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Deploying Nanoparticle-Doped Polymeric Membranes in Treating Water Contaminated with Ciprofloxacin †

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Abstract: The antibiotic Ciprofloxacin HCl (CPH) is a representative example of pharmaceutical contaminants of emerging concern which are frequently released in wastewater effluents and can cause hazardous health effects. In this work, we investigate the potential of utilizing porous polymeric membranes incorporating metal nanoparticles for removing CPH from water. In this regard, polylactic acid/polyurethane membranes were impregnated in situ with single, binary and tertiary systems of nanoparticles of cobalt, copper and nickel, among others. Membranes loaded with cobalt exhibited the best performance among all the examined membranes. They yielded removal efficiencies above 80% at an initial CPH concentration range of 10–50 ppm and pH 6.5, thus exceeding those of the bare membranes by about 1.3 times under the same conditions. As confirmed by Brunauer, Emmet and Teller (BET) analysis, the incorporation of cobalt nanoparticles into the mesoporous membranes increased their surface area and pore volume by 5 and 10 times, respectively. Thermogravimetric analysis (TGA) showed that cobalt nanoparticles had no catalytic influence on the dissociation of the membrane polymeric chains. Fourier Transform Infra-red (FTIR) and zeta potential measurements suggested that binding could possibly occur via physical interactions along with catalytic degradation.

Keywords: Ciprofloxacin HCl; nanoparticles; porous polymeric membranes; contaminants of emerging concern

1. Introduction

In recent years, there has been an increased human consumption of chemicals such as pharmaceuticals, personal care products, industrial chemicals, disinfectants and pesticides, among others. When released in water streams, even in minute amounts, these compounds can pass to the soil and ground water and then to the surface water which human and animals consume [1,2]. Without applying the proper water treatment methods, they will accumulate in the environment posing major health effects over prolonged periods of time [1]. Thus, they are referred to as “contaminants of emerging concern” or CECs since they have been often overlooked in the past with regard to their detection and treatment; however they recently gained much attention [3].

One of the CECs commonly found in wastewater is the pharmaceutical Ciprofloxacin HCl (CPH) that belongs to the fluoroquinolone group of antibiotics. It is active against gram-positive and gramnegative bacteria and performs its activity by inhibiting the enzyme catalytic activity involved in the bacterial nucleic acid synthesis [4]. The antibiotic was detected, at the microgram scale concentration, in various water streams including hospital effluents, sewage treatment plants' influents and effluents, as well as in drinking water [4]. It was also detected in maize tissue that had been irrigated with water containing the antibiotic, thus leading to possible bacterial resistance [5]. The presence of CPH in water leads to potential ecotoxicity to the heterobacteria *Pseudomonas fluorescens* at EC50 of 0.175 μg/L, reduced growth of the mycrophyte *phragmitis australis* at a concentration of 2 mg/L after 5 days and increased length and weight of the fish *Cyprinus carpio* in its early stages at a concentration of 1 mg/L [6]. It was confirmed that CPH is a persistent drug in wastewater which cannot be removed efficiently with conventional water treatment methods such as biological degradation and flocculation [7].

Several approaches have been investigated for the removal of CPH from wastewater including reverse osmosis, advanced oxidation processes and adsorptive removal [8–10]. One recently adopted method involved the use of metal nanoparticles due to their catalytic activity beside their sorptive properties [11,12]. In this work, we investigate the potential of removing CPH using metal nanoparticles incorporated into a polymeric porous membrane of the biopolymer blend, polylactic acid/polyurethane. This approach addresses the challenges associated with one or more of the previously reported materials by providing environmentally-friendly, high surface area nanoporous membranes that can be deployed within a low-energy process that does not require high pressure demands as encountered with the regular sorption polymeric systems [13]. It can also mitigate the possible toxicity arising from the release of free metal nanoparticles in water [14].

2. Materials and Methods

2.1. Materials and Chemicals

Ciprofloxacin HCl was brought from EIPICO Pharmaceuticals, Sharqia Governorate, Egypt. Polylactic acid (PLA) of density 1.24 g/cm^3 was purchased from Nature Works, Minnetonka, Minnesota, USA under the code name 4060D, while polyester-based polyurethane (PU) pellets with the commercial name "polyurethane" of density 1.21 g/cm^3 were obtained from Alfa Aesar (Kandel, Germany). As for metal precursors and reducing agents, sodium chloride was purchased from Alfa Aesar (Kandel, Germany), while cobalt chloride hexahydrate, anhydrous copper chloride, nickel chloride hexahydrate and sodium borohydride were purchased from Loba Chemie, Maharashtra, India. Solvents, such as *N,N* dimethyl-formamide (≤99%), absolute ethanol (anhydrous) and 1,4-dioxane were purchased from Fisher Chemical Company (Hampton, VA, USA).

2.2. In-Situ Preparation of Metal Loaded Porous Membranes

The nanoporous membranes were prepared using the solvent casting technique with a mixture of PLA and PU as described in [15], with 10% cellulose acetate (CA) and 50% NaCl crystals (pore formers). They were then soaked in 0.1 M of the metal salt solution for 3 days on an orbital shaker, then added to a 0.5 M $NaBH_4$ aqueous solution and kept shaking for 24 h on an orbital shaker at room temperature to allow all the metal salt ions to be reduced to metal nanoparticles.

2.3. Characterization

Fourier Transform Infra-Red (FTIR) spectroscopy measurements were performed for the prepared membranes before and after adsorption using the KBr disc method in the range of 400–4000 cm^{-1}. Dynamic light scattering (DLS) measurements were performed to determine the zeta potential of the membranes before and after adsorption. Scanning electron microscopy (SEM) and Brunauer, Emmett and Teller (BET) measurements were also performed to determine the morphology and surface characteristics of the membranes, while Thermogravimetric analysis (TGA) was applied to investigate their thermal stability.

2.4. Adsorption Experiments

Cut membranes of dimensions 1*2 cm^2 and predetermined weight were added to 15 mL of CPH solutions of concentrations (2.5, 5, 10, 25, and 50 ppm) into 15-mL falcon tubes. They were then left on a shaker in the dark, at room temperature and pH 6.5. The adsorption experiment was halted after 8h. Afterward, the absorbance of CPH was determined using a UV/Vis spectrophotometer at 286 nm wavelength and the corresponding concentration of CPH was then calculated from a pre-prepared calibration curve. Percent removal and adsorption capacity were determined from the following equations:

$$\%\ \boldsymbol{Removal} = \frac{\boldsymbol{c}_{\mathrm{i}} - \boldsymbol{c}_{\mathrm{e}}}{\boldsymbol{c}_{\mathrm{i}}}, \qquad (1)$$

$$q_e = \frac{(\boldsymbol{c}_{\mathrm{i}} - \boldsymbol{c}_{\mathrm{e}})\boldsymbol{V}}{\boldsymbol{X}} \qquad (2)$$

where C_i is the initial CPH concentration, C_e is the equilibrium concentration, q_e is the equilibrium adsorption capacity, V is the total volume of the solution in the falcon tube, and X is the dry mass or surface area of the cut membranes.

3. Results and Discussion

3.1. Screening of the %Removal of Several Metal Loaded Polymeric Membranes

Initially, a screening study was performed to identify the most efficient membranes with regard to their removal for CPH. Fourteen different membranes were examined, non-porous polymeric membrane which was prepared in absence of NaCl (np), porous polymeric membrane (p), and porous polymeric membranes loaded with Co, Ni, Cu, ZnO, TiO_2, WO_3, Fe_2O_3, graphene oxide (GO), Fe/Co, Fe/Ni, Ni/Co, or Fe/Co/Ni. The removal efficiencies of these membranes (Figure 1a) were obtained after 8 h of adsorption using 50 ppm of CPH. Clearly, the cobalt-loaded membranes exhibited the highest removal efficiency of 80.7%, followed by the copper–loaded ones (70.9%) then the nickel-loaded ones (68.8%). On the other hand, the bare porous (p) and non-porous membranes (np) yielded comparable efficiencies of 61.8% and 61.9%, respectively implying that the removal is independent on porosity. This may suggest that the mechanism of adsorption is mainly governed by surface interactions rather than pore diffusion. Having lower efficiencies than those of cobalt-loaded, copper-loaded or nickel-loaded membranes suggests that the nanoparticles contribute to the adsorption. Meanwhile, titanium dioxide, ferric oxide, zinc oxide, GO and WO_3 loaded membranes showed removal efficiencies that ranged from 40% to 52%. Interestingly, utilizing binary or tertiary nanoparticle mixtures of Co or Ni with other metals reduced the removal efficiency relative to that of the single component nanoparticles of Co or Ni, showing the lowest recorded removal efficiencies among all the deployed membranes (7–22%). This antagonistic effect could be owed to possible interaction between the components of the mixture [16].

Since Co,Cu,Ni-loaded membranes showed the best removal, we focused on studying their removal efficiencies and adsorption capacities over a range of different initial CPH concentrations (Figure 1b–d). As depicted in Figure 1b, the removal efficency slightly increases with increasing the concentration in the range of 5–50 ppm, then remains almost constant in the range of 10–50 ppm indicating saturation of adsorption sites. Similar trend was observed in previous literature where 3.6–100 ppm methylene blue was biosorbed on fava bean peels [17]. The corresponding equilibrium adsorption capacities were then calculated per unit area or dry mass of the membrane as shown in Figure 1c,d, respectively. A clear linear correlation can be realized between the adsorption capacity and the initial CPH concentration. The adsorption capacity increases proportionally with concentration probably due to a decrease in the mass transfer resistance resulting from the higher concentration gradient as previously reported [18]. Adsorption capacities of 37, 33 and 32 mg/g corresponding to 3027, 2660 and 2578 mg/m^2, for Co, Cu and Ni-loaded membranes, respectively were obtained at 50 ppm of CPH, as opposed to 29 mg/g (2324 mg/ m^2) and 28 mg/g (2317 mg/m^2) pertaining to non-porous and porous membranes, respectively. Given that cobalt-loaded membranes showed the best performance probably due to the highest catalytic activity of Co nanoparticles relative to the other investigated nanoparticles, it will be the focus of the following characterization studies.

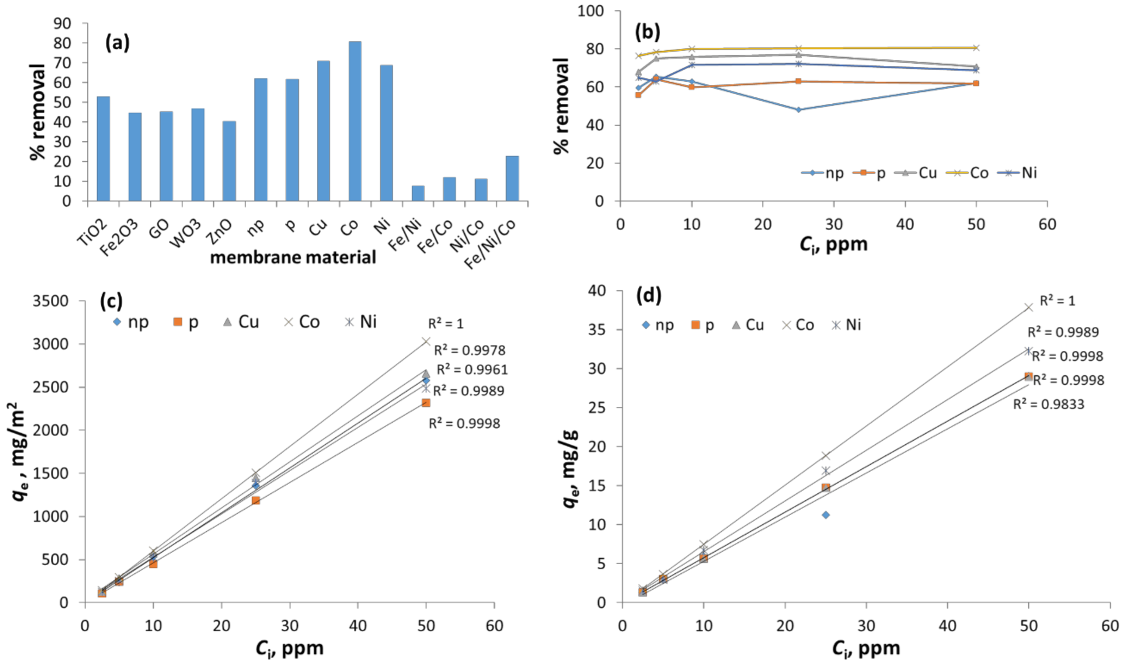
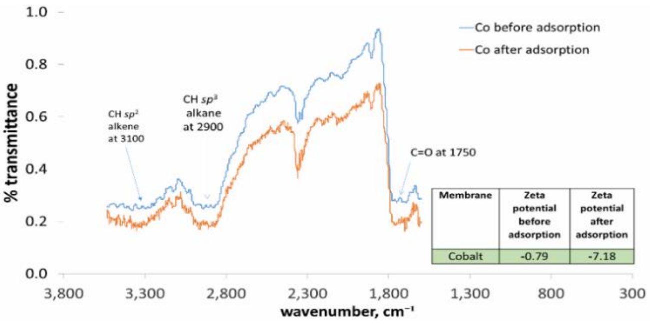


Figure 1. (**a**) Percentage removal of CPH using various metal loaded polymeric membranes, at an initial CPH concentration of 50 ppm and pH 6.5, (**b**) Percentage removal of different concentrations of CPH using the most efficient employed membranes, (**c**) equilibrium adsorption capacity in m^2/g and (**d**) equilibrium adsorption capacity in mg/g onto the most efficient employed membranes.

3.2. *Characterization of Membranes*

3.2.1. FTIR and DLS Measurements

DLS measurements showed that cobalt-loaded membranes maintained its neutrality after adsorption which suggests that it bound with CPH through physical interactions and possibly catalytic degradation. This is supported by the FTIR measurements (Figure 2) for this membrane where almost no apparent shift in peak energies for CH *sp*^{2} alkene, CH *sp*^{3} alkane and C=O was observed before and after adsorption. Besides, the disappearance of some of the peaks typical of CPH may be likely a result of the catalytic degradation.



Membrane	Zeta potential before adsorption	Zeta potential after adsorption
Cobalt	-0.79	-7.18

Figure 2. FTIR spectra and zeta potential values for Co-loaded membranes before and after adsorption.

3.2.2. SEM Measurements

The SEM images, shown in Figure 3, reveal the porous structure of the unloaded membranes; while the cobalt-loaded ones possess a rough surface owing to the impregnated cobalt nanoparticles.

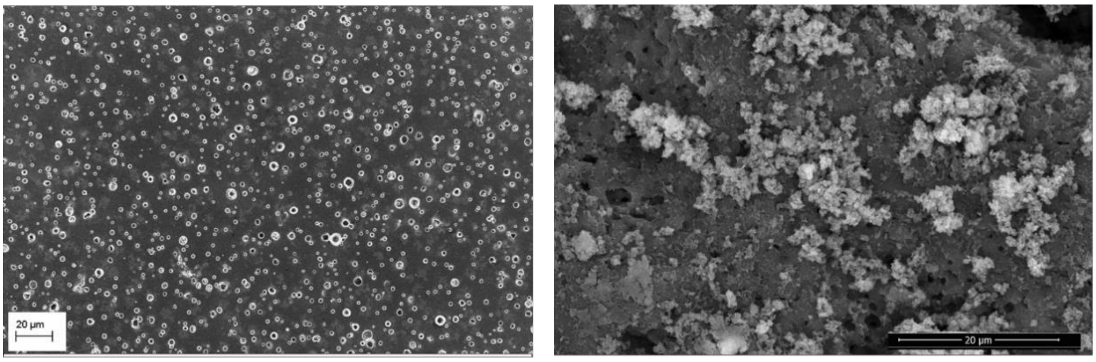


Figure 3. SEM images for unloaded porous membranes (**left panel**), and Co-loaded membranes (**right panel**).

3.2.3. TGA and BET Measurements

The TGA profiles in Figure 4 (left panel) show a two-step degradation mechanism with no apparent temperature shifts between the unloaded and cobalt-loaded membranes, implying that the nanoparticles had no catalytic influence on the degradation of the polymer chains. BET isotherms in Figure 4 (right panel) confirm a mesoporous structure with pore sizes ranging from 2 to 50 nm where surface area and pore volume for Co-loaded membranes (0.399 m^2/g and 0.002 cm^3/g) were 5-10 times larger than those of the unloaded ones (0.083 m^2/g and 0.0002 cm^3/g).

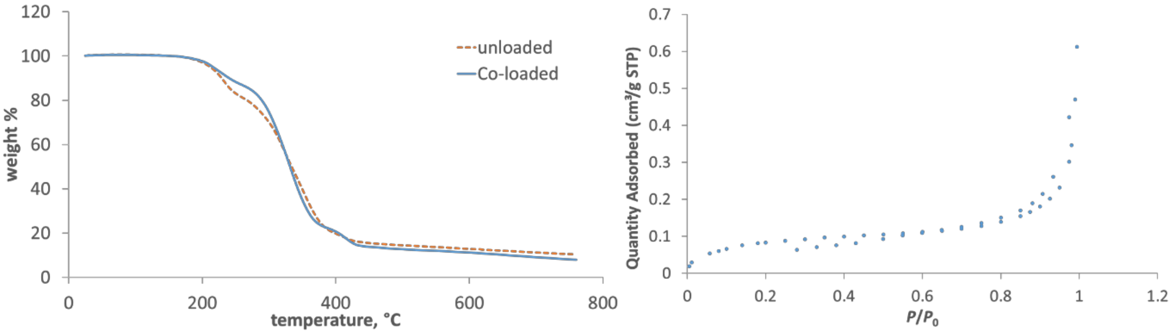


Figure 4. TGA for unloaded and cobalt-loaded membranes (**left panel**), and BET for cobalt-loaded membranes (**right panel**).

4. Conclusions

Cobalt-loaded mesoporous membranes successfully removed CPH from aqueous solutions with an efficiency of more than 80%. FTIR and zeta potential measurements suggest that binding took place through physical interactions and catalytic degradation mechanisms.

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