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Porous Polymer Nanocomposite Materials for Environmental Protection

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Abstract

The major directions of applying polymer nanocomposite materials for the protection of the environment and humans are considered in the review. The potential of using highly porous materials and cross-linked hydrogels with incorporated nanoparticles for the purification of waste and natural waters from heavy metals, dyes, and antibiotics is demonstrated. Highly porous polymer materials with magnetic nanoparticles can be used as efficient sorbents for oil-spill cleanup from the surface of water bodies. Incorporation of anisotropic carbon and metal nanoparticles into highly porous polymer materials is a promising strategy for creating nanocomposite materials for electromagnetic radiation shielding.

Keywords: polymer nanocomposite materials, porous polymer materials, sorbents, water purification, electromagnetic radiation

INTRODUCTION

Intensive industrialization and an increase in the human population caused problems in providing stable supply of pure water to agriculture, food industry, energy generation, extraction of fossils, and chemical industry [1]. As a result of anthropogenic action, water bodies are polluted with heavy metals (Pb^{2+}, $Cr_2O_7^{2-}$, Hg^{2+}, *etc.*); organic compounds: dyes, pesticides, detergents, antibiotics; dissociating inorganic compounds: nitrates, sulphides, fluorides, phosphates of metals [2]. Pollution of water bodies with oil products during oil mining, transportation and processing leads to distortions of ecological balance and does not allow efficient functioning of biological systems.

During recent years, porous polymer materials containing various nanoparticles (NP) have been extensively investigated for the purification of waste waters [3]. These nanocomposite materials are composed of a polymeric matrix of natural or artificial origin, and a filler, which is composed of inorganic or organic NP. The porosity of these materials may reach 95 % and more. Due to the porous structure and corresponding high specific inter-phase surface, high sorption capacity is achieved, providing a high degree of water purification from pollutants. Along with the purification of aqueous media, porous polymeric nanocomposite materials (PPNCM) may be applied for air purification and for gas detection [4–6].

A promising area is the use of PPNCM to absorb and shield electromagnetic radiation (EMR) [7]. The most essential advantages of these materials (along with a high degree of shielding from electromagnetic interference) are low density and flexibility, which allows using them in modern electronic devices.

Undoubtedly, porous materials can be used to purify various natural objects: water bodies, air, and soil. In the present review, we focused on the most promising potential areas of PPNCM application, which are described in subsequent sections.

REMEDIATION OF WATER BODIES AND PURIFICATION OF WASTE WATERS FROM WATER-SOLUBLE POLLUTANTS

The processes that are used to purify waste waters include chemical oxidation and chemical deposition, adsorption and ion exchange, electrochemical treatment, aerobic and anaerobic degradation, and membrane filtration [8]. Adsorption is one of the basic physicochemical processes used to purify industrial and household waste waters, allowing pollutant removal to very low concentrations.

As a rule, adsorbents that are used to sorb heavy metals have surface functional groups -OH, -COOH, -SH, $-NH_2$, $-PO_4^{3-}$ or -CONH [9]. Functional groups may be either on the surface of the pores of the polymer matrix or on the surface of NP partially incorporated into pore walls. To purify water bodies, polymer nanocomposite materials of different structures were studied: solid porous polymers and hydrogel granules with incorporated NP.

Solid highly porous polymer materials may be obtained through polymerization of the dispersion medium of inverted highly concentrated emulsions [10]. For example, porous polymers with triazole-functionalized NP of magnetite in the matrix of styrene and divinyl benzene copolymer have been synthesized [11]. The studies of these materials showed that the capacity with respect to heavy metals increased with an increase in the concentration of magnetic NP. The authors explained this fact by an increase in the amount of functional groups on the surface with an increase in the content of magnetite NP. The highest sorption capacity with respect to lead cations (157 mg/g) was that of nanocomposite materials containing 30 mass % magnetite NP.

Highly porous polymer nanocomposite materials were obtained through polymerization of the dispersing medium of inverted emulsions containing styrene, 2-ethylhexylacrylate and divinyl benzene. To enhance mechanical strength, silica NP were included in their composition. After grafting the sulphonic groups to the pore surface, the sorption capacity of the resulting PPNCM with respect to nickel was ~40 mg/g [12].

To increase the mechanical strength of highly porous polymer materials, anisotropic NP are added into them, for example, multilayer carbon nanotubes [13], graphene particles [14], nanorods of titanium oxide [13], cellulose nanocrystals [15], silica NP [12, 16], the particles of montmorillonite [17] and technical carbon [18].

Nanoparticles of different nature may be included into the matrix of the polymer hydrogel. For example, porous polymer materials based on carboxymethylcellulose with the particles of graphene oxide have been synthesized. The capacity of these materials for adsorption of Ni^{2+}, Co^{2+} and Cd^{2+} cations was 65, 58 and 43 mg/g, respectively [19]. As a result of the modification of graphene oxide particles with hyperbranched aminopolymer, the capacity of PPNCM increased substantially and reached 153 and 138 mg/g for the sorption of Pb^{2+} and Cu^{2+}, respectively [9].

Investigation of porous materials composed of montmorillonite particles in a chitosan matrix cross-linked with glutaric aldehyde showed that their capacity was 40 and 38 mg/g for the sorption of Pb^{2+} and Hg^{2+}, respectively [20]. Nanocomposite materials with magnetite NP with the grafted carboxylic groups and acid-activated bentonite in cellulose matrix were studied for the sorption of Pb^{2+} [21].

The use of chitosan-based hydrogel granules with TiO_2 and SiO_2 NP was studied for the sorption of Cd^{2+} from aqueous solutions [22]. The sorption capacity of the tragacanth polymer material with incorporated calcium carbonate NP was 192 mg/L for the sorption of Pb^{2+} from aqueous solutions [23].

The hydrogel of sodium alginate with the particles of graphene oxide modified with polyaniline and polypyrrole was used to purify aqueous solutions from chromium and copper. The capacity of this sorbent was 134 mg/g for the sorption of Cr(VI) and 87 mg/g for the sorption of Cu^{2+} [24]. Maghemite nanoparticles with a shell of silica with the grafted carboxymethylchitosan molecules were studied for the efficiency of Cu^{2+} sorption. The sorption capacity of this sorbent was 160–170 mg/g [25]. The characteristics of sorbents with different NP and different compositions of the polymer matrix are presented in Table 1.

The descriptions of the use of highly porous polymer materials as matrices for catalyst immobilization on the inner surface of pores are reported. For example, platinum NP were included into highly porous polymers as the catalyst for allyl alcohol hydrogenation [28] and 4-nitrophenol reduction [29], as the catalyst for Suzuki reaction [30], and gold NP for eosin Y reduction [31]. Nanocomposite materials containing magnetite NP as a catalyst for the destruction of methyl orange during Fenton's reaction were synthesized [32], and materials based on cellulose with

TABLE 1

Characteristics of porous polymer nanocomposite materials for the recovery of water-soluble pollutants from aqueous solutions

Polymer matrix	Nanoparticles	Pollutant to be removed	Capacity, mg/g	Reference
Carboxymethyl-β-cyclodextrin	Fe_3O_4	Cu^{2+}	47.2	[26]
Copolymer of styrene and divinyl benzene	Fe_3O_4	Pb^{2+}	157	[11]
Cellulose	β-FeOOH	As^{3+}	99.6	[27]
		As^{5+}	33.2	
Carboxymethylchitosan	Fe_2O_3@SiO_2	Cu^{2+}	160–170	[25]
Copolymer of styrene, 2-ethylhexylacrylate and divinyl benzene	SiO_2	Ni^{2+}	~40	[12]
Carboxymethylcellulose	Graphene oxide	Ni^{2+}	65	[19]
		Co^{2+}	58	
		Cd^{2+}	43	
		Pb^{2+}	78	
		Cu^{2+}	77	
Carboxymethylcellulose	Graphene oxide modified with hyperbranched amino polymer	Pb^{2+}	153	[9]
		Cu^{2+}	138	
Sodium alginate	Graphene oxide modified with polyaniline and polypyrrole	Cr^{6+}	134	[24]
		Cu^{2+}	87	
Chitosan	Montmorillonite	Pb^{2+}	40	[20]
		Hg^{2+}	38	
Tragacanth	$CaCO_3$	Pb^{2+}	192	[23]

the NP of graphene oxide and magnetite for the destruction of acid orange 7 [33].

Photocatalytic methods are used to purify water from persistent organic pollutants [34]. Using PPNCM made of polystyrene with incorporated SnO_2 NP, it was demonstrated by the example of rhodamine B that 98.2 % of the dye was removed under the action of UV radiation. The photoactivity of PPNCM was conserved for 5 cycles. The high catalytic capacity was due to a large inter-phase surface containing many catalytically active centres, which promoted the interaction between the dye molecules and OH radicals on the surface of the porous polymer, and caused dye degradation [35]. Hollow polypyrrole fibres with porous Sn_3O_4 NP attached to the surface exhibited several times higher activity than non-porous tin oxide NP [36].

Purification of waste waters from dyes may also be carried out with the help of photocatalytic destruction using NP of different nature as catalysts. In many publications, photocatalytic decomposition of water-soluble dyes was carried out for methylene blue as an example. The sorbents studied with this reaction were porous polystyrene with TiO_2 NP [37], polyacrylamide with maghemite NP [38], and the particles of hydrogel composed of a copolymer of acrylic and vinylsulphonic acids with Fe_3O_4 NP [39], cellulose with TiO_2 NP [40], sodium alginate with halloysite nanotubes [41], calcium alginate with maghemite NP and the particles of activated coal [42], chitin with the nanoparticles of graphene oxide and Fe_3O_4 [43].

The photocatalytic decomposition was investigated by the examples of destruction of crystal violet in chitin matrix with the nanoparticles of graphene oxide and Fe_3O_4 [43], reactive black 5 in chitosan matrix with graphene NP [44], methylene orange in the hydrogel of calcium alginate with maghemite NP and the particles of activated carbon [42]. Hydrogel of sodium alginate and polyacrylamide with graphene oxide NP was used to purify aqueous solutions from methylene blue, brilliant green, malachite green, methylene orange, Bordeaux red, rose bengal, rhodamine 6G, calcein [45]. A review on waste water purification from dyes with the help of hydrogels from natural saccharides with graphene oxide NP was published [46].

Another problem existing at present in environmental pollution with antibiotics due to ineffective purification of waste waters. This may

cause elevation of the stability of bacteria in soil and water against antibiotics, followed by the horizontal transfer of antibiotic-resistant genes in the environment. It should be stressed that the number of publications dealing with the photocatalytic decomposition of antibiotics over catalysts immobilized in PPNCM is substantially smaller. For instance, a material composed of natural extracellular matrix with magnetite NP was used to adsorb tetracycline [47]. Hydrogel of sodium alginate with graphene oxide NP was used for photocatalytic destruction of ciprofloxacin in ground water [48]. It should be stressed that this direction is highly promising because materials of this kind may be used to purify waste waters to very low concentrations of pharmaceutical substances, in particular it is possible to remove trace amounts of pollutants [49].

ELIMINATION OF OIL PRODUCT SPILLAGE

Oil spillage in the case of accidents with oil carrier ships and pipelines brings about a substantial danger to the environment causing the loss of energy carriers and the pollution of water bodies. To remove oil spillage, a number of ecological measures are taken, including oil collection with the help of special collecting devices. After the application of oil collecting devices, oil spots often remain on water surface; they can be efficiently removed with the help of sorbents [50, 51].

The sorbents of oil products may be divided according to material type into mineral (zeolites, clay, coal), natural organic (products and wastes from agriculture and textile industry), and synthetic [51]. The potential of the use of mineral sorbents is limited by their relatively low sorption capacity, fragility and impossibility of mechanical desorption of oil products without destruction of the material. Natural organic sorbents are usually hydrophilic and are characterised by low floatability. Their sorption capacity in comparison with synthetic sorbents is also not very high.

At present, the materials of the highest interest are highly porous synthetic polymer nanocomposites. These materials are mostly characterized by high sorption capacity with respect to oil products because they possess hydrophobic surfaces and high floatability [52–55]. Their use enables regeneration of the adsorbed oil products, so the sorbent may be used many times [56–58].

The materials that are under most thorough investigation for these purposes are porous polymers obtained by electromoulding [59]; crosslinked cryogels formed through freezing the polymer gel and subsequent sublimation drying [57, 60–62]; highly porous materials formed through polymerization of the dispersion medium of highly concentrated W/O emulsions [10, 53–55, 58].

Polymerization of the dispersion medium of highly concentrated emulsions may lead to polymer materials with controlled porosity and pore size [10]. The selectivity of the sorption of oil products by these sorbents from water surface depends on pore size. An oil product is rapidly sorbed in the pores with a size smaller than the critical value, while water is sorbed in larger pores [54, 55]. SEM microphotographs of the sorbents with different pore sizes are shown in Fig. 1, along with the illustration of sorbent impregnation with transmission oil [54]. These sorbents are developed to remove oil films using the traditional method, which involves deposition of the sorbent on the water surface, followed by its removal. In addition, continuous pumping was proposed to remove the oil product when it rises to a definite height in the sorbent [63].

A rather essential factor is the biodegradability of polymer sorbents and the possibility of their utilization. From this point of view, polymer sorbents based on collagen [60, 64], polylactide [61], polycaprolactone [62] are of great interest. These sorbents are cheap because they may be obtained from wastes; they are biodegradable, and their resources are renewable. However, these sorbents are hydrophilic, so it is necessary to make their surface hydrophobic in order to provide efficient collection of oil products.

The inclusion of NP into the structure of highly porous polymer materials may improve their sorption properties and render special functional properties. Nanoparticles with lyophilic surface, located on pore surface, enhance sorbent hydrophobicity. In addition, these NP cause an increase in the roughness of the pore surface [56], which also promotes more rapid sorption of oil products in comparison with water.

To increase hydrophobicity and to make roughness, NP and microparticles of different nature were deposited on the inner surface of pores. Nanocomposite materials were obtained from a copolymer of styrene and divinyl benzene with calcium stearate microparticles [53], porous polyurethane and epoxy resin with multilayer carbon nanotubes (MCNT) [65]. Nanoparticles of silica were used to make roughness on the surface of cellulose acetate fibres [66] and the fibres of poly-*m*-phenyleneisophthalamide reinforced with

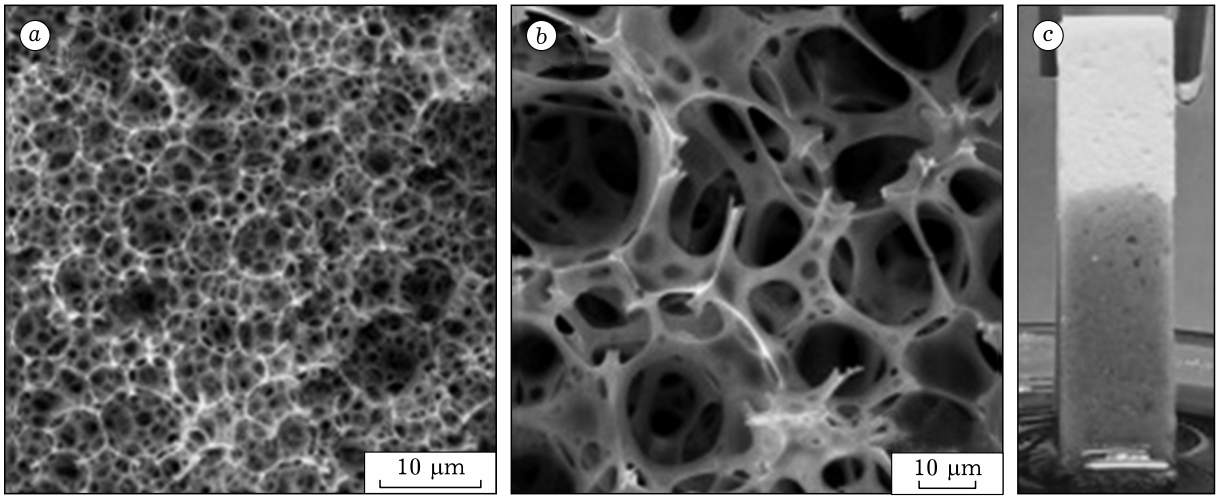

Fig. 1*. SEM microphotographs of sorbents composed of copolymer of styrene and divinyl benzene with average pore diameter 3 (*a*) and 20 μm (*b*); rise of transmission oil in the sorbent in contact with the surface of transmission oil (*c*) [54].

MCNT [67]. To enhance hydrophobicity of incorporated NP, their surface was modified with polydimethylsiloxane when obtaining porous materials from polyurethane with carbon nanotubes [68, 69] and porous melamine with silica NP [63].

Inclusion of reduced graphene oxide in the amount of 2 mass % into the composite material based on polylactide caused an increase in sorption capacity. The sorption capacity for diesel fuel and lubricant oil was 44 and 48 g/g, respectively [61]. An increase in sorption capacity was due to an increase in the edge angle of wetting of the porous polymer material in comparison with porous polylactide without the particles of reduced graphene oxide, as well as by the higher porosity of the sorbent due to its lower shrinkage during drying as the stage of sorbent preparation.

Incorporation of magnetic NP into a polymer matrix allows more efficient collection of the sorbent from the water surface with the help of magnetic field. For the collection of oil products and separation of water-oil emulsions, porous polymer materials containing magnetic NP were synthesized from polyurethane [70], polyurethane and cellulose acetate [71], polystyrene [72], copolymer of styrene and divinyl benzene [73, 74], copolymer of styrene and 4-*tert*-butylstyrene [75], natural caoutchouc and epoxy resin [76].

Porous polymer nanocomposite materials were obtained on the basis of aerogels of cellulose with magnetite NP [77, 78]. To make cellulose fibres with magnetic NP hydrophobic, a thin layer of titanium oxide was deposited on their surface [77], magnetite NP modified with oleic acid were incorporated into aerogels of cellulose nanocrystals [78].

The data on the sorption capacity of PPNCM with respect to various oil products and mineral oils are presented in Table 2.

So, in many cases PPNCM are characterized by the high capacity with respect to oil products and may be used as sorbents to eliminate the consequences of emergency spillage. Biocompatible polymers allow reducing the toxic load on the environment during their application or processing. Incorporation of hydrophobic NP of different nature into polymer composites causes an increase in hydrophobicity of these materials and consequent improvement of sorption properties. Porous materials with magnetic NP possess an additional advantage because the efficiency of the collection of this sorbent from the water surface increases.

ELECTROMAGNETIC RADIATION SCHIELDING

Intense scientific and technological advance has caused a sharp decrease of the safety of our habitat due to the appearance of new sources of electromagnetic pollution, such as cellular, satellite radio communication, navigation and radiolocation systems, radiotechnical installations, medical devices, household devices and other technical means intended for transmission and use of electromagnetic energy. Electromagnetic radiation

* Fig. 1 is reprinted from [54] on permission from Elsevier publishers.

TABLE 2

Characteristics of porous polymer nanocomposite materials for the recovery of oil products

Polymer matrix	Particles	Porosity, %	Sorbed liquid	Sorption capacity, g/g	Reference
Polylactide	Reduced graphene oxide	98.2	Diesel fuel	44	[61]
			Vacuum oil	47	
			Lubricating oil	48	
			Hydrocarbon oil	50	
Polyurethane and epoxy resin	MCNT	63	Cyclohexane	9.1	[65]
			Motor oil	10.0	
			Chloroform	32.2	
Polyurethane	Carbon nanotube	–	Petrol	18	[68]
			Diesel fuel	19	
			Motor oil	24	
Polyurethane	Carbon nanotubes	–	Lubricating oil	27	[69]
			Crude oil	30	
Copolymer of styrene and divinyl benzene	Calcium stearate	98.4	Diesel fuel	62.6	[53]
			Crude oil	67.2	
Polyurethane	Fe_3O_4	–	Kerosene	11.5	[70]
			Lubricating oil	12.0	
			Petrol	17.5	
Polyurethane and cellulose acetate	Fe_3O_4	–	Mineral oil	12.2	[71]
Polystyrene	Fe_3O_4	98.9	Lubricating oil	40	[72]
Copolymer of styrene and divinyl benzene	Fe_3O_4	98	Petroleum ether	18	[73]
			Diesel fuel	24	
Copolymer of styrene and divinyl benzene	Fe_3O_4	98.1	Lubricating oil	23.2	[74]
			Diesel fuel	22.7	
			Petrol	21.9	
Copolymer of styrene and 4-*tert*-butylstyrene	Fe_3O_4	–	Crude oil	10	[75]
			Lubricating oil	12.5	
Natural caoutchouc and epoxy resin	Fe_3O_4	–	Petrol	6.8	[76]
Cellulose/TiO_2	Fe_3O_4	–	Mineral oil	28	[77]
Cellulose	Fe_3O_4	–	Vacuum oil	33.2	[78]

Notes. 1. MCNT – multilayer carbon nanotubes. 2. Dash means the absence of data.

(EMR) generated by various sources may cause failure in the operation of devices; in addition, long-term exposure to EMR is hazardous for human health [79, 80]. Some medical implants or devices (for example, hearing kits, insulin pumps and cardiostimulators) are prone to failures when operating in the alternating electromagnetic field [81].

As a rule, isolating (shielding) or absorbing materials and coatings are used for EMR shielding. In the case of isolating materials being used, during wave reflection from the surface of the material (shield) the reflected signal is often amplified due to wave interference. Isolating materials include electroconductive materials, as a rule, these include metal sheets or metal grids made of latten brass, aluminium, silver, nickel, and steel [82]. However, their high density and high susceptibility to corrosion limit their application in modern electronic devices. It is more promising to use metal-coated polymer materials. For example, a composite nanomaterial based on polyurethane modified with carbon nanotubes was obtained. The external layer of this material was conductive because it contained silver nanofibres, of which the surface was electroplated with silver [83]. To provide EMR shielding, nickel NP were synthesized on the surface of polyester cloth [84].

At present, radio-absorbing materials with different radiotechnical characteristics, structure and composition are under development. These mate-

rials are able to protect against EMR in different frequency ranges. Gradient materials have multilayer structure with smooth or step-like change of permittivity over thickness. Thorn-like structures with the relief formed on their outer surface by lumps shaped as thorns, cones and pyramids are conventionally considered gradient materials. A decrease in reflection coefficient for these materials is promoted by multiple reflections of the waves from the surfaces of thorns, with partial absorption of the wave energy at each reflection. For these materials to exhibit not only interference properties but also absorption, ferromagnetic NP, carbon nanotubes, graphene, and carbon black are added into these materials [85]. For instance, polymer nanocomposite materials were obtained using polystyrene as a matrix; nickel ferrite NP as magnetic filler, and polyaniline fibres as electrically conducting filler [86]. In [87], the properties of the material formed from the polyethylene matrix and a mixture of nickel ferrite and copper particles were investigated.

Currently, the most promising materials are porous polymer materials containing electrically conducting fillers: these are usually carbon NP or polyaniline and polypyrrole fibres [85]. Due to porosity, these materials are characterized by low density. To achieve the percolation limit, when filler particles form a continuous conducting network within the polymer matrix, substantially lower filler concentrations are required than those necessary for nonporous polymers. The action of these materials is based on the multiple reflection of EMR inside the pores and absorption in polymer walls. It should be stressed that the fillers in these materials often play a binary role: they scatter EMR and enhance the mechanical strength of the polymer framework. For example, composite films and porous polymer materials were made of polyvinylidene fluoride containing MCNT 9.5 nm in diameter and ~1.5 μm long, and the particles of Ti_3AlC_2 MXene. Due to the possibility to govern the anisotropy of characteristics, a material with high thermal conductivity and mechanical strength was developed [88]. A comparison of the efficiency of composite films and porous materials with the pores 10–30 μm in size in EMR shielding showed that for MXene concentration 1 and 12 mass % in PPNCM, EMR shielding was 45.2 and 65.1 dB, which was 4–5 time higher than shielding provided by non-porous materials of the similar composition. Electromagnetic radiation entering a porous material was reflected many times from pore surfaces and scattered in pore walls on conducting surfaces of filler interfaces in the form of thermal energy.

Porous materials with MCNT [89–93], graphene [94, 95] were obtained. Polymer materials containing combinations of different fillers were investigated: MCNT and preliminarily synthesized magnetite NP [96]; MCNT with magnetite NP deposited on the surface of nanotubes [97]; MCNT and graphene [98]; reduced graphene oxide [99].

The high degree of EMR shielding, low density and good thermal stability were characteristic of porous polyamide with MCNT [100]. For EMR shielding, aerogels made of a mixture of graphene and reduced graphene oxide with the addition of epoxy resin as a binder were proposed [101]. Flexible composite materials were obtained from polyester imide with the graphene filler and with Fe_3O_4 NP [102]. In these nanocomposite materials, EMR is multiply reflected and absorbed.

Porous polymer materials with metal NP are also of interest for EMR shielding. Both EMR attenuation in pores and reflection due to the presence of metal particles usually occur in materials of this type. Results of the investigation of porous polymethylvinylsiloxane with pore surface coated with silver layer are presented in [103]. The high shielding efficiency was achieved at a rather low silver concentration in the porous material: 0.51 vol. %. An essential advantage of these PPNCM was the possibility of multiple sample bending-unbending without any change in the function of EMR absorption. Porous materials composed of polyurethane with silver nanofibres were obtained [104]. In materials based on porous epoxy resin with silver nanoplates, as demonstrated in [105], EMR absorption dominated over reflection.

The data on the protective effect of PPNCM with different fillers under the action of EMR are presented in Table 3. In the majority of works, the action of EMR within the frequency range 8.2–12.4 GHz was investigated. However, it should be stressed that it is not quite correct to compare only the results on shielding efficiency because the thickness and density of the samples were different in those works.

Thus, efficient materials for EMR shielding were obtained using porous polymers as matrices: polyurethane, polystyrene, polymethylmethacrylate, biodegradable polylactide. Carbon nanostructures and metal NP are most thoroughly studied as fillers. Inclusion of fillers into porous polymers allows not only substantial enhancement of the effi-

TABLE 3

Characteristics of porous polymer nanocomposite materials used for electromagnetic radiation (EMR) shielding

Polymer matrix	Particles	Filler concentration, mass %	EMR shielding, dB	Reference
Polystyrene and polymethylmetacrylate	MCNT	1.61	23.1	[93]
Polylactide	MCNT	10	~23	[90]
Polyvinylidene fluoride	MCNT	15*	56.7	[91]
Polyvinylidene fluoride	MCNT	1	18.6	[92]
		2	31.5	
		5	88.3	
		8	132.6	
Epoxy resin	MCNT	5	20.5	[89]
Polyvinylidene fluoride	Ti_3AlC_2 MXene	12	65.1	[88]
	MCNT	~5		
Polymethylmetacrylate	MCNT with Fe_3O_4 NP on surface	10	25.1	[97]
Methylvinylsilicon	MCNT	10	27.5	[96]
	Fe_3O_4 NP	20		
Polymethylmetacrylate	MCNT	8	~36	[98]
	Graphene	4		
Polyurethane, epoxy resin	MCNT	0.35	37.1	[99]
	Reduced graphene oxide			
Polyurethane	Graphene	10	57.8	[94]
High-pressure polyethylene	Graphene	19*	31.6	[95]
Epoxy resin	Graphene	20.4	51.0	[101]
	Reduced graphene oxide	0.1		
Polyester imide	Graphene with Fe_3O_4 NP on surface	10	18.2	[102]
Polyvinylsiloxane	Silver on pore surface	0.51*	30.5	[103]
Polyurethane	Silver nanofibres	28.6	64.0	[104]
Epoxy resin	Silver nanoplates	10	<20	[105]
		30	49.7	

Note. MCNT – multilayer carbon nanotubes; NP – nanoparticles.
* vol. %.

ciency of EMR shielding, but also renders necessary mechanical strength to the resulting materials.

CONCLUSION

In the present review, the actively developing areas of the application of PPNCM for environmental protection are considered. These materials are promising for the purification of waste and natural waters from various pollutants: heavy metals, phosphates and nitrates, dyes, antibiotics.

In case of emergency spillage, after collection of the major amount of oil products, an oil film remains on the surface of water bodies. This film may spread over great distances covering large areas of the surface of water bodies. The presence of this film causes distortion of the energy and gas exchange between the water body and the atmosphere, which has a hazardous effect on the vital activities of plankton, fish, and aquatic birds. Porous polymer materials are efficient sorbents of oil products due to their hydrophobic pore surface. These sorbents possess high floatability, so they do not sink to the bottom of water bodies after adsorption of the pollutants. This does not cause accumulation of oil products in the ground at the bottom of a water body, which is especially important for near-shore zones. Inclusion of magnetic NP into the composition of porous sorbents simplifies the collection of these sorbents from the water surface, and secondary pollution of the water body is substantially decreased.

One of the intensively developing directions is the use of PPNCM for EMR shielding. Due to the inclusion of various NP, high shielding efficiency is achieved, first of all due to multiple reflections in the pores and absorption of the radiation.

Porous polymer nanocomposite materials are promising not only for the purification of water bodies but also for air and soil purification. Encapsulation of fertilizers, insecticides in the porous structure provides gradual and prolonged release, which enhances their efficiency. Porous polymer composites are the basis for the development of detectors for various gases. The potential of the application of these materials for the protection of the environment and humans is undoubtedly very broad.

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