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Review

Development of polymeric and polymer-based hybrid adsorbents for pollutants removal from waters

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ABSTRACT

In the past decades polymeric adsorbents have been emerging as highly effective alternatives to activated carbons for pollutants removal and subsequent recovery from industrial effluents. More recently, the development of polymer-based hybrid adsorbents has opened up the new opportunities of their application in deep removal of inorganic pollutants like heavy metals from waters. The present review focuses on preparation of these polymeric-based adsorbents, their physicochemical properties, adsorption characteristics and mechanism, as well as their application in water purification.

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1. Introduction

Adsorption is one of the most effective and simplest approaches to removing toxic and recalcitrant pollutants from aqueous systems, and activated carbon is one of the most widely used adsorbents for this purpose. The traditional pollutants including phenols, dyes, organic acids, and heavy metals, can be effectively trapped by activated carbons originated from different sources [1–5]. However, it is well recognized that activated carbon adsorption still suffers from costly regeneration and high attrition rate. Moreover, they tend to adsorb organic chemicals indiscriminately, making it difficult to selectively recover certain organic chemicals for reuse. Meanwhile, low-cost adsorbents have been widely prepared for water purification [6–11]. These adsorbents are produced on the basis of low-cost materials [6,7] or even wastes [8–11] and seem economically attractive for practical application. However, their adsorption capacities, mechanical strength, and other properties need further improvement for wider application.

In the past decades, polymeric adsorbents have been emerging as potential alternative to activated carbon in terms of their vast surface area, perfect mechanical rigidity, adjustable surface chemistry and pore size distribution, and feasible regeneration under mild conditions. Generally, polymeric adsorbents can effectively trap many of the ubiquitous organic pollutants, namely, phenolic compounds [12,13], organic acids [13–15], aromatic or polyaromatic hydrocarbons [16,17], alkanes and their derivatives [18]. Upon regeneration, the adsorbed organic chemicals are desorbed and may be recovered for further use [19,20]. To further improve adsorption performance of a given polymeric adsorbent toward other pollutants such as highly water-soluble compounds (e.g., sulfonated pollutants) and heavy metal ions, surface modification or functionalization has proved to be an effective approach because the functional groups bound to the polymeric matrixes are expected to provide specific interaction with the target pollutants [21,22].

More recently, polymer/inorganic hybrid adsorbents have emerged as a new class of adsorbent materials for deep removal of trace pollutants from waters. Generally speaking, these hybrid adsorbents can be fabricated by irreversibly dispersing inorganic nanoparticles (e.g., metal oxides, inorganic ion exchangers, zero-valent Fe) within different polymeric supports. One of the basic reasons for designing these new hybrid adsorbents relies on the fact that fine or ultrafine inorganic particles are unusable in fixed beds or any flow-through systems because of excessive pressure drops and poor mechanical strength, though most of them exhibit specific affinity toward target pollutants in waters. For example, metal (hydr)oxides namely Fe(III) [23–26], Mn(IV) [25,27,28], and Al(III) [24,25,29] oxides offer specific adsorption affinity toward charged pollutants like heavy metal ions [23–25,27,29] and phosphate or arsenate [26,28]. In addition, zero-valence Fe can effectively decontaminate some of the disinfection byproducts (DBPs) [30,31] in drinking waters. Thus, they have to be impregnated into porous supports of larger particle size to overcome the technical bottleneck, and porous polymeric materials seem more attractive than activated carbon [32–34], cellulose [35], alginate [36,37], diatomite [38,39], and sand [40–43] due to their excellent mechanical strength and adjustable surface chemistry.

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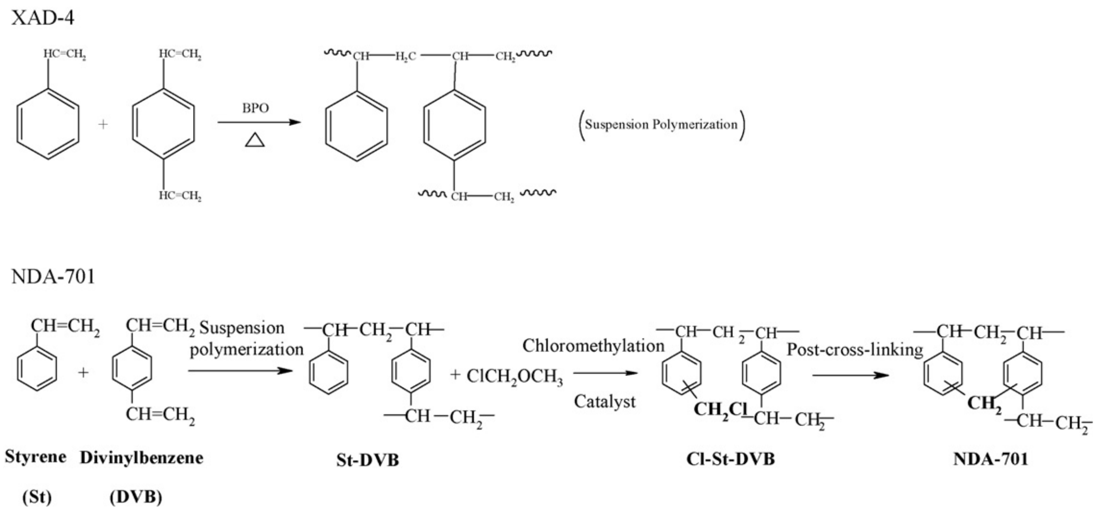


Scheme 1. Schematic illustration of synthetic procedures for a polystyrene adsorbent (XAD-4) and a hypercrosslinked polymeric adsorbent (NDA-701) [48].

The present review focuses on synthesis and characterization of these environmentally benign polymer-based adsorbents, their adsorption performance and mechanism, as well as their application in pollutant removal from water. Also, the forthcoming development in the field was discussed.

2. Polymeric adsorbents

Traditional polymeric adsorbents were first developed in the 1960s [44], and they were originally developed for use in gel permeation chromatography, but their outstanding physical properties have made them a very popular material for adsorption and filtration processes. Now they have been widely used in removal of organic pollutants from industrial wastewaters or natural waters [12–16]. These adsorbents exhibit vast surface area and perfect skeleton strength, and their basic physicochemical properties like internal surface area and pore size distribution are adjustable by varying the polymerization conditions [45–47]. As compared to activated carbon, the exhausted polymeric adsorbents can be amenable to an efficient regeneration under mild conditions like acid or alkaline rinsing [20,48]. As for the environmental concerns, the main polymeric adsorbents are based on polystyrene or polyacrylic ester matrix.

2.1. Polystyrene adsorbents

2.1.1. Synthesis and characteristics

Polystyrene adsorbents can be directly synthesized through suspension polymerization by using styrene as the monomer and divinylbenzene as the crosslinking agent [49], and polymerization occurs in the presence of pore-forming agents (Porogens) like toluene [50] or xylene [51]. These agents will be removed from the polymeric network after polymerization, resulting in a porous nature of the polymers [52]. Note that any residual free monomeric or crosslinking agents will be completely removed by extraction with organic solvent (e.g., ethanol) prior to practical use. Surface area and pore structure of a given polystyrene adsorbent mainly depend upon the usage of the crosslinking agents, and higher crosslinking agent ratio is generally believed to result in higher surface area and narrower pore. These adsorbents have been commercially available for decades, such as XAD-2 (4, 12 or 16) and Duolite ES-861 from Rohm Haas Co. (USA), Diaion HP-20 from Mitsubishi Chemical Co. (Japan), and H-5 from Nankai Chemical Plant (China). In general, they are highly durable due to the polystyrene nature, and always possess high surface area as well as high adsorption capacity. However, most of the inner pores of these adsorbents fall within the scope of macroporous ($d > 50$ nm) or mesoporous (d: 2–50 nm) ranges, and only a little fraction (always <5%) is microporous ($d < 2$ nm). For example, one of the most widely used adsorbent, Amberlite XAD-4, possesses about 880 m^2/g of BET surface area and its average pore diameter is ~11 nm [48]. The specific

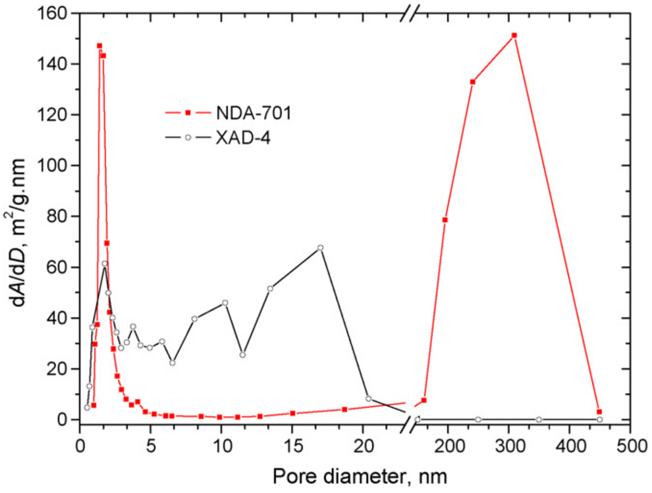
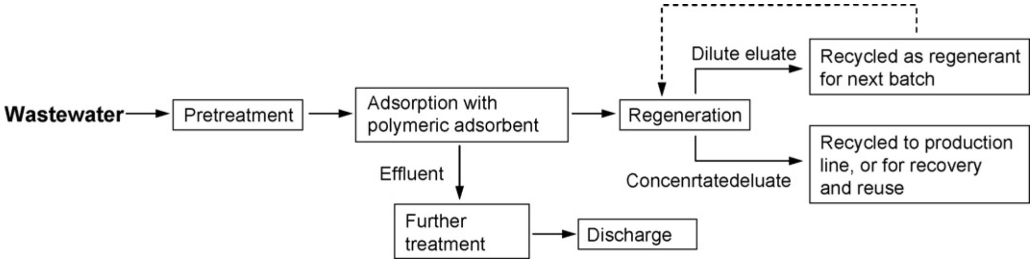


Fig. 1. Pore size distribution of the polystyrene adsorbents NDA-701 and XAD-4 [48].

Table 1
Characteristics of the polystyrene adsorbents XAD-4 and NDA-701 [48].

Adsorbent designation	NDA-701	XAD-4
Matrix	Polystyrene	Polystyrene
Average pore diameter (nm)	2.24	5.61
BET surface area (m^2/g)		
Total	824	886
Macropore	306	196
Mesopore	88	651
Micropore	430	39
Pore volume (cm^3/g)	0.58	1.22
Micropore volume (cm^3/g)	0.22	0.0043
Density (wet, g/ml)	1.08	1.04
Particle size (mm)	0.5–1.0	0.5–1.0
Swelling ratio in benzene (%)	<5	>15
Osmotic-attrited perfect ball ratio (%)	>99.5	~92



Scheme 2. A typical flow chart of industrial wastewater treatment by polymeric adsorbents [88].

pore distribution implies that, though high adsorption capacity is still available as a result of high surface area, micropore filling plays insignificant role in adsorption and the adsorption affinity between adsorbate and adsorbent may be relatively weak in the absence of other specific interactions. Consequently, deep removal of a given pollutant by these adsorbents always needs further improvement.

To further improve the adsorption performance, another polystyrene adsorbent, namely hypercrosslinked polymeric adsor-

Table 2
Polystyrene adsorbents used for organic pollutants removal from waters.

Polymeric adsorbents	Type	Organic chemicals	Maximum sorption capacities	Ref.
XAD-16	Polystyrene	Phenol, *p*-chlorophenol	1.5029 mmol/g (phenol), 2.2702 mmol/g (*p*-CP)	[12]
XAD-4	Polystyrene	Amino acids, phenylalanine, tryptophan	Not available	[14]
XAD-2, 4; Indion 1014 MN-2	Polystyrene	Phenol, Salicylic acid, *p*-hydroxy benzoic acid	0.2–3 mmol/g	[15]
XAD-2	Polystyrene	1-Naphthol, 2-naphthol, 1-naphthylamine, 2-naphthylamine	125.3 mg/g (1-naphthol), 109.3 mg/g (2-naphthol), 180.2 mg/g (1-naphthylamine), 208.6 mg/g (2-naphthylamine)	[16]
XAD-4	Polystyrene	1-Naphthol, 2-naphthol, 1-naphthylamine, 2-naphthylamine	307.4 mg/g (1-naphthol), 320.4 mg/g (2-naphthol), 473.6 mg/g (1-naphthylamine), 479.7 mg/g (2-naphthylamine)	[16]
XAD-1600	Polystyrene	Dichloromethane	27 mmol/g	[18]
XAD-2	Polystyrene	Di-2-pyridyl ketone salicyloylhydrazone	2.2 mg/g	[61]
XAD-4, 12, 16	Polystyrene	Benzoic acid	Not available	[62]
XAD-4	Polystyrene	Diethyl phthalate	649 ± 75.3 mg/g	[63]
XAD-2, 4	Polystyrene	Benzene	730 mg/g (XAD-2), 1400 mg/g (XAD-4)	[64]
XAD-2, 4	Polystyrene	Carbon tetrachloride	1250 mg/g (XAD-2), 2600 mg/g (XAD-4)	[64]
XAD-2, 4	Polystyrene	Chlorobenzene	825 mg/g (XAD-2), 2060 mg/g (XAD-4)	[64]
Duolite ES-861	Polystyrene	*m*-Cresol	141 mg/g	[65]
XAD-4, 16	Polystyrene	Phenol	Not available	[66]
XAD-4	Polystyrene	4-Chlorophenol	30.89 mg/g	[67]
XAD-2, 4	Polystyrene	Cephalosporin C, deacetylcephalosporin C	Not available	[68]
XAD-2, 4	Polystyrene	Atrazine	Not available	[69]
XAD-4	Polystyrene	Sodium 6-dodecyl benzene sulfonate, reactive brilliant blue KN-R	1.95 mmol/g (6-NaDBS), 0.4 mmol/g (KN-R)	[70]
XAD-2, 4	Polystyrene	Phenol, 4-chlorophenol, 2,4-dichlorophenol	≈0.4–2.5 mmol/g	[71]
XAD-2, 4	Polystyrene	Linalool	Not available	[72]
XAD-4, NDA-16	Polystyrene	Chloronitrobenzene	325 mg/g (NDA-16)	[73]
XAD-4	Polystyrene	phenol, *p*-cresol, *p*-chlorophenol, *p*-nitrophenol	0.603 mmol/g (phenol), 1.176 mmol/g (*p*-cresol), 1.428 mmol/g (*p*-CP), 1.200 mmol/g (*p*-NP)	[74]
XAD-4	Polystyrene	Phenol	Not available	[75]
XAD-4	Polystyrene	Caffeine, cephalosporin-C	28.505 mmol/g (caffein), 23.353 mmol/g (cephalosporin-C)	[76]
XAD-4	Polystyrene	Aniline, phenol	0.716 mmol/g (aniline), 0.521 mmol/g (phenol)	[77]
XAD-4	Polystyrene	Phenol, 4-chlorophenol	1.22 mmol/g (phenol), 1.47 mmol/g (4-CP)	[78]
NDA-701	Hypercrosslinked	4-Nitrophenol	≈600 mg/g	[48]
NJ-8	Hypercrosslinked	Phenol, *p*-cresol, *p*-chlorophenol, *p*-nitrophenol	1.455 mmol/g (phenol), 2.489 mmol/g (*p*-cresol), 2.891 mmol/g (*p*-CP), 2.364 mmol/g (*p*-NP)	[74]
Sample 390	Hypercrosslinked	Aniline, phenol	1.931 mmol/g (aniline), 1.390 mmol/g (phenol)	[77]
ZCH-101	Hypercrosslinked	Dyes, phenol	384.6 mg/g (phenol), 232.6 mg/g (RO), 20.9 mg/g (MB)	[79]
NDA-100	Hypercrosslinked	Resorcinol, catechol	0.814 mmol/g (resorcinol), 1.012 mmol/g (catechol)	[80]
NDA-150	Hypercrosslinked	Diethyl phthalate	825 mg/g	[81]
NDA-150	Hypercrosslinked	Sorbic acid	120 mg/g	[82]
CHA-111	Hypercrosslinked	Lipoic acid	12.2 mg/g	[83]
CHA-101	Hypercrosslinked	Terephthalic acid	90 mg/g	[84]
HXLGp	Hypercrosslinked	Oxamyl, methomyl, desisopropylatrazine	Not available	[85]
CHA-111	Hypercrosslinked	Phenol, benzoic acid, *o*-phthalic acid, benzene sulfonic acid, 2-naphthalenesulfonic acid	174.8 mg/g (phenol), 293.3 mg/g (benzoic acid), 202.8 mg/g (*o*-phthalic acid), 208.3 mg/g (BSA), 266.0 mg/g (2-NSA)	[86]
Hypersol-Macronet MN-200	Hypercrosslinked	Phenol, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol	0.922 mmol/g (phenol), 1.060 mmol/g (2-CP), 1.355 mmol/g (3-CP), 1.270 mmol/g (4-CP)	[87]

bent, was developed at the end of 1960s [53,54]. It can be available by suspension polymerization of styrene and divinylbenzene, followed by chloromethylation and post-cross-linking of the resulting polystyrene beads [55]. The commercial hypercrosslinked adsorbents are NDA-701, CHA-101, and NDA-150 from N&G Environ. Co. (China), and Hypersol-Macronet MN-200 & -250 from Purolite (UK). For comparison, synthetic procedures of XAD-4 and NDA-701 are briefly depicted in Scheme 1 [48], and their key structure data are listed in Table 1. In addition, their pore size distributions are illustrated in Fig. 1 [48].

One can see that NDA-701 possesses a little higher surface area and much more microporous volume than XAD-4. In fact, micropore region of a given adsorbent is believed to greatly enhance adsorption toward organic pollutants through micropore filling. Thus, higher capacity can be available at relatively low solute concentration for hypercrosslinked polymeric adsorbent [48]. However, the high degree of crosslinking may abate the diffusion of the solutes into the polymer bulk and consequentially decrease the adsorption capacity.

2.1.2. Application in water and wastewater treatment

Polystyrene adsorbents are now widely used for removal of organic pollutants particularly discharged from industrial effluents. Unlike activated carbon, polymeric adsorbents could be tailor made and their adsorption is generally a reversible process, i.e., the adsorbed organic chemicals from waste streams could be effectively desorbed under mild conditions for resource recovery or further treatment. The desorption reagents required depend mainly on the properties of the adsorbed pollutants, the typical ones being inorganic acids (e.g., HCl, H_2SO_4), alkaline (NaOH, Na_2CO_3), or organic solvents (methanol, alcohol, acetone) [20,51,57–60]. Table 2 summarizes recent literatures and patents on polystyrene adsorbents employed for organic species removal from industrial effluents or natural waters.

Generally, fixed-bed adsorption-regeneration process is frequently proposed for their industrial application. Scheme 2 presents a typical flow diagram for the process [48,88].

2.1.3. Case study

2.1.3.1. Case 1. 2,3-acid manufacturing effluent treatment. NDA-708, a hypercrosslinked polystyrene adsorbent manufactured by N&G Environmental Co. (China), was chosen to treat the 2-napthol-3-carboxylic acid (2,3-acid) manufacturing effluent based on a fixed-bed process [57]. The acidic effluent contained 700–800 mg/L of 2-naphthol and 2,3-acid totally, and its COD (chemical oxygen demand) value was about 1500–500 mg/L. After being treated, 99.5% of naphthalene derivatives as well as 98.5% of COD were effectively removed, and the effluent quality met the national emission standard of China after pH adjustment to 6–9. 2,3-acid and 2-naphthol adsorbed on the polymeric adsorbent could be effectively rinsed by NaOH solution with desorption efficiency nearly to 100%. The concentrated 2,3-acid and 2-naphthol solution was then recycled to the production process for resource recovery without any further treatment. In china, there are eight 2,3-acid manufacturing plants adopting the above-mentioned process to treat their organic effluents, and more than 700,000 m^3 of the effluent was effectively disposed of annually for safe discharge. Moreover, more than 500 ton of naphthalene derivatives were recovered.

2.1.3.2. Case 2. Phenylacetic acid manufacturing effluent treatment. A hypercrosslinked polystyrene adsorbent (NDA-999, manufactured by Jinxiang Chemical Plant, China) was employed to treat phenylacetic acid manufacturing effluent [20]. The effluent contained 3.5–3.7 g/L of phenylacetic acid, 0.1–0.5 g/L benzyl alcohol and benzaldehyde, and ~5% NaCl. Its COD value was near to 13,700 mg/L. After NDA-999 adsorption, over 99.5% of the organic pollutants could be removed before the significant breakthrough occurred. The effluent containing the residual NaCl was then transferred to an electrolysis process to produce NaOH. Phenylacetic acid loaded on NDA-999 could be effectively rinsed by dilute NaOH solution, while other organics like benzyl alcohol and benzaldehyde could be desorbed by methanol. The eluted solution containing concentrated phenylacetic acid was directly recycled into the production line for recovery of phenylacetic acid. As for the used methanol, it can be recovered by distillation, the residues disposed of by incineration. The exhausted adsorbent after regeneration could be employed for repeated use without any capacity loss. The process was employed to treat the industrial effluent (about 40 ton per day) in a chemical plant (Shandong province, China).

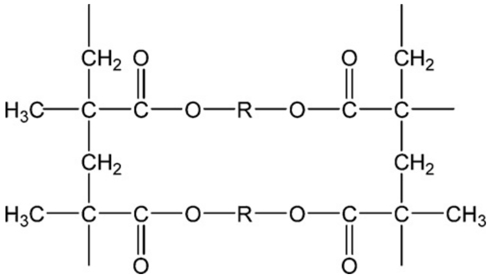


Fig. 2. Schematic structure of polyacrylic ester adsorbent (R denotes the crosslinking reagent, e.g., dimethyl acrylate glycol ester) [89].

2.2. Polyacrylic ester adsorbent

2.2.1. Synthesis and characteristics

Polyacrylic ester adsorbent can be synthesized according to a similar process to polystyrene adsorbent, except that the monomer is acrylate instead of styrene for the latter one. Its chemical structures can be generally represented by Fig. 2 [89]. Acrylate exhibits relatively larger reactivity than styrene during the copolymerization process and thus, the polyacrylic ester adsorbents seem mechanically more stable than the polystyrene adsorbents [90]. In addition, they are polar and hydrophilic due to the presence of acrylic ester groups. Commercially available polyacrylic ester adsorbents include Amberlite XAD-7, -7HP and -8 from Rohm Haas (US), Wofatit EP62 and Y59 from Chemie AG Bitterfeld (Germany), and NDA-7 from Jiangsu N&G Environ. Co. (China).

2.2.2. Application in water and wastewater treatment

Due to their polar and hydrophilic characteristics, the polyacrylic ester adsorbents have been successfully applied for removal and recovery of highly water-soluble compounds from water and wastewater, typical of which are reactive dyes and some sulfonated compounds. Also, the polyacrylic ester adsorbents show easier regeneration characteristic as compared to polystyrene adsorbents, this characteristic may offer excellent opportunities conducive to decolourisation of a wide array of dye from contaminated water bodies. Table 3 is a compilation of literature and patents on organic removal by polyacrylic ester adsorbents.

As for the adsorption mechanism, hydrophobic interaction, ionic attraction, hydrogen bonding, and even complex formation possibly occur under different operation conditions [97]. Our recent study [89] elucidated that hydrophobic interaction and electrostatic interaction play a synergetic role in effectively scavenging sulfonated pollutants by a polyacrylic ester adsorbent NDA-801. It is well recognized that the hydrophobic interaction plays a favorable role in adsorption [87,77]. Besides, the ester groups bound to porous polymeric matrix are partially positively charged under acidic solution and thereby, electrostatic interaction occurs between the positively charged ester groups and anionic adsorbates.

Table 3
Organic pollutants removal by polyacrylic ester adsorbent.

Polyacrylic adsorbents	Organic chemical	Maximum sorption capacities	Ref.
XAD-7, 8	2-Naphthylamine	232.5 mg/g (XAD-7), 263.2 mg/g (XAD-8)	[16]
XAD-7, 8	1-Naphthol	278.0 mg/g (XAD-7), 296.5 mg/g (XAD-8)	[16]
XAD-7, 8	1-Naphthylamine	256.4 mg/g (XAD-7), 267.1 mg/g (XAD-8)	[16]
XAD-7	Dichloromethane	17.76 mmol/g	[18]
XAD-7	Phenol	78.7 mg/g	[51]
XAD-7	Di-2-pyridyl ketone salicyloylhydrazone	10.4 mg/g	[61]
XAD-8	Phenol	Not available	[62]
XAD-7	Diethyl phthalate	480 ± 49.9 mg/g	[63]
XAD-7, YWB	Sodium 6-dodecyl benzene sulfonate, reactive brilliant blue KN-R	0.65–1.6 mmol/g	[70]
XAD-7	Linalool	Not available	[72]
XAD-7	Caffeine, cephalosporin-C	58.322 mmol/g (caffein), 62.676 mmol/g (cephalosporin-C)	[76]
XAD-7	Phenol, 4-chlorophenol	0.84 mmol/g (phenol), 1.31 mmol/g (4-CP)	[78]
NDA-801	Sodium 2-naphthalene sulfonate	123 mg/g	[89]
NDA-7; XAD-7	Dimethyl-isophthalate-5-sulfonic acid	Not available	[91]
XAD-7	*p*-Cresol, *N*-methylaniline	Not available	[92]
NDA-7	5-Sodiosulfoisophthalic acid	Not available	[93]
Wofatit EP62, Y59	Ethoxylated aliphatic mines	Not available	[94]
XAD-6 (7 or 8), YWB-38	4,4′-Dinitrostilbene-2,2′-disulfonic acid (DNS)	Not available	[95]
XAD-7	Alachlor, trifluralin, prometryn, amitrole	Not available	[96]

3. Chemically modified polymeric adsorbent

Chemical modification is generally an effective approach to improving adsorption performance of a polymeric adsorbent toward some specific pollutants. For example, many environmentally significant aromatic compounds, namely, aromatic carboxylic acids, naphthalene and benzene sulfonic acids, and quaternary benzylammonium compounds exist as ions in the aqueous phase over a wide range of pH. They are often referred to as hydrophobic ionizable organic compounds (HIOCs) [98,99]. Because of their high water solubility, they cannot be effectively trapped by traditional nonpolar polystyrene adsorbents from aqueous systems. In view of theory, it is viable to solve the technical difficulty by modifying surface chemistry of a polystyrene adsorbent and thereby enhancing the adsorbate–adsorbent affinity. Till now there are numerous chemically modified polymeric adsorbent available for this purpose. Table 4 summarizes recent literature and patents on chemically modified polymeric adsorbents for pollutants removal from waters.

To further elucidate the characteristics and possible application of a chemically modified polymeric adsorbent, here an amine-modified polystyrene polymeric adsorbent M-101 was selected as a

Table 4
Pollutants removal by functionalized polymeric adsorbents.

Polymeric matrix	Functional group	Pollutants	Maximum sorption capacities	Ref.
Hypercrosslinked polystyrene	Tertiary amino group	Sodium benzene sulfonate	1.2 mmol/g	[21]
Hypercrosslinked polystyrene	Carboxyl group	p-Nitroaniline	3.2 mmol/g	[22]
Polystyrene	Tertiary amino group	Resorcinol, catechol	1.0–1.8 mmol/g	[80]
Hypercrosslinked polystyrene	Tertiary amine	Phenol, benzoic acid, *o*-phthalic acid, benzene sulfonic acid, 2-naphthalenesulfonic acid	90–270 mg/g	[86]
Polystyrene	Tertiary amine	Methomyl	40 mg/g	[100]
Polystyrene	Sulfonic acid group	Methomyl	5 mg/g	[100]
Polystyrene	Dicyandiamide	Reactive brilliant blue KN-R	28.1 mg/g	[101]
Hypercrosslinked polystyrene	Amidocyanogen	Phenol, aniline	Not available	[102]
Polystyrene	Sulfonic group	Acetylaminophenol	428.5 mg/g	[103]
Polystyrene	Amino group	Naphthalene sulfonates	108 mg/g	[104]
Polystyrene	Polyethylene glycol group	Yellow 5GL	Not available	[105]
Polystyrene	2-Carboxy-3/4-nitrobenzoyl, 2,4-dicarboxybenzoyl	Oxamyl, methomyl, desisopropylatrazine, phenol, dimethoate, atrazine, 2,4-dichlorophenoxy acetic acid, hydroquinone, resorcinol, catechol, orcinol, guaiacol	Not available	[106]
Polyacrylamide	Lateral alkyl quaternary ammonium group	Cholate, taurocholate, chenodeoxycholate	1.35–1.73 mmol/g	[107]
Polystyrene	Nitrosonaphthol	Cu(II), Ni(II)	6–10 mmol/g	[108]
Polystyrene	Dithiooxamide	Cu, Zn(II), Cd(II), Pb(II)	0.97 mmol/g (Cu), 0.12 mmol/g (Zn, Pb), 0.08 mmol/g (cd)	[109]
Polystyrene	Bis-2[(*O*-carbomethoxy)-phenoxy]ethylamine	La(III), Nd(III), Sm(III)	0.5–0.7 mmol/g	[110]
Polystyrene	Palmitoyl quinolin-8-ol	Mn(II)	0.03 mmol/g	[111]
Polystyrene	1,2-Bis(*o*-aminophenylthio)ethane	Hg(II), MeHg(I)	0.38 mmol/g (Hg), 0.30 mmol/g (MeHg)	[112]
Polystyrene	Catechol	Cd(II), Cu(II), Ni(II), Pb(II)	25–90 umol/g	[113]
Polystyrene	2-Naphthol-3,6-disulfonic acid	Cr(III), Cr(VI)	1.35 mmol/g	[114]
Polystyrene	1-(2-Thiazolylazo)-2-naphthol	Zr(IV), Hf(IV)	0.92 mmol/g (Zr), 0.87 mmol/g (Hf)	[115]
Polystyrene	Amino group	Hg(II), U(VI), Pb(II)	0.8 mmol/g (Hg), 1.13 mmol/g (U), 0.36 mmol/g (Pb)	[116]
Polystyrene	Palmitoyl hydroxyquinoline	Ga(III)	Not available	[117]
Polystyrene	Bicine	La(III), Nd(III), Tb(III), Th(IV), U(VI)	0.35 mmol/g (La), 0.40 mmol/g (Nd), 0.42 mmol/g (Tb), 0.25 mmol/g (Th), 0.38 mmol/g (U)	[118]

Table 5
Salient properties of an aminated polystyrene adsorbent M-101 [21].

Crosslink density (%)	>35
BET surface area (m^2/g)	671.5
Macropore volume (cm^3/g)	0.16
Mesopore volume (cm^3/g)	0.028
Micropore volume (cm^3/g)	0.40
Total anion exchange capacity (mequiv./g)	1.53
Quaternary ammonium group (mmol/g)	0.027

representative one because of its wide application in HIOCs removal from industrial streams in China.

3.1. Synthesis and characterization of an amine-modified polystyrene adsorbent M-101

The amine-modified polystyrene adsorbent M-101 of high surface area could be synthesized according to a proprietary technique [119]. In brief, its synthesis consists of three basic steps. First, polystyrene beads were synthesized through suspension polymerization of styrene and divinylbenzene. Second, the resulting polystyrene beads were chloromethylated to create possible bond bridge for sequent amination. Third, the chloromethylated beads were aminated by dimethylamine and we obtained M-101, an aminated polystyrene adsorbent [56]. Salient properties of the aminated polystyrene adsorbent M-101 were listed in Table 5 [21].

From Table 5 one can see that M-101 possesses not only basic properties of a hypercrosslinked polystyrene adsorbent (e.g., high surface area and micropore volume), but a large amount of amine groups, which is similar to a weakly basic anion exchanger. Such interesting structure of M-101 renders it to be an effective adsorbent for many HIOCs like sulfonated compounds. Our earlier study [21] demonstrated that M-101 exhibited much higher adsorption capacity toward sulfonated aromatics (e.g., benzene sulfonate, naphthalene sulfonate) than a hypercrosslinked polystyrene adsorbent CHA-101. Moreover, its adsorption preference toward these sulfonated aromatics over sodium sulfate is much higher than a weakly basic anion exchanger D-301. Such satisfactory performance of M-101 is mainly attributed to the π–π interaction between the aromatic nature of polymeric matrix and nonpolar moiety of the adsorbate, as well as electrostatic interaction between the positively charged amine groups under acidic pH and the sulfonated anions [56].

3.2. Field application of M-101 in chemical wastewater treatment

The aminated polymeric adsorbent M-101 has been widely applied for removal of aromatic sulfonates from industrial wastewater. For example, M-101 was successfully adopted to remove 1- and 2-naphthalene sulfonates (NS) from 2-naphthol manufacturing effluent (500 m^3/d, Chuanqing Chemical Plant, China) [120]. The feeding wastewater contains about 1500 mg/L 1-NS, 5000 mg/L 2-NS, and 7–12% of sodium sulfate. Field application results showed that total NS was removed to below 40 mg/L. The regeneration efficiency of about 99% could be achieved by using 2 M NaOH as regenerant. The concentrated eluate solution was further treated by condensation and recycled to the production line for NS recovery. The above process has been employed in four plants in China, treating about 400,000 m^3 of industrial effluent annually. Another example is to treat the manufacturing wastewater for DSD acid (4,4′-dinitrobenzyl ethylene-2,2′-disulfonic acid) in Huaihua Chemical Co.(Jiangsu, China) and Huayu Chemical Group (Hebei, China). This industrial stream contained about 3500 mg/L DNS acid (4,4′-diaminobenzylethylene-2,2′-disulfonic acid) and as high as 10–15% of sodium sulfate [121]. Field application results demonstrated that, after adsorption with M-101, DNS acid in the effluent decreased to less than 30 mg/L. Its superior property of M-101 was manifested by more than 2-year continuous running performance in industrial scale.

4. Polymeric chelating adsorbents

Polymeric chelating adsorbents have been tailor made to selectively adsorb toxic heavy metals from industrial streams or other aqueous systems, and widely applied in concentration control (preconcentration of the trace elements from solutions) for analytical purposes [50,122–134]. Such adsorbents generally consist of two sections: the polymeric matrix and the immobilized chelating groups. We were particularly interested in different chelating groups, which are expected to offer specific interactions with targeted metals through complex formation. Such specific interactions are generally interpreted by Lewis acid–base principle, where the chelating groups can be taken as Lewis bases while the heavy metal ions, Lewis acids. Some of recent developments on polymeric chelating adsorbents employed for heavy metals removal are summarized in Table 6.

Table 6
Polymeric chelating adsorbents for selective heavy metals removal from aqueous media.

Polymeric adsorbents	Chelating groups	Targeted pollutants	Maximum sorption capacities	Ref.
Iminodiacetate chelating resins	Iminodiacetate groups	Cu(II), Co(II), Ni(II)	3.257 mmol/g (Cu), 2.6 mmol/g (Co), 2.809 mmol/g (Ni)	[50]
Poly(MMA-MAGA)	Methacryloylamidoglutamic acid groups	Hg(II), Cd(II), Pb(II)	29.9 mg/g (Hg), 28.2 mg/g (Cd), 65.2 mg/g (Pb)	[122]
Chelex 100	Iminodiacetic acid groups	Ni(II)	2.15 mmol/g	[123]
Poly(GMA-co-EGDMA)-en	Ethylene diamine	Pt(IV), Cu(II), Pb(II), Cd(II)	1.30 mmol/g (Pt), 1.10 mmol/g (Cu), 1.06 mmol/g (Pb), 0.67 mmol/g (Cd)	[124]
GMA/DVB magnetic resin	Iminodiacetic acid groups	Pb(II), Cd(II), Zn(II), Ca(II), Mg(II)	2.3 mmol/g (Pb), 2.0 mmol/g (Cd), 1.65 mmol/g (Zn), 1.60 mmol/g (Ca), 1.48 mmol/g (Mg)	[125]
Amberlite IRC-718	Iminodiacetate groups	Fe(III), Al(III), Ni(II), Zn(II)	Not available	[126]
Gel-type chelating resins	Dithiocarbamate groups	Hg(II), Pb(II), Cd(II)	Not available	[127]
Dowex M 4195	Bispicolylamine groups	Cr(VI)	29.7 mg/g (Cr)	[128]
2,3-DHBA-XAD	2,3-Dihydroxy benzoic acid groups	Fe(III)	Not available	[129]
PASP chelating resin	Aspartate groups	Cu(II), Cd(II)	1.40 mmol/g (Cu), 1.28 mmol/g (Cd)	[130]
Chelex 100	Iminodiacetic acid groups	Cu(II)	1.6 mmol/g	[131]
Benzothiazole-based chelating resin	Benzothiazole groups	Cu(II), Cd(II), Pb(II)	5.68 mmol/g (Cu), 1.03 mmol/g (Cd), 1.55 mmol/g (Pb)	[132]
PGLY chelating resin	Glycine groups	Cu(II), Ni(II), Cd(II)	1.22 mmol/g (Cu), 1.07 mmol/g (Ni), 0.96 mmol/g (Cd)	[133]
Azophenolcarboxylate -based chelating resin	Azophenolcarboxylate groups	Cr(III), Cr(VI)	0.38 mmol/g Cr(III), 0.69 mmol/g Cr(VI)	[134]

Table 7
Polymer-based hybrid adsorbents for inorganic pollutants removal.

Polymeric substrate	Inorganic nanoparticles	Targeted pollutants	Detailed performance	Ref.
Polymeric cation exchanger	$Zr(HPO_4)_2$	Pb(II)	Pb(II) removed from 40 to <0.05 mg/L within 2000 BV	[140]
Polymeric anion exchangers	Hydrated ferric oxide	Phosphate	P(V) removed from 100 to <5 ppb within 10,000 BV	[141]
Polymeric anion exchangers	Hydrated ferric oxide	Arsenic	As(V) removed from 23 to <0.5 ppb within 33196 BV	[143]
Polyacrylamide	Hydrated ferric oxide	Pb(II), Hg(II), Cd(II)	Adsorption capacities are 211.4 mg for Pb(II), 155.0 mg for Hg(II), 147.2 mg for Cd(II) per g of adsorbent	[144]
Polymeric anion exchangers	Hydrated ferric oxide	Arsenic	As(V) removed from 50 to <10 ppb within 4000 BV, As(III) removed from 100 to <10 ppb within 2000 BV	[145]
Polymeric anion exchangers	Hydrated ferric oxide	Arsenic	As(V) removed from 300 to <10 ppb within 3500 BV, As(V) removed from 20 to <10 ppb within 17,500 BV	[146]
Polystyrene adsorbents	Hydrated ferric oxide	Arsenic	Arsenic removed from 100 to <10 ppb within 60 BV	[147]
Cation exchange adsorbents	Fe(III) oxides	Se(IV); As(V)	Se(IV) removed from 100 to <0.5 ppm, As(V) removed from 100 to <0.5 ppm	[148]
Fibrous polymeric ion exchangers	Hydrated ferric oxide	As(III), As(V)	Arsenic removed from 60 to <10 ppb within 10000 BV	[149]
Polymeric cation exchanger	$Zr(HPO_3S)_2$	Pb(II), Cd(II), Zn(II)	Pb(II) removed from 50-130 to <10 ppb within 50,000 BV, Cd(II) removed from 80–140 to <3 ppb within 9000 BV	[150]
Polymeric cation exchanger	Hydrated ferric oxide	Pb(II), Cu(II), Cd(II)	Metal ions removal from 1 ppm to <5 ppb within 7000 BV	[151]
Polymeric cation exchanger D-001, 001 × 7; D-113	Hydrous manganese oxide	Pb(II), Cd(II), Zn(II)	Kd increased by 20–800 times as compared to host exchangers, sorption capacities increased by 50–300%	[152]

Though heavy metals can be selectively trapped by chelating adsorbents, it is noteworthy that regeneration of the exhausted chelating adsorbents for repeated use is still a challenging and costly task due to the strong affinity between the adsorbents and heavy metals. Therefore, how to balance the adsorption and regeneration properties of a given chelating adsorbent is still an important but somewhat difficult aspect in future.

5. Polymer-based inorganic hybrid adsorbents

Water pollution by inorganic pollutants, e.g., heavy metals, arsenic, has adverse effects on ecosystems and human health, and exposure to heavy metals even at trace level is believed to be a risk for human beings [135,136]. It has been a major preoccupation for many years to develop efficient technologies for enhanced removal of these toxic pollutants from waters. In the past decades, many environmentally benign inorganic particles, namely, metal (hydr)oxides (e.g., Fe(III) [23–26], Mn(IV) [25,27,28], and $M(HPO_4)_2$ (M = Zr, Ti, Sn) [137,138]) have been exploited as efficient adsorbents for enhanced removal of these targeted pollutants. Unfortunately, these inorganic adsorbents are usually present as fine or ultrafine particles and suffer from issues involving mass transport and excessive pressure drops when applied in fixed bed or any other flow-through systems [139]. An effective approach to overcoming this technical bottleneck is to fabricate hybrid adsorbents by impregnating or coating the fine particles onto the porous supports of larger particle size [32–43]. The widely used support materials include activated carbon [32–34], cellulose [35], alginate [36,37], diatomite [38,39] and sand [40–43]. In recent years, porous polymeric adsorbents or ion exchangers proved to be ideal alternatives

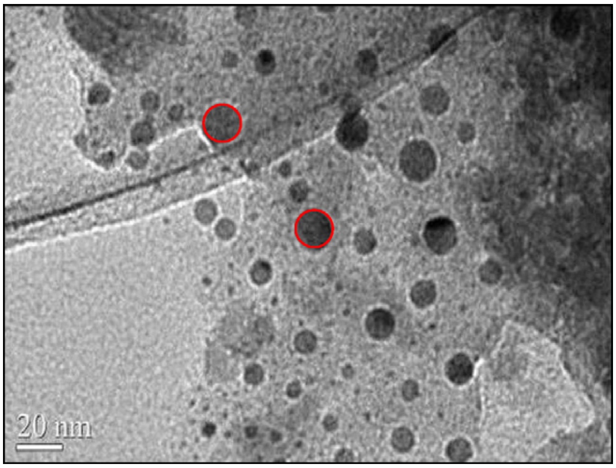


Fig. 3. Transmission electron micrographs of ZrP-loaded D-001 (ZrP-001).

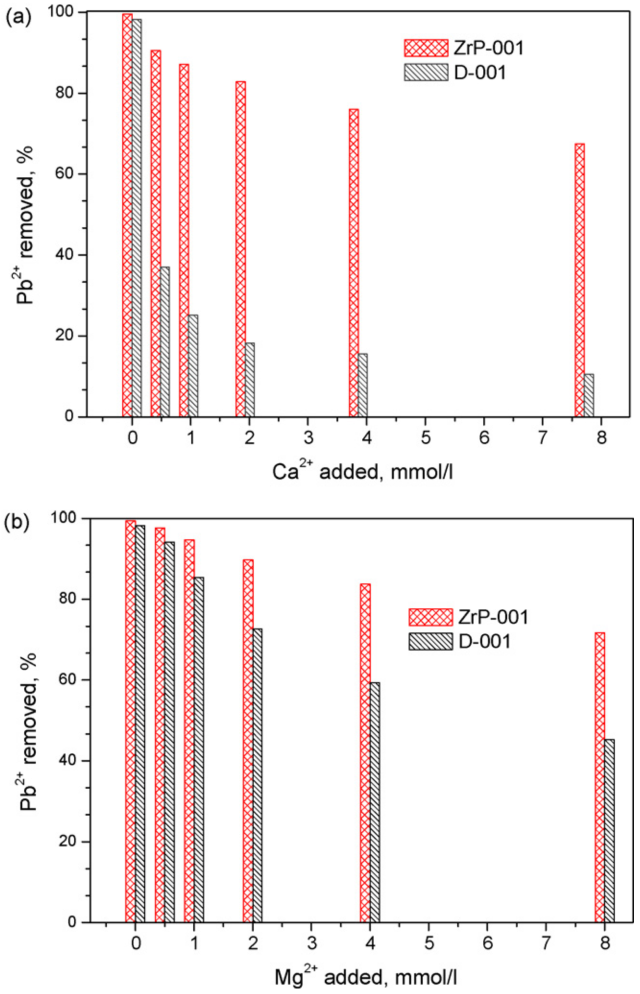


Fig. 4. Effect of competing cations on lead removal by ZrP-001 and D-001 at pH 4.0 and 303 K. (a) Ca^{2+}, (b) Mg^{2+} (0.25 g of each sorbent was introduced into 100-mL solution containing 0.25 mM Pb^{2+}) [140].

to fabricate similar hybrid adsorbents [140,141]. This is mainly because of the excellent mechanical strength and adjustable surface chemistry of the polymeric supports. For example, when a polymeric exchanger is chosen as support material of a given hybrid adsorbent, the immobilized charged functional groups bound to the polymeric matrix would greatly enhance permeation of inorganic pollutants of counter charges, which is called Donnan membrane effect [139,142]. Table 7 summarized some typical hybrid adsorbents based on polymeric materials. Also, we exemplify two typical hybrid adsorbents to further elucidate their unique properties for removal of trace pollutants from waters.

5.1. Polymer-supported zirconium phosphate (ZrP) for lead removal

In our earlier study we impregnated zirconium phosphate (ZrP) onto a porous strongly acidic cation exchanger D-001 and obtained a new hybrid adsorbent ZrP-001 [140]. TEM of ZrP-001 depicted in Fig. 3 indicated that ZrP preloaded within D-001 was nanosized, which is understandable because the average pore size of D-001 was about 34.1 nm. The ZrP content in ZrP-001 is about 30% in mass. The new hybrid adsorbent inherited excellent mechanical and hydraulic properties of the support exchanger D-001. Moreover, $Zr(HPO_4)_2$ nanoparticles immobilized within D-001 are expected to exhibit preferable adsorption toward lead ion over other innocuous but ubiquitous cations like Ca^{2+}, Mg^{2+}, and Na^+.

Compared to D-001, ZrP-001 exhibited more favorable lead adsorption even in the presence of Ca^{2+} or Mg^{2+} at greater levels (Fig. 4). Such unique performance of ZrP-001 was mainly attributed to two aspects, the host material D-001 and the loaded ZrP particles. As for D-001, the non-diffusible negatively charged sulfonic acid groups bound to D-001 matrix would greatly enhance permeation and preconcentration of lead ion from solution to inner surface of the polymeric phase [140,150], which would greatly facilitate enhanced lead removal by ZrP particles. Moreover, lead ion can be selectively sequestrated by ZrP particles through possible inner–sphere complexation of Pb(II) and ZrP [137]. Additionally, the exhausted ZrP-001 beads can be efficiently regenerated by 2% HNO_3 or HCl solution at 303 K for repeated use without any significant capacity loss.

Similarly, other inorganic particles exhibiting specific affinity toward heavy metal ions, namely, hydrated ferric oxides (HFOs), $Zr(HPO_3S)_2$, $Ti(HPO_4)_2$, hydrated manganese oxide (HMO), can also be dispersed within porous cation exchanger to obtain heavy metal-specific hybrid adsorbents [142,150,152].

5.2. Polymer-based hydrated ferric oxides (HFOs) for arsenic removal

Hydrated ferric oxides can selectively bind anionic ligands (e.g., arsenate, phosphate) through inner–sphere complex formation [153–155]. Also, they are environmentally benign and cost effective. Like ZrP, they cannot be directly employed in fixed-bed columns or any other flow-through systems due to the fine or ultrafine particles. Polymer-supported hydrated ferric oxides were then developed to overcome its inherent defect. Due to the anionic nature of arsenate, a polymeric anion exchanger is desirable as host material according to the Donnan membrane principle. However, Fe^{3+}, the precursor of HFO, cannot be directly exchanged onto an anion exchanger due to the electrostatic repulsion. Till now there are two patented techniques developed by Sengupta et al. [156] and Pan et al. [157], respectively, to fabricate HFO-loaded anion exchanger for arsenic removal from waters. Sengupta and his coworkers first loaded oxidant anions (ClO^- or $MnO_4{}^-$) onto an anion exchanger AP-500 and then rinsed the exchanger beads with Fe(II) ions. During the rinsing process Fe(II) ion was oxidized and simultaneously deposited as HFO particles. As for the technique invented by Pan et al. [157], $FeCl_4{}^-$ was used as the precursor of HFO and HFO nanoparticles were immobilized within D-201, a polymeric anion exchanger, by rinsing the $FeCl_4{}^-$ loaded D-201 beads with NaOH–NaCl binary solution and subsequent thermal treatment.

Comparison of As(III) or As(V) effluent histories between D201-HFO and the host substrate D-201 under otherwise identical conditions was shown in Fig. 5 [142]. While As(III) and As(V) broke through quickly for D-201, satisfactory adsorption breakthrough results were observed for both arsenic species on D201-HFO even when the competing anions are about 3000 times more than the targeted species.

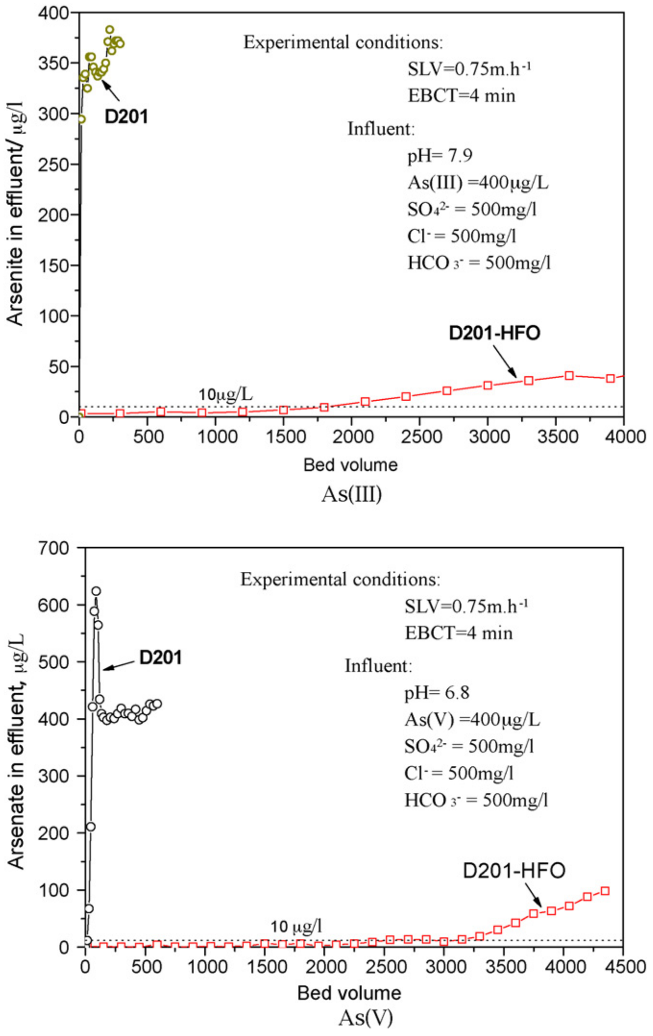


Fig. 5. Breakthrough curves of As(III) and As(V) onto D201-HFO and D-201 for separate column runs under otherwise identical conditions [142].

6. Concluding remarks

Polymeric adsorbents and their derivatives have been widely used as a potential alternative to activated carbon for pollutants removal from contaminated waters. However, there are still many challenging issues on synthesis and application of ideal polymeric adsorbents for environmental concerns. In detail, although polymeric adsorbents of desirable matrix, pore structure and functional groups may be tailor made, molecular design of a polymeric adsorbent for highly selective adsorption of a given pollutant is still difficult and thus, its recovery from concentrated eluate solution is still a costly task as limited by low purity. In addition, adsorption capacities of polymeric adsorbents toward water-soluble pollutants, i.e., hydrophobic ionizable organic compounds, are relatively low and frequent regeneration is thus required for repeated use, resulting in high operation cost in industrial application. As for the polymer-based inorganic hybrid adsorbents, they have opened the possibility to enhance removal of trace inorganic pollutants from waters. However, almost all these adsorbents are still fabricated in laboratory scale, and further study is required on how to obtain these high-performance adsorbents in larger scale. Moreover, as a new type of highly effective adsorbents, their adsorption mechanism toward targeted species needs further elucidation, and more experimental evidences and mathematical modeling are required to achieve the goal.

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