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Polymeric Particles for the Removal of Endocrine Disruptors

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Endocrine disruptors (EDs) have threatened our daily life severely through drinking water, cosmetics, foodstuff, and drugs. Various treatment processes for removal of EDs are studied in recent years, including membrane filtration, advanced oxidation process, biological treatment and adsorption. In this present paper, the progress of researches on various polymeric particles used as adsorbents of EDs including porous polymeric particles, hybrid polymeric particles, and imprinted polymeric particles, have been reviewed.

KEYWORDS Endocrine discruptors, polymeric particles, removal, adsorption, hybrid, imprinted polymer

INTRODUCTION

Endocrine disruptors (EDs), also known as endocrine-disrupting compounds or hormonally active agents, are "exogenous substances or mixtures that alter function(s) of the endocrine system and consequently causes adverse health effects in an intact organism or its progeny or (sub)populations" (1). According to US Environmental Protection Agency (USEPA), EDs can interfere with the "synthesis, secretion, transport, binding, action or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development and/or behavior" (2).

Basically, EDs may be classified in two categories, those occurring naturally and those that are synthesized (3). EDs enter in the environment from

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various different sources (3); today, people are exposed to EDs in everyday life, because they are found in low doses in literally thousands of products (drinking water, cosmetics and other personal care products, drugs and foodstuffs, and so on) (4–11), including Polychlorinated biphenyl (PCB), Bisphenol A (BPA), Polybrominated diphenyl ethers (PBDE), a variety of phthalates, and so on (12). This has provoked more and more national and international organizations, as well as scientific and public interest groups, to initiate research programs, conferences, workshops and expert panels to address and evaluate EDs-related issues (1, 3, 5, 6, 8, 10, 11, 13–41). Studies have revealed that low-level exposure of EDs might cause similar effects in animals and human beings (1). Therefore, there is a growing interest in removal of Eds effectively (1).

Presently, there are various treatment processes for removal of EDs. Basically, they belong to 4 categories:

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Membrane Filtration

Membrane filtration techniques, especially nanofiltration and reverse osmosis, can screen some EDs directly (42–49). However, the removal efficiency was affected by raw water fouling potential and membrane integrity (50). High raw water fouling potential and low membrane integrity may lead to leakage of EDs and serious results (42, 48).

Advanced Oxidation Processes

Advanced Oxidation Processes (AOP), a very useful for cleaning EDs in wastewater, refers to a set of chemical treatment procedures designed to remove organic and inorganic materials in wastewater by oxidation (51). During AOP process, contaminants are oxidized by different reagents: ozone (52–68), hydrogen peroxide or other peroxides (58, 69), oxygen (70–74), and air (75–79), in precise, pre-programmed dosages, sequences, or combinations (59, 77). These procedures may also be combined with UV irradiation and specific catalysts such as titanium dioxide (68, 70, 80–86).

Biological Treatment

Biological treatment processes have a high efficiency in removal of EDs (33, 87–111). It is reported that, when combined with adsorption of the solids, it may lead to 45% up to 99% removal of EDs from influent wastewater (112). When compared with membrane rectors, biological processes performed in conventional (activated sludge) treatment plants demonstrated quite reduced efficiency in removing EDs from wastewater (3, 113), although activated sludge treatment remains a workhorse technology for controlling pollution of aquatic environment (114).

Membrane bioreactors are considered an alternative to conventional treatment plants, because the membrane of bioreactors could not only act as a complete barrier to solids onto which many EDs are adsorbed, but also retains the EDs (88,112). It is reported that the removal of EDs within a membrane bioreactor prior to disinfection led to 96% removal of cholesterol, coprostanol and stigmastanol from municipal wastewaters compared to around 85% removal achieved in a conventional treatment plant receiving the same influent (112).

Adsorption

Adsorption is almost the way most frequently used in removal of EDs (3, 115). As an adsorbent, it is desirable to get a big specific surface area as much as possible; therefore, activated carbon is the most popular adsorbent used for non-specific removal of EDs (116–117); in order to achieve specific adsorption, ion exchange resin (118), carbon nanomaterials (42), and polydimethylsiloxane (PDMS) membrane (119, 120) are also used. Moreover, adsorption is usually combined with biological treatment (96) and advanced oxidation processes (113). Therefore, adsorption always attracts much attention of researchers.

In recent years, because of the hydrophobicity and porosity, polymeric particles and their derivates have been intensively studied as adsorbents for removal of EDs. In this present paper, the progress of these studies on various polymeric particles used as adsorbents for EDs removal has been reviewed.

Basically, polymeric particles that have been used as adsorbents for EDs removal could be classified as the following 3 types: (1) simple porous polymeric particles; (2) hybrid polymeric particles, which could be subdivided as (a) activated carbon/ polymer hybrid particles, (b) Montmorillonite/ polymer hybrid particles, and (c) DNA/ polymer hybrid particles; (3) imprinted polymeric particles.

POROUS POLYMERIC PARTICLES

Preparation of porous polymer membranes with big specific surface area by means of liquid-liquid phase separation technique has a long history (121). On this basis, researchers started to prepare porous and hydrophobic polymeric particles by means of a liquid-liquid phase separation technique, and explored their adsorption to EDs. It was expected that hydrophobic area and relatively large specific surface area could lead to good adsorption to EDs (122). Like membranes prepared by liquid-liquid phase separation technique, the polymeric beads obtained also had a skin on the outer surface, on which there were nano-scaled pores; under the skin, there were many bigger pores inside (Figure 1a).

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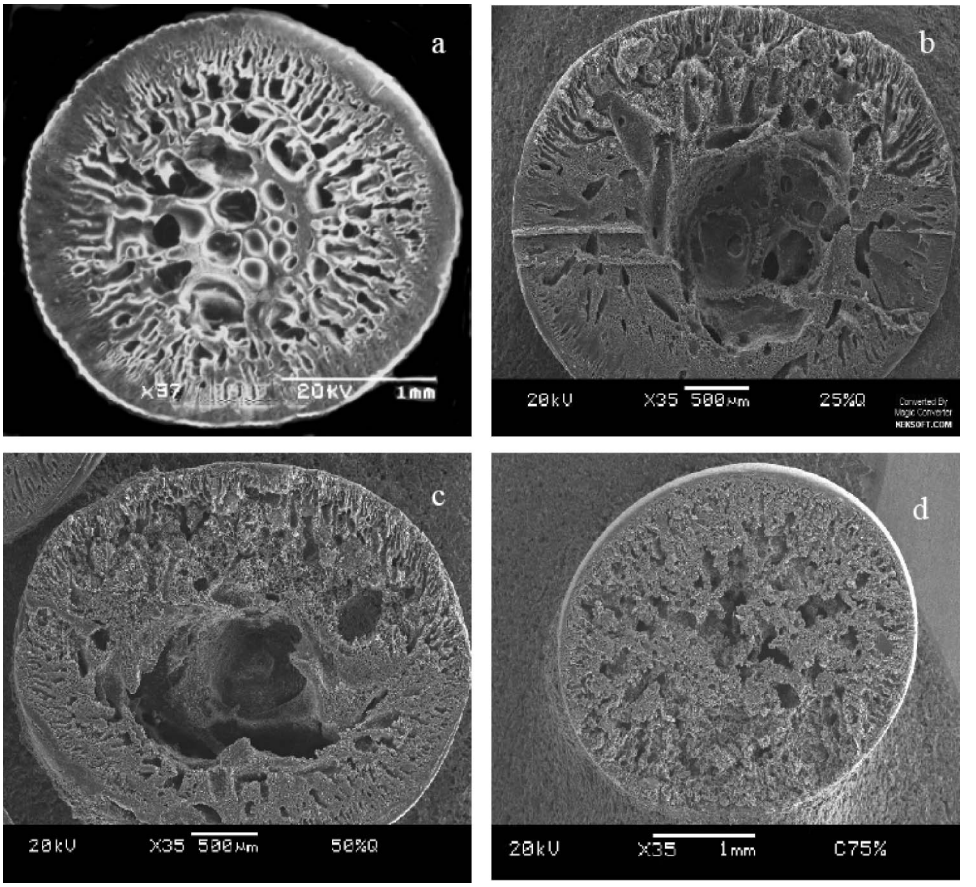

FIGURE 1 SEM pictures of different polyethersulfone (PES)/activated carbon (AC) hybrid particles. AC proportion for the particles in a, b, c, d were 0%, 25%, 50%, and 75%, respectively. Adapted from Ref. (126).

As a highly hydrophobic material, polysulfone (PSF) also has good mechanical properties, oxidation resistance, and acid and alkali resistance. Therefore, it was often used as adsorbents for EDs. Zhao et al. (122, 123) had prepared porous PSF beads by means of a liquid-liquid phase separation technique: *N*-methyl-2–pyrrolidone (NMP) was used as solvent, and water acted as non-solvent. The obtained particles had a size ranging from about 1 mm to about 2.5 mm. Therefore, the specific surface area of this kind of PSF beads ranged from about 20 m^2/g to about 150 m^2/g, depending on the polymer concentration used to prepare the particles, the particle diameter and porosity, which was very useful for adsorption.

Because of the hydrophobicity, high porosity and big specific surface area, PSF beads could be used to remove EDs from environment. It was noted that PSF porous beads had a better specific adsorption to the EDs with big octanol-water partition coefficient (Log P_{OW}) (122). Under a certain

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condition, the removal ratios for the EDs dibenzo-p-dioxin (DBD), dibenzofuran (DBF), Biphenyl (BP), diethylstilbestrol (DES), and BPA from their aqueous solutions after 24 h reached 98, 94, 82, 49, and 31%, respectively (122). (The values of Log *P*OW of them were 4.37, 4.27, 3.16, 2.8, and 2.20, respectively.) Comparing with the reported results, the removal capacities of this kind of PSF porous beads were 40 times and 11 times larger for DBF and DBD than those of polydimethylsiloxane membranes, respectively (120). Moreover, the adsorbed EDs in the PSF beads could be effectively removed by 2-propanol or ethanol, which indicated that the beads could be reused.

As mentioned previously, removal of EDs by the PSF porous beads resulted from the hydrophobic interaction between PSF and EDs and the microsphere porosity. Therefore, it is significant to control the hydrophobicity of materials, particle sizes, pore sizes and porosity for the achievement of expected adsorption. Moreover, it was reported that the removal ratio of the endocrine disruptors by the porous PSF beads increased with the increase of Log P_{OW} (124).

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HYBRID POLYMERIC PARTICLES

Activated Carbon/Polymer Hybrid Particles

Because of the large specific surface area, powdered materials, such as activated carbon (AC) and montmorillonite, have been most extensively used as adsorbents for removal of EDs non-specifically (59, 117). However, if AC contacted blood directly in some cases, fine carbon particles together with soluble organic compounds in the carbons would be eluted and non-compatibility with blood would be observed (125). Therefore, researchers explored the possibility of combining AC with polymeric particles, to achieve a better adsorption and avoid the disadvantages mentioned here.

Wang et al. prepared PES-AC hybrid particles by liquid-liquid phase separation technique (126). The powered AC was added into the PES/DMAc solution at certain proportions with sufficient stirring to obtain the PES-DMAC-AC mixtures, which were then injected into water to obtain PES-AC hybrid particles and incubated in water for over 24 h to elute the solvent from the particles. This hybrid particle had a porous structure and a relatively dense skin layer due to rapid phase separation, and the AC was embedded in the matrix of PES (Figure 1 b–d). The skin layer restricted the AC from being eluted. The porous structure led to large specific surface areas, which were essential for adsorbents (126).

The effect of the AC content in the hybrid particles on the removal ratio of PB was illustrated in Figure 2. It was indicated that PES-AC hybrid particles could remove up to 70% of the PB from its aqueous solution. Moreover, it was easy to prepare the particle column using these kinds of hybrid particles and the hybrid particle column could more effectively remove PB (126).

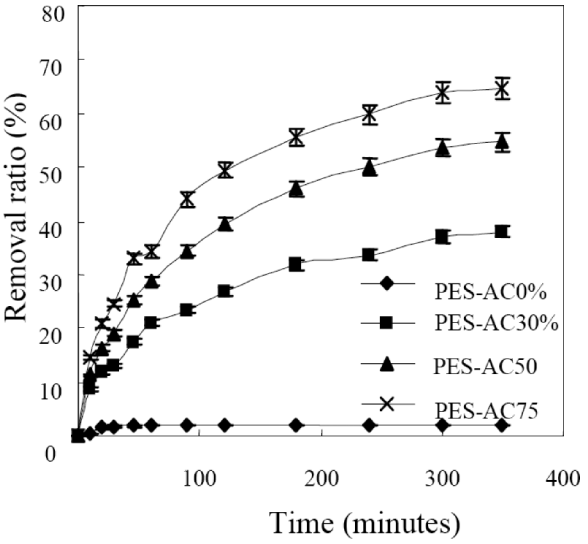

FIGURE 2 Phenobarbital (PB) adsorption on the polyethersulfone (PES)/activated carbon (AC) hybrid particles with different proportions of activated carbon. PB solution: 10 ml, 145 μmol/l; particles: 500 mg; Data were expressed as the mean ± SD of 3 independent measurements. Adapted from Ref. (126).

Mao et al. (127) and Deng et al. (128) prepared PSF/ AC hybrid particles and PES/AC hybrid particles respectively, of which the processes of preparation were similar to that of Wang (126). Both the hybrid particles also had skin layers outside and porous structures inside (127, 128).

The PSF/AC hybrid particles could adsorb BPA with high efficiency, and the adsorbed BPA to the hybrid particles could be effectively removed by ethanol, which indicated that the hybrid particles could be reused (127). The PES/AC hybrid particles show strong ability to adsorb creatine (128).

Montmorillonite/Polymer Hybrid Particles

Montmorillonite (MMT), another kind of natural adsorbent, has large specific surface area, low price, special mechanical property, and some other special properties. Therefore, it was also be used as adsorbent for removal of EDs (129–131). However, when the MMT or modified MMT is used directly, cations together with soluble compounds will be eluted. Therefore, hybrids of MMT and polymeric matrixes are studied extensively.

In a study by Chen et al. (132), Na-MMT was modified with Cetyltrimethylammonium bromide (CMAB) first to get an organic Na-MMT, which was then added into PES/DMAc solution to get a well-distributed suspension solution. The resultant suspension was injected into distilled water to get the hybrid MMT/PES hybrid beads. It was demonstrated that the modified MMT hybrid beads showed excellent adsorption ability to BPA. This may be due to

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m-MMT that has a larger interlayer spacing, which leads to a larger porosity and specific surface areas, and better hydrophilicity.

Cao et al. (133) carried out similar research, in which organic MMT modified by hexadecyl trimethyl ammonium bromide (HDTMA) was used. The process of preparation of hybrid beads was similar to that of Chen (132). These hybrid particles had a good performance on BPA adsorption, and the adsorption capacity per unit mass of the particles increased with the increase of the OMMT amounts in the particles. The BPA adsorbed could be effectively removed by ethanol, which indicated that the hybrid particles could be reused. Moreover, since the inter-surface chemical structure of MMT could be modified, it could be estimated that molecules with different sizes and chemical nature could be removed by the corresponding types of organophilic MMT (132).

In addition, Salipira et al. took advantage of cross-linked cyclodextrin polyurethanes copolymerized with functionalized multi-walled carbon nanotubes as adsorbents for organic pollutants, and very useful result was obtained (134).

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DNA/Polymer Hybrid Particles

To get rid of EDs with a higher efficiency in a wider range, some researchers have paid attention to DNA (135, 136). It is well-known that DNA is one of the most important genetic materials of living organisms (137). Moreover, as a naturally occurring and highly specific functional biopolymer, DNA has a double-stranded structure, which allows it to have various specific functions, such as intercalation, groove binding, and electron transfer (138–140). Therefore, it is possible to achieve broad-spectrum and specific adsorption of EDs with the help of DNA. Films and fibers can be prepared from DNA; however, utilization of DNA as an adsorbent of EDs is limited, because they are water-soluble and have low mechanical strength (135).

According to the reports of Nishi et al., water-insoluble and nuclease-resistant DNA films were prepared by ultraviolet (UV) irradiation, and insolubilized DNA immobilized onto porous glass beads was also prepared by treatment with UV irradiation (141–143); the DNA films and DNA-immobilized glass beads could remove DNA-intercalating compounds, such as ethidium bromide (EB), dioxin derivatives, benzo(a)pyrene, and metal ions (141–143).

However, as an adsorbent of EDs, DNA has another disadvantage—some harmful EDs that lack a planar structure, such as BPA and DES, did not bind the water-insoluble DNA films (144). Therefore, researchers tried to combine DNA with other materials to achieve a more broad-spectrum adsorption.

Yamada et al. prepared the water-insoluble DNA-β-Cyclodextrin (β-CD) composite material by mixing the double-stranded DNA and β-CD-immobilized poly(allylamine) (PCD) (144). As a result, these composite

materials had properties of both the double-stranded DNA, such as intercalation, and the cyclodextrin, such as encapsulation of an organic molecule into the intramolecular cavity. Therefore, these materials could accumulate, not only the EDs with planar structures, but also the nonplanar molecules, such as BPA, EDS, and nonylphenol.

Zhao et al. had modified PSF membranes with DNA; the hydrophilicity of the modified membranes increased, and the membranes showed better blood compatibility (145, 146). To get a higher capacity of adsorption to EDs, DNA-blended PSF microspheres were prepared by means of a liquid–liquid phase separation technique (123, 135, 136): PSF was dissolved in NMP to get a PSF solution; double-stranded DNA from salmon milt (a relatively cheap source) was dissolved in distilled water with various concentrations.

The DNA solution was then dropped into the PSF solution to obtain mixed solutions, which were injected into water with stirring to get the microspheres. The DNA-incorporated PSF microspheres were stable in water, especially the microspheres prepared by high PSF concentration solution (136). The release rate of DNA from the microspheres could be controlled by manipulating the microsphere structure (135, 136). The DNA-loaded PSf microspheres could effectively accumulate harmful DNA-intercalating pollutants and EDs, such as EB, acridine orange (AO), BP, DBF, and DBD. The amounts of removed EB after 24 h were 25.8, 54.5, 71.2, and 91.4%, for the microspheres prepared by 0, 0.002, 0.004, and 0.008 of DNA/ PSF (wt) solution respectively (Figure 3). Moreover, about 80% of the

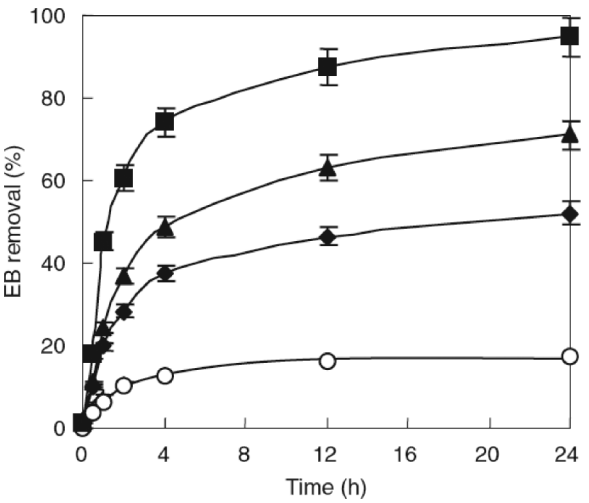

FIGURE 3 Influence of the amount of encapsulated DNA on the removal of ethidium bromide (EB) from aqueous solution. The data points corresponded to the following DNA/polysulfone (PSF) ratios: ○, 0; ♦, 0.002; ▲, 0.004; ■, 0.008. The PSF concentration was 10% in all cases. The data points corresponded to the mean obtained from 3 independent experiments. Adapted from Ref. (123).

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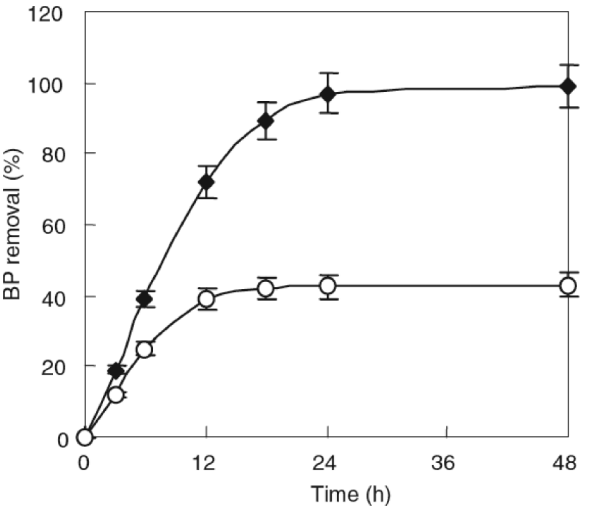

FIGURE 4 Kinetics of the removal of biphenyls (BP) from its aqueous solution by the polysulfone (PSF) particles in the presence or absence of DNA: ♦, DNA-blended particles (DNA/PSF ratio, 0.004); ○, particles without blended DNA. The data points corresponded to the mean obtained from three independent experiments. Adapted from Ref. (123).

DBD and almost all the BP was removed by the DNA-loaded microspheres, while only about 41% of the BP was removed by the PSF microspheres without DNA (Figure 4) (123). The amount of pollutants removed by the microspheres was dependent on the amount of incorporated DNA and on the porosity of microsphere (123, 135, 136).

As a parent polymeric materiel of PSF, polyethersulfone (PES) shows more outstanding oxidative, thermal and hydrolytic stabilities as well as good hydrophilic properties; therefore, attempts have also been carried out to prepare various DNA-blended PES porous beads (147–150).

The DNA-blended PES porous beads were prepared by liquid-liquid phase separation technique, just as that mentioned above for DNA-blended PSF porous beads (147, 149, 150). The DNA-blended PES microspheres are stable in water and NaCl solution, while DNA could be hydrolyzed under acidic conditions. As PES has a higher hydrophilicity than PSF, about twice amount of DNA could be incorporated into the PES microspheres compared to the PSF microspheres. Thus, the DNA-blended PES particles could remove a larger amount of organic compounds. The DNA-loaded porous PES particles could accumulate harmful DNA intercalating pollutants (e.g., EB and AO) (147, 149) and EDs (e.g., BP, DBF, and DBD). (150).

Yang et al. tried to encapsulate DNA inside PES hollow particles (148) to get a more stable DNA/PES blended particle: Double-stranded DNA aqueous solution was injected into a PES/DMAc solution with mild stirring (60 rpm) for a short time (20 s); as water is a non-solvent of PES, the PES would precipitate outside the droplets due to the rapid phase separation, and a

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skin layer would form outside the droplets. The nascent hollow particles obtained were removed out and exposed to air for some seconds, and then were incubated into water for over 24 h for solidification and elution of the residual DMAc. The double-stranded DNA was encapsulated in the PES hollow microspheres, while water molecules and other small molecules could freely pass through the wall of the microspheres because there were many pores in the wall. The DNA encapsulated PES particles could remove EDs such as BP and DBF effectively (148). Moreover, as the DNA was encapsulated in the particle, a high encapsulation rate of DNA (up to 80%) could be achieved. After the hollow particles were dried, the solid DNA inside was very stable. Once the hollow particles were put into water, water could enter the inside and form DNA aqueous solution again.

To introduce a more stable DNA component on the outer surface of PSF porous beads, chemical bonding was considered. DNA-immobilized porous beads were prepared and characterized (151): PSF/NMP solution was injected into water with stirring to obtain PSF beads. After post-treatment, the PSF beads were immersed in aqueous DNA solution (20 mg/ml DNA in H_2O) for 24 h. After drying at room temperature, the beads were irradiated with UV light at 254 nm for 5 h, and the beads were shaken once every 20 min. The amount of immobilized DNA onto the PSF beads increased with the increase of the concentration of the DNA solution used to treat the PSF beads. After UV-irradiation, DNA became water-insoluble and immobilized onto the PSF beads.

The DNA-immobilized porous PSF beads were stable in water, and no more than 3% of the initial immobilized DNA was eluted from the beads, even after being incubated for 24 h (145). However, about 70% of the initial immobilized DNA was eluted from the beads when it was incubated in hydrochloric acid solution (1 M), which suggested that DNA phosphodiester bonds might be hydrolyzed (145); about 20% of the initial immobilized DNA was eluted into the sodium dodecylsulfate (SDS) solution. Therefore, these DNA-immobilized PSF beads were applicable to adsorption in neutral solution. The experiments indicated that removal ratios were 83% and 100% for the EB and AO, respectively; the PSF beads without DNA also removed small amounts of the compounds, only 14.6% and 18.4% for the EB and AO (Figure 5) (151).

In DNA-hybrid PSF and PES porous particles, the biological molecules are combined with polymeric particles very well. DNA could function smoothly because the activity is ensured in the hybrid particles. The DNA hybrid polymeric particles have higher removal rates for EDs, not only those with high log P_{OW}, but also those with low P_{ow} but has planar structure. For the PSF microspheres without DNA, the removal ratios increased as the octanol–water distribution coefficients (log P_{OW}) increased. However, different results were obtained for those DNA-modified microspheres; almost all the BP and DBF were removed from their aqueous solutions, although the removal ratio for DBD only increased slightly under these conditions. (123).

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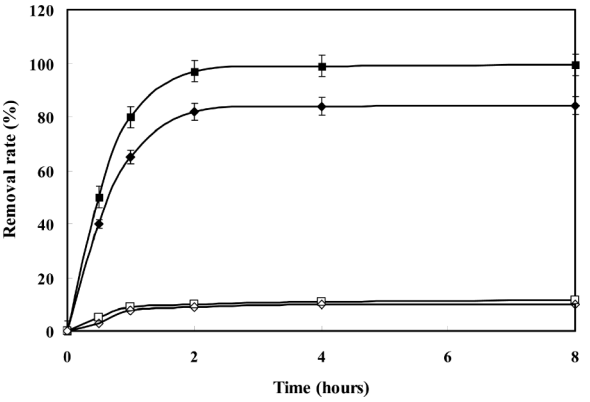

FIGURE 5 Removal rate of DNA-intercalating compounds by the DNA-immobilized porous polysulfone (PSF) beads (30 mg, n = 3): (■) DNA-immobilized beads in acridine orange solution (5 μM); (♦) DNA-immobilized beads in ethidium bromide solution (5 mM), (□) PSF beads without DNA in acridine orange solution; (◇) PSf beads without DNA in ethidium bromide solution. Adapted from Ref. (151).

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IMPRINTED POLYMERIC PARTICLES

However, for EDs with low log P_{ow} but without planar structure, methods mentioned above are not satisfactory. Moreover, with the development of technique of adsorption and separation, specific adsorption is a tendency, which, however, could not be realized by hybrid polymeric particles mentioned above. Therefore, adsorbents having specific molecular recognition ability are quite desirable. (152, 153) As molecularly imprinted polymers (MIPs) possess high selectivity and sensitivity for corresponding low molecular mass compounds, they attract attention of researchers in the field of EDs removal (154, 155).

Kubo et al. (156) prepared a kind of molecularly imprinted particles as follows: The polystyrene seed particles were prepared first through an emulsifier free emulsion polymerization (156); then ethylene glycol dimethacrylate (EDMA, cross-linking agent) and 4-vinyl pyridine (functional monomer), *p-tert*-butylphenol (TBP, template molecule) were polymerized with polystyrene seed particles; after rinsed with methanol and tetrahydrofuran (THF), the prepared polymeric particles were filtered with a membrane filter to get a product with excellent size uniformity. In this procedure, *p-tert*-butylphenol acted as a pseudo template molecule of the MIP for removal of Bisphenol A (BPA). The resultant MIP quantitatively concentrated dilute BPA up to 1000-fold. Since BPA cannot be utilized as the template molecule, this method can be a useful tool for analysis and removal of BPA in environmental water.

On this basis, Watabe et al. (157) replaced TBP with 4,4'-methyleneBisphenol (MBP) as the pseudo template molecule, because the

latter was structurally closer to BPA than the former. Moreover, It was demonstrated that the MBP template was more effective than the ordinary TBP template for chromatographic retention and selectivity.

In another case, taking advantage of a modified phase inversion imprinting, a non-covalent molecular imprinting approach, Yang et al. (158) prepared BPA-imprinted PES microspheres for the binding and recognition of Bisphenol A as follows: PES (24 wt%) and BPA (5 wt%) were added in DMAc respectively, and the resultant polymer solution was dropped into distilled water at room temperature to prepare porous microspheres. Because of the poor solubility of BPA in water, the BPA remained in the solid PES microspheres when the exchange between DMAc and water proceeded. After incubation in water for over 24 h, the microspheres were washed with methanol, ethanol or 1,4-butylene glycol for several days at 40°C to extract the template molecules. Thus, after the extraction of BPA from the solid particles, imprinting sites of the template were formed (158).

The FTIR results suggested that the PES and BPA interacted by hydrogen bonds. The imprinted microspheres showed the selectivity for BPA and structurally BPA-related compounds (158). However, it took more than 20 days for the template molecules in the microspheres to be extracted in ethanol during the preparation, which would limit the commercial application of the BPA-imprinted PES microspheres effectively. Therefore, in their subsequent research, Yang et al. (159) studied the BPA-imprinted PES microspheres when ethanol, acetone, acetone/ethanol solutions were used for the extraction of template molecules from the solidified polymeric particles.

It was found that acetone destroyed the inside structure, while ethanol and acetone/ethanol mixed solution (V : V = 25 : 75) could extract the template molecules but not change the porous structure in the imprinted particles; no recognition behavior was found in the imprinted particles extracted by the acetone, while the imprinted particles which were extracted by acetone/ethanol (V : V = 25 : 75) had similar recognition ability with ethanol-extracted particles (Figure 6). But it took much more time for the ethanol extraction than the acetone/ethanol extraction. Therefore, the acetone/ethanol mixed solution provided an efficient way to extract the BPA from the imprinted PES particles. Unfortunately, the binding and recognition ability for the imprinted particles disappeared under alkali condition, but they recovered as soon as possible when the solution changed from alkali condition to neutral or acid condition (159) .

In BPA and BPA-related compounds mixed solutions, the imprinted particles showed selectivity for the template molecule BPA. With the addition of Na^+, Mg^{2+}, and Cl^-, the binding amounts for the imprinted particles and non-imprinted control were not changed heavily, which indicated that these imprinted particles might be used in removal of EDs from seawater (159).

To extend the research and application of BPA-imprinted polymer, Yang et al. (160) prepared BPA-imprinted PSF particles. The process of preparation

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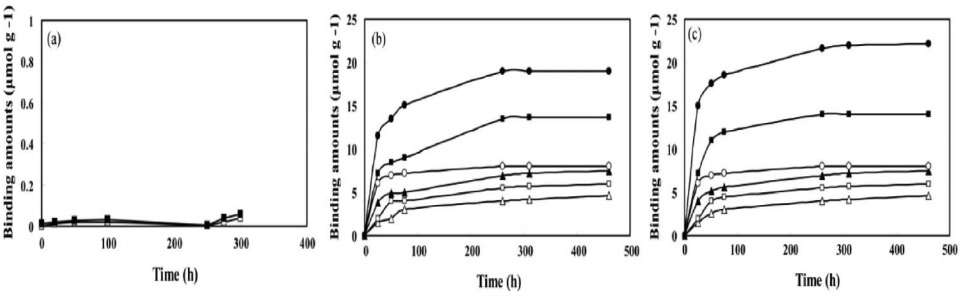

FIGURE 6 Time course of binding to the imprinted and the nonimprinted particles with different extraction methods. (a) was extracted in acetone, (b) was extracted in ethanol, (c) was extracted in acetone/ethanol (V : V = 25 : 75). In 50 μM, for the imprinted (▲) and the nonimprinted (△); in 100 μM, for the imprinted (■) and the nonimprinted (□); in 200 μM, for the imprinted (●) and the nonimprinted (○). Adapted from Ref. (159).

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was similar to that of BPA-imprinted PES particles: PSF (24 wt%) and BPA (5 wt%) were dissolved in DMAc respectively, and the resultant polymer solution was dropped into distilled water with stirring at about 300 rpm at room temperature to prepare porous particles. After incubation in water for over 24 h, the microspheres were extracted with ethanol by means of a Soxhlet extractor for 96 h at 90°C. The result indicated that, with the increase of BPA concentration in solution, the recognition ability of the imprinted particles increased.; with the increase of the BPA amounts in the PSF solution used to prepare the imprinted particles, the specific recognition sites increased, and thus the recognition capability increased; the binding amounts and the recognition coefficient became larger when the pH value decreased from 7 to 2, but the binding and recognition ability disappeared under alkali condition. Meanwhile, the imprinted PSF has the similar recognition ability as the imprinted PES, but the general prices of PSF are only 40%–70% of that of PES (160).

On the basis of BPA-imprinted PES particles (158), Zhao et al. (161) developed a kind of pH-sensitive imprinted PES particles by filling cross-linked polyacrylamide (PAA) gels into the pores of BPA-imprinted PES particles as follows: the nascent BPA-imprinted PES particle samples were soaked in acrylic acid aqueous solutions containing N,N-methylenebis (acrylamide) and 2,2'-azo-bis-iso-butyronitrile for 6–8 h before polymerization was carried out in an oven at 65°C for 24 h. After the polymerization, the particles were thoroughly extracted with boiling deionized water to remove the unreacted monomers. It was found that the structure of the particle had been substantially altered by incorporation of PAA. The void volume of the modified particle was occupied, at least in part, by the pore-filling polymer, which indicated that the pore size decreases as PAA gel was incorporated in the particles (161).

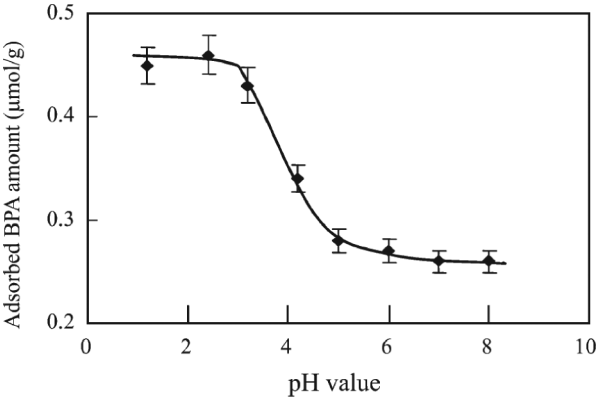

FIGURE 7 Adsorbed Bisphenol A (BPA) amount in 4 h as a function of pH value. Adapted from Ref. (161).

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The effect of pH changing from 1.5 to 8 on BPA uptake to the pore-filled imprinted particles was shown in Figure 7. From the figure, the BPA uptake of the pore-filled particles exhibits chemical valve behavior at pH between 3 and 6, and hardly changes at pH values lower than 2.5 or higher than 6.5. The chain configuration of weak polyacid is a function of pKa of the polymer. The pKa of PAA in solution is about 4.3–4.9, depending on the measurement method, which is consistent with that from Figure 7.

Thus, in the experiments at pH lower than 3, there were at least 90% (with respect to pKa around 4.6 from Fig. 7) of all the carboxyl groups in their unionized state; PAA gel segments coiled down resulting in pore opening. At pH values greater than 6, about 90% carboxyl groups dissociated and extended resulting in pore closing. A further decrease or increase in pH after the pH reached 2.5 or 6.5, respectively, would not change the PAA gel configuration significantly. Therefore, it could be verified that the introduction of PAA gels into the particles was essential for the creation of pH responsiveness, as shown in Figure 8 (161), and changing acidity of the solution reversibly controls the rebinding ability toward BPA.

As a specific adsorbent for selective remove of some EDs, imprinted polymers have attracted more and more interest of researchers. It can be expected that, with the development of new technique and new materials, various specific polymer-particle-based adsorbent will appear, which can remove EDs with more efficiency and higher selectivity.

CONCLUSION

Nowadays, more and more endocrine disruptors (EDs) threaten our daily life through drinking water, cosmetics and other personal care products,

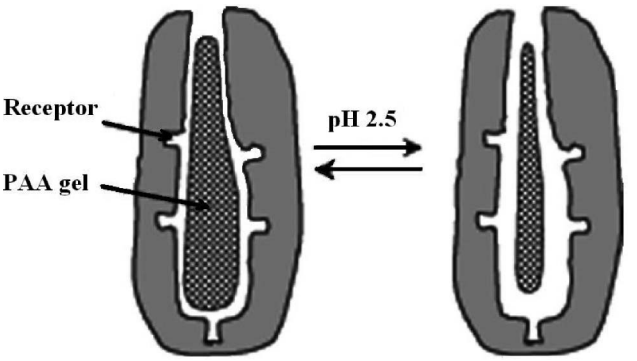

FIGURE 8 Schematic diagram of Switching of the substrate affinity of MIP receptors resulting from the swelling of polyacrylamide (PAA) gel. Adapted from ref (161).

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drugs, and foodstuffs. Therefore, researches on adsorption and separation of various EDs are in the ascendant. Compared with conventional techniques of adsorption and separation, polymeric particle-based materials are still in the early stage.

As hydrophobic porous polymeric particles prepared by means of liquid-liquid phase separation technique have relatively big specific surface area, non-specific adsorption can be achieved through the hydrophobic interaction. Selection of appropriate materials and reasonable control of the particle size, pore size and porosity are significant for achievement of the function of polymeric particles. Powders/ polymer hybrid materials, including AC/polymer and MMT/polymer hybrid particles, have stronger non-specific adsorption effect. DNA/polymer hybrid particles have good selectivity to EDs with planar structure. As for imprinted polymeric particles, as specific EDs or analogues act as template, the resultant adsorbents have significant effect of specific adsorption.

However, it is a pity that, at present, in the studies of various polymeric particles adsorbents, the matrixes are only limited in several polymer materials such as PSF, PES and cyclodextrin. It can be expected that, in the future, with the progress of new materials and new technique, increasingly more polymer-based adsorbents with specific adsorption capacity will be researched and developed.

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