the same time, polymers which are characterized by reactive functional groups containing O, N, S and P (electrondonor atoms), constitute an important class of versatile polymeric materials that are found widespread in environmental applications [15]. The composition of these materials confers them the possibility to coordinate with different metal ions [16–18]. As one of the novel conducting polymers, polypyrrole (PPy) has been widely studied due to its good thermal and environmental stability, superior electric conductivity as well as ease of preparation [19]. PPy is a conjugated polymer with alternating single and double bonds which its conductivity originates from the $nC_4H_4NH + 2FeCl_3 \rightarrow (C_4H_2NH)_n + 2FeCl_2 + 2HCl$ electrons delocalized over the conjugated system and from the doping ions. It has been proved that PPY is an effective adsorbent that can be employed for removal of heavy metals including copper ions [19]. L. Seid and co-workers [15] investigated the potentiality of employing PPy as an adsorbent for heavy metal removal from aqueous solution. They found polypyrrole particles as the effective adsorbents in the removal of cadmium (II) and cobalt (II) ions from wastewaters. In another study, Hosseini et al. [19] employed this polymer for adsorption of copper ions from aqueous solution. They reached to 100% efficiency in the removal of copper ions.

Ghorbani et al. [20] modified carbon nanotubes with polyaniline and polypyrrole and used them for removing anions (S^{2-} and SO_4^{2-}) and heavy metals ions (Cu (II), Fe (II and III) and Zn (II)) from paper mill wastewater. Polypyrrole/maghemite (γ-Fe_2O_3) and polyaniline/maghemite (γ-Fe_2O_3) nanocomposites were prepared by A.E. Chávez-Guajardo et al. [21] as some active agents for removal of Cr (VI) and Cu (II) ions from aqueous media. They claimed that theses nanocomposites have great potential for being used as magnetic adsorbents for removal of Cr (VI) and Cu (II) ions from aqueous solutions. Moreover, it was found that the polypyrrole/γ-Fe_2O_3nanocomposite showed higher adsorption capacity for adsorption of both Cr (VI) and Cu(II) ions compared to polyaniline/γ-Fe_2O_3. With regard to these studies, PPy can be applied as an efficient modifier to achieve higher heavy metal uptake onto the appropriate adsorptive nanoparticles.

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Nomenclature

Symbols & abbreviations

A	membrane area (m^2)
A'	surface of membrane sample (cm^2)
AFM	atomic force microscopy
C_e	equilibrium concentration of copper ion (mg/l)
C_f	copper ion concentration in feed (mg/l)
C_i	initial concentration of copper ion (mg/l)
C_p	copper ion concentration in permeate (mg/l)
DMAc	N,N-dimethylacetamide
DW	distilled water
d_w	water density (0.998 g/cm^3)
$Eq._{Ads.}$	equilibrium adsorbed amount of copper ions on the membrane (mg/g)
FTIR	Fourier transform infrared
l	membrane thickness (cm)
m	mass of the adsorptive membrane (g)
NP	nanoparticle
NPs	nanoparticles
PES	polyethersulfone
PyAl	nanocomposite membrane prepared with PPy@Al_2O_3 nanoparticle
$PyAl_{0.01}$	nanocomposite membrane prepared with 0.01 wt.% of PPy@Al_2O_3 nanoparticle
$PyAl_{0.1}$	nanocomposite membrane prepared with 0.1 wt.% of PPy@Al_2O_3 nanoparticle
$PyAl_1$	nanocomposite membrane prepared with 1.0 wt.% of PPy@Al_2O_3 nanoparticle
$PAl_{0.1}$	nanocomposite membrane prepared with 0.1 wt.% of Al_2O_3 nanoparticle
PPy	polypyrrole
PPy@Al_2O_3	Al_2O_3 nanoparticles coated by polypyrrole
PVP	polyvinylpyrrolidone
Q	permeate weight (kg)
SEM	scanning electron microscopy
V	volume of the solution (l)
WCA	water contact angle (°)
W_d	dry membrane weight (g)
W_w	wet membrane weight (g)
Δt	permeate gathering time (h)

Regarding the conspicuous properties of alumina (Al_2O_3) e.g. high adsorption capacity, hydrophilicity and resistance to chemical agents [22–27], in this study, alumina nanoparticles were selected as nanofillers. PPy@Al_2O_3 nanoparticles (NPs) as a polymer modified adsorbent were prepared and added into the PES matrix to obtain a new nanocomposite membrane with enhanced affinity toward heavy metals. By the method of coating a thin PPy layer on the alumina nanoparticles, it would be possible to employ simultaneously the adsorptive capability of both alumina and PPy using the very small amounts of these adsorbents. Besides, the common problems of powder-form adsorbents (such as separation of adsorbents from final product, cost and difficulty of regeneration of adsorbents as well as the environmental problems due to unwanted entrance of nanoparticles into the surrounding media) might well be controlled when the nano-adsorbent is introduced into the membrane matrix. In this work, the performance of prepared membranes was tested for removing copper ions from diluted Cu (II) aqueous solution. Cu (II) has been selected for removal experiments because of the serious risks that it can offer to human health. For example, an excessive intake of Cu (II) can lead to gastrointestinal problems, kidney and liver damage, headaches and nausea [21]. Moreover, as a heavy metal, copper ions might be considered as a representative for bunch of heavy metals. SEM, AFM and FTIR tests were applied for characterization of prepared membranes and nanoparticles. The reusability of membranes was examined using EDTA as regenerator.

Experimental

Materials

The chemicals used in the current study are listed in Table 1. All reagents were used without further purification. Distilled water (DW) was employed throughout the experiments.

Preparation and characterization of PPy@Al_2O_3 nanoparticles

A method of in situ polymerization was employed to encapsulate the alumina NPs by PPy. As the pyrrole monomer can be polymerized through a chemical polymerization reaction in the aqueous media, pyrrole was dissolved in DW (1.2 wt.%). Then, 2 g of Al_2O_3 NPs was added into 40 ml of the solution and sonicated for 5 min. The solution was stirred (400 rpm) at room temperature for 1 h to ensure the adequacy of contact time between NPs and monomer. Afterward, 20 ml of 13 wt.% $FeCl_3$ aqueous solution was mixed with that solution. Immediately, the following oxidative polymerization reaction was started and the color of the suspension turned to black.

$$nC_4H_4NH + 2FeCl_3 \rightarrow (C_4H_2NH)_n + 2FeCl_2 + 2HCl$$

Stirring the reaction mixture was continued for 1 h to complete the polymerization. Polymer coated NPs was filtered and carefully washed with DW and then, dried in an oven at 40 °C.

Fortunately, the color change during encapsulation of white alumina was as clear that strongly confirms the prosperity of coating process. However, FTIR spectroscopy (Shimadzu, FTIR spectrophotometer, Japan) was applied to validate the formation of functional groups on new PPy@Al_2O_3 NPs.

For the morphology evaluation, a field emission scanning electron microscope (FE-SEM, Mira 3-XMU, Czech Republic) was employed and the microphotographs of both alumina and polymer modified alumina particles were recorded and analyzed for particle size and morphology.

Fabrication of PPy@Al_2O_3 nanocomposite membrane

Mixing nanofillers into the polymer bulk is simply approached during a phase inversion method. In preparation procedure, the

Table 1
Identifications of chemicals.

Chemical	Supplier
Al_2O_3 (<100 nm)	Nanosav, Iran
$Cu(NO_3)_2 \cdot 3H_2O$	Ghatran shimi, Iran
DMAc	Merck, Germany
EDTA	Merck, Germany
$FeCl_3$, $6H_2O$	Merck, Germany
NaCl	Merck, Germany
Na_2SO_4	Merck, Germany
PES (Ultrason E6020P, MW 58,000 g/mol)	BASF, Germany
PVP (MW 25,000 g/mol)	Merck, Germany
Pyrrole	Merck, Germany