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НАНОМАТЕРІАЛИ ТА НАНОТЕХНОЛОГІЇ В ОЧИЩЕННІ ВОДИ. ОГЛЯД

Висвітлено останні досягнення та застосування нанотехнологій для очищення стічних вод. Наноматеріали мають високу реакційну здатність і високий ступінь функціоналізації, велику специфічну поверхню, що робить їх придатними для застосування в очищенні стічних вод та для опріснення води. Розглянуто застосування різних наноматеріалів, таких як наночастинки металів, оксиди металів, вуглецеві сполуки, цеоліт, фільтраційні мембрани тощо, у нанофільтрації, адсорбції, розділенні органічних та неорганічних речовин та фотокаталітичній деградації органічних забруднювачів, зокрема теоретичні основи та механізми.

Ключові слова: очищення стічних вод, наноматеріали, опріснення, нанофільтрація, наносорбент, фотокаталіз.

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NANOMATERIALS AND NANOTECHNOLOGY IN WATER PURIFICATION. REVIEW

This article briefly reviews the recent advances and application of nanotechnology for wastewater treatment. Nanomaterials have high reactivity and a high degree of functionalization, large specific surface area, which makes them suitable for applications in wastewater treatment and for water desalination. Application of various nanomaterials such as metal nanoparticles, metal oxides, carbon compounds, zeolite, filtration membranes, etc., in nanofiltration, adsorption, separation of organic and inorganic substances and photocatalytic degradation of organic pollutants is discussed, including theoretical fundamentals and mechanisms.

Key words: wastewater treatment, nanomaterials, desalination, nanofiltration, nanosorbent, photocatalysis.

Introduction The issue of drinking water is one of the most important nowadays for most countries, especially for densely populated and developing countries. For example, in India, 80 % of diseases are caused by contamination of drinking water, in particular bacterial [1]. The main reasons for such situation are population growth; drought; extraction of minerals, in particular oil; the widespread use of chemicals in the farm, etc., which are today that critical “pressure” on nature that prevents it from fully performing water purification from pollution. Therefore, minimizing the negative impact on nature and improving the technology of water purification are the main directions of solving such a global issue. Well-known physical, chemical and physicochemical methods do not always provide a suitable level of purification. So, disinfection with UV light is not able to inactivate the microorganisms of individual diseases; chlorine easily reacts with organic substances present in many waters with the formation of toxic halogen-containing compounds; ozonization is effective for local use, which is not always practically feasible [2]. Therefore, the first successes for the use of nanomaterials, which are given only in the review articles of the last decade, show the wide possibilities of nanotechnologies in water purification [1–8]. The most intensive research is carried out in the following areas: filtration, adsorption and separation, photocatalysis (table).

Main directions of application of nanomaterials in water purification

Materials	Functional properties and application	Ref.
Ultra- and nanofiltration		
Nanofiber membranes: polyacrylonitrile, polyvinylpyrrolidone	For remove bacteria and other microorganisms in order to eliminate fouling.	[8]
A hollow-fiber-type polymeric membrane	Double-stage integrated micro- and nanofiltration plus reverse osmosis for treating dairy wastewater.	[9]
Nine commercial NF membranes: cellu-lose, polyamide, polypiperazinamide	For nanofiltration of dairy wastewater	[10]
Commercially available ultra-filtration polymeric membrane	For improving water quality of treated textile wastewater by ultrafiltration membrane modules	[11]
Modificatednanopore membranes	For ultrafiltration of wastewater	[7]
Denrimers polymers	Desalination and recovery of metal ions from aqueous solutions	[12]
Well-organized multilayer structures of membranes	For water purification, with applications in wastewater treatment, biomedicine, food industry	[13]
Ceramic ultra- and nanofiltration membranes	In the separation of oils, emulsions and silts by pressure-driven membrane processes	[3]
Microporous/nanoporoustermed ceramic water filters	For applications in water filtration: to remove bacteria and chemical contaminants	[14]
Ceramic membrane	For separates dyes and salts in industry	[15]
Nanomembranes with Al_2O_3 and TiO_2nanocrystallites	For reject partially the ions and could successfully separate all the microorganisms	[16]
Polyurethane nanofibers filters, modified by nanoparticles of copper oxide	Water filtration with antibacterial treatment	[17]
Inkjet printed grapheme oxide membranes on polymeric supports	For highly effective water purification by nanofiltration	[18]
Industrial micro- and nanofilters pumps	Water Purification. Water treatment pressure-driven membrane processes by membrane module	[19]
Adsorption and separation		
Nanoporous zeolite membranes	For dehydration of water/ethanol mixture	[22]
Ceramic/polymeric fibers	Oil/water emulsions separation	[23]
Amphi-functional mesoporoussilica nanoparticles	For various dyes (cationic and anionic) removal from water with easily regeneration	[24]
Zeolite. Silica hybrids porous materials	Adsorption of heavy metal ions	[2,25]
Phosphoryl functionalized mesoporous silica	For uranium (VI) adsorption in a wide range of pH values and removal of U (VI) sorbent	[26]
3D porous graphene hydrogel	For adsorbing and removing different pollutants (antibiotics, dyes, and heavy ions)	[27]
Magnetic nanoparticles	As high capacity/selectivity for toxic metal ions, radionuclides, organic and inorganic solutes/anions	[1]
Photocatalytic degradation		
Electrophoretic deposited nano-TiO_2	For waste water purification systems for light industries before discharge into the ecosystem	[28]
Flexible ceramics with nano zinc oxide tetrapods and hybrid metal oxides	Photocatalysis for degradation of organic substensis (methylene blue)	[29]
Iron-doped ZnO nanowires	Water purification of organic dyes by photocatalysis	[30]

1. Ultra- and nanofiltration of water

The development of nanofiltration technology (NF) over the last decade has led to its use in the textile industry, the separation of pharmaceuticals from enzymatic broths, dairy industry, the removal of viruses and heavy metals from sewage, for the removal of natural organic substances and inorganic pollutants in surface waters [4–19].

Byusing the filters with pore sizes between 1–100 nm, nanofiltration (pores 1–10 nm) and ultrafiltration (10–100 nm) are carried out. However, the authors [5] propose to classify nanofiltration membranes not by size of pores, but by the functional characteristics of the membrane process, in particular the size or molecular weight of the separated component, using selectivity. Thus, by ultrafiltration there are macromolecular substances removed from the solution with sizes greater than 10 nm, while nanofiltration allows water to be purified from cations of heavy metals and cations of calcium and magnesium, sulfate, nitrate, hydrogencarbonate anions, which allows to receive drinking water from waste water and sea water. However, ultra- and nanofiltrationare carried out in combination with other methods, as shown in the diagram (Fig. 1). In addition, nanotechnologies for obtaining conditioned water are preceded by a preliminary treatment of wastewater treatment, in particular macrofiltration, lighting, coagulation, sedimentation, etc. Thus, for the removal of colored and precious metals, cementation is used, for example "green" by the use of magnesium as a reducing agent [20], for the intensification of wastewater neutralization – an ultrasound field [21].

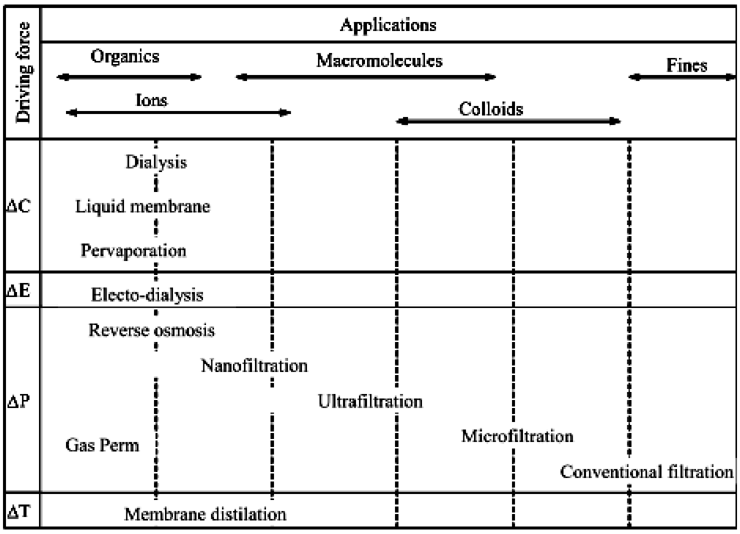


Fig. 1. Effective range of membrane processes [6]

Ultra- and nanofiltration in recent years are based on the study and application of the following types of filters: 1) membrane based on organic polymers [4–13]; 2) ceramic [3, 14–16] and 3) hybrid [17–19]. The first type is mostly widespread due to the possibility of synthesis of different structures of pores and their large specific surface volume, lightness of industrial production, cheapness. However, as noted in [7], high pressures during filtration (20 atm or more) cause their rapid deterioration. In addition, requirements for the selectivity of filtration processing and productivity are increasing. Ceramic filters are characterized by higher selectivity and durability, but they are expensive and unstable to mechanical deformations. Therefore, a lot of attention has been given in recent years to polymer modifications [7, 12, 13] and the production of hybrid nanomembranes [17–19].

1.1. Polymeric membranes

The paper [7] describes the characteristics of a wide range of industrial membranes that were used in the membrane process for landfill leachate treatment. The basis for these are the following polymers: polyethylene, polypropylene, polytetrafluoroethylene, polyethersulfone, poly (vinylidene fluoride), cellulose nitrate, etc., preferably with structural particles – hollow fiber, cross-flow, tubular. Moreover, depending on the functional purpose (nano-, ultra- or microfiltration), the pore sizes are in the range of 40–400 nm.

The commercial membranes for nanofiltration are made on the basis of regenerated cellulose, polyamide, poly (piperazinamide, permeability range of from 8.1 to 72.4 ($L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$) [10], which primarily is caused by their different structure and, above all, the different pore size (Fig.2), as well as the different nature of the surface. This allows the use of nanofiltration of organic substances (dairy products, lactose), and the removal of ions.

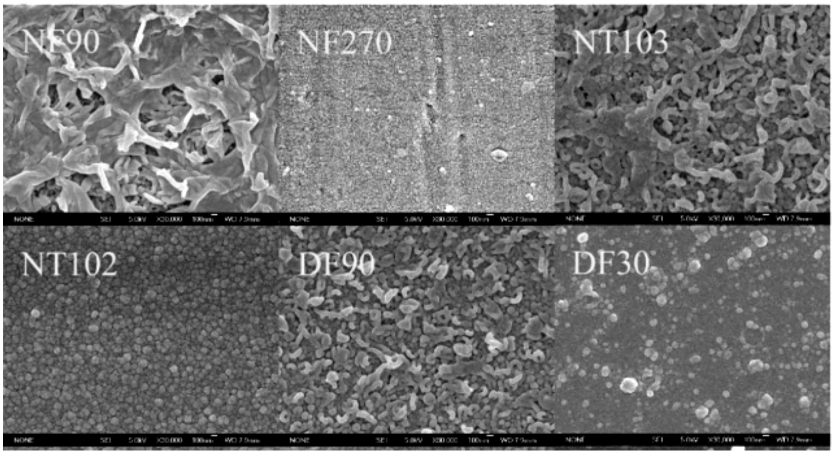


Fig. 2. SEM images of surface morphology of NF membranes [10]: polyamide (NF90, NT103, DF90); poly (piperazinamide NF270, NT102, DF30)

With the use of dendritic polymers (denrimers), nanofiltration of ions can be combined with the regeneration of heavy metal salts and the reuse of nanofilters (Fig. 3).

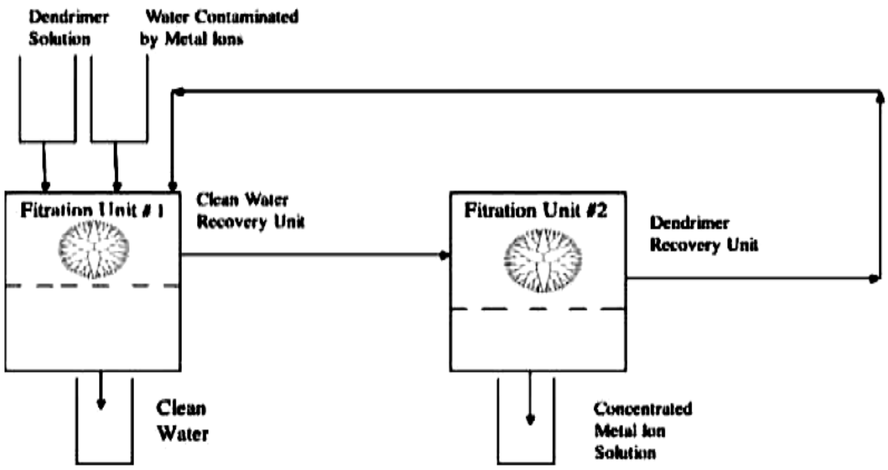
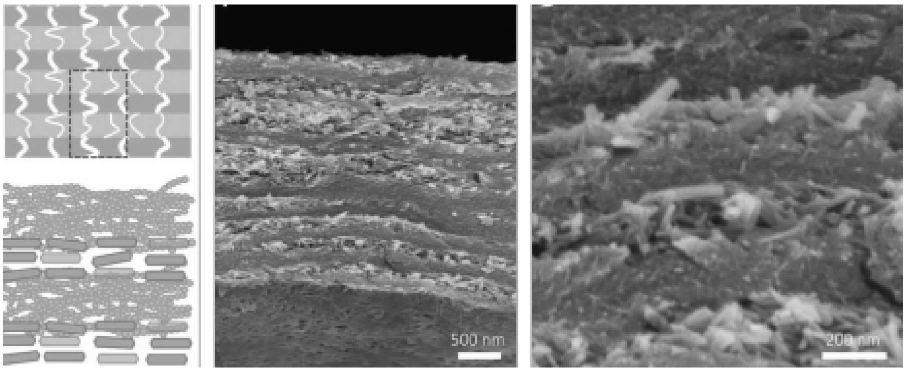


Fig. 3. Scheme of recovery of metal ions from aqueous solutions by dendrimer enhanced filtration [12]

One of the directions of modification of filtration membranes is the formation of multilayer architecture, which allows to increase the throughput of filtration and provide high purity of water [13]. In addition, such membranes are effective in reuse of contaminants, including heavy metal ions, dyes, proteins, and other nanoparticles in water. This is a new direction in membrane filtration, which is in the stage of computational simulation and experimental fabrication. Multilayer filtration membranes (Fig. 4) are formedof protein nanofibrils and mineral plates, the link between which is weak.

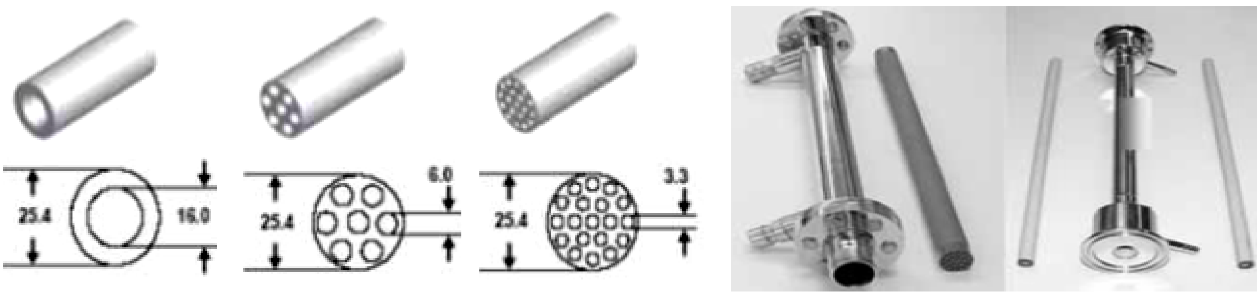


a *b* *c*

Fig. 4. Schematic of multilayer structures (a). Cross-sectional SEM image of a multilayer membrane (b). High-resolution cross-sectional SEM image of a multilayer membrane (c) [13]

1.2. Ceramic water filters

Ultra- and nanoporous ceramic membranes are of interest, especially for cleaning where high chemical or thermal stability is required. Ceramic membranes are also characterized by high performance characteristics. However, considering the low mechanical characteristics, especially the fragility, they can be used in filtering devices only with metal cases made of stainless steel (Fig. 5). High temperatures and appropriate chemical treatment of ceramic membranes with reagents make it easy to regenerate them without changing the structure and, consequently, the filtering characteristics. It distinguishes them favorably from polymer membranes, in particular in purifying water from contamination by oil, petroleum products, organic substances, etc. The basis for such ceramic filters is nanoporous alumina [3], ceramic based on a mixture of clay [14]. Commercial nano filtration ceramic membranes have been used to separate dyes and salts in industry [15].



a *b*

Fig. 5. Ceramic membrane designs, adapted from atech innovations (a) and ceramic membranes and steel housings (b) [3]

Ceramic nanofilters are promising for desalination of water [15, 16]. Moreover, besides the nature of porous ceramics, the selectivity of absorption of ions is influenced by the conditions of filtration. Thus, tubular nanocomplexes based on the γ-alumina and titaniananocrystallites with the avarage pore size of 5.8 nm change their permeability with increasing pressure (Fig. 6). Moreover, depending on the size of the ions and their charge, there is a difference in the dependence of ***ion permeability – the pressure*** on the general tendency to decrease permeability. Acidity of water significantly affects the permeability of ions, but there is no general pattern (Fig. 7). So, for Ca^{2+} it is absent in acidic medium, while in alkaline it is quite large. Chloride ions are impervious to neutral solutions, whereas for sulfate-ion permeability is high in a wide range ofpH. Consequently, only such two parameters can significantly affect the salt content of desalinated water and the content of individual ions in it.

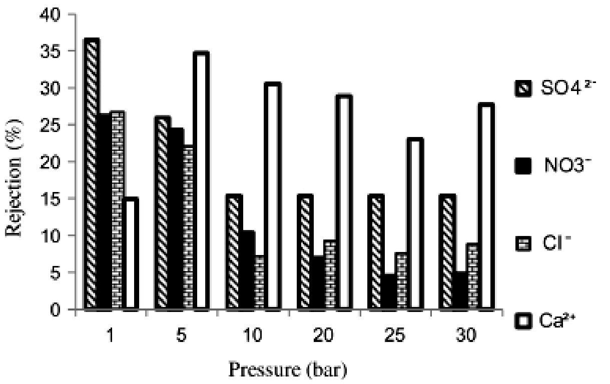


Fig. 6. Rejection ratio of some ions as a function of pressures for nanomembrane in pH 6.5 [16]

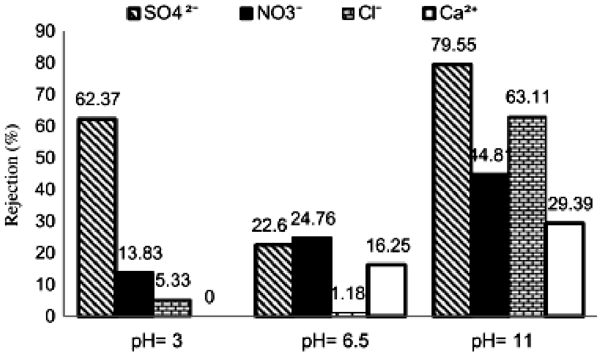
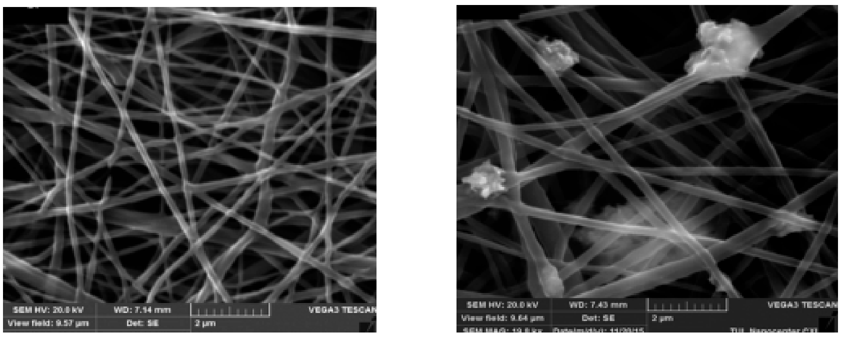


Fig. 7. Rejection ratio of four ions in acidic, normal, and alkaline pH for nanomembrane [16]

1.3. Hybrid nanofilters

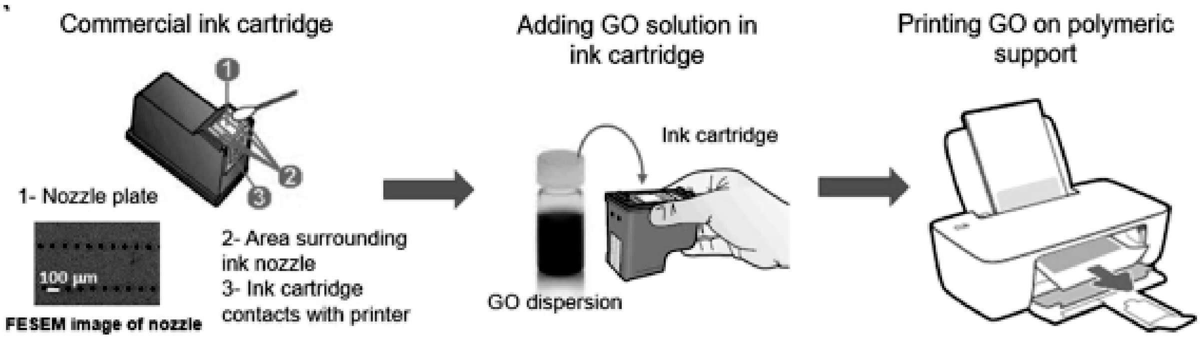
One of the directions for expanding the functional properties of nanofilters is their modification with antibacterial components. Thus, the [17] shows the effectiveness of CuO nanoparticles deposited on polymeric nanofibers of which filters are formed (Fig. 8). In view of the industrial production of polymeric nanofibers (polyacrylonitrile and polyvinylpyrrolidone) [8] and hollow fiber type polymeric (poly (ether sulfonate) / poly (vinyl pyrrolidone) [9], membranes based on them are promising in terms of commerciality. At the same time, the latter can be formed with a wide range of porosity - from several nanometers to submicron sizes [8, 9, 17]. This enables nanofiltration, providing antibacterial activity with a high proportion of nanoparticles of metals and their compounds.



a *b*

Fig. 8. SEM images of nanofibers (a) with micro- and nanoparticles of CuO (b) [17]

The production of nanofiltering membranes by inkjet printing is fundamentally new, for example, with the application of layers of graphene oxide (GO) in the thickness of 7.5…60 nm on a polymeric basis [18]. Choosing GO is due to its main characteristics: two-dimensional (2D) nanomaterial, which is commercial; excellent mechanical properties, ultra-low thickness; good dispersion in water; it easily forms high-quality lamellar structures with subnanometricnanochannels. In addition, the functional groups of graphene oxide cause the formation of a strong bond through the donor-acceptor mechanism (GO:←M^{n+}) with ions of heavy metals, which helps to clear water from them. The proposed method, based on these properties of graphene oxide, makes it possible to make homogeneous membranes of large areas. The dosage of GO “ink” concentration and/or printing time (Fig. 9) makes the process controlled by the thickness of the filtering layer, the porosity and hence the permeability and selectivity. Thus, the GO membrane, which was successfully printed on a modified polyacrylonitrile, has an order of magnitude higher permeability compared to commercial polymer nanofiltration membranes and much higher than the absorption of small organic molecules.



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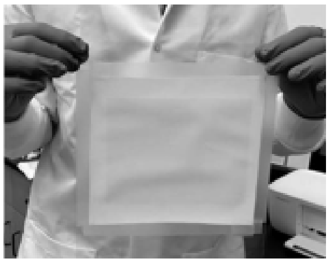


b

Fig. 9. Printed, ultrathin grapheneoxide (GO) membranes:
a – schematic showing the procedure for printing ultrathin GO membranes;
b – digital picture of a printed GO membrane (15×15 cm^2) on modified PAN (M-PAN) support [18]

2. Adsorption and separation

Adsorption with the use of nanomaterials, in addition to increasing the active area, pore geometry, is intensively investigated in the last decade in the direction of surface modification with the provision of their differential properties. Thus, the fundamentally new nanosorbent is the so-called colloidal Janus particles - asymmetric particles with two opposite surface properties, where one sphere is polar, the other is nonpolar [24]. It is the polar part at the expense of functional groups, for example, COOH, $-NH_2$, selective adsorption of organic substances, heavy metal ions is carried out. Often, colloidal Janus particles consist of SiO_2 oxide, which makes it easy to chemically modify the surface (Fig. 10). The particles, due to the equilibrium of *adsorption↔desorption* processes, provide reusable use of such nanomaterials with the removal of valuable components.

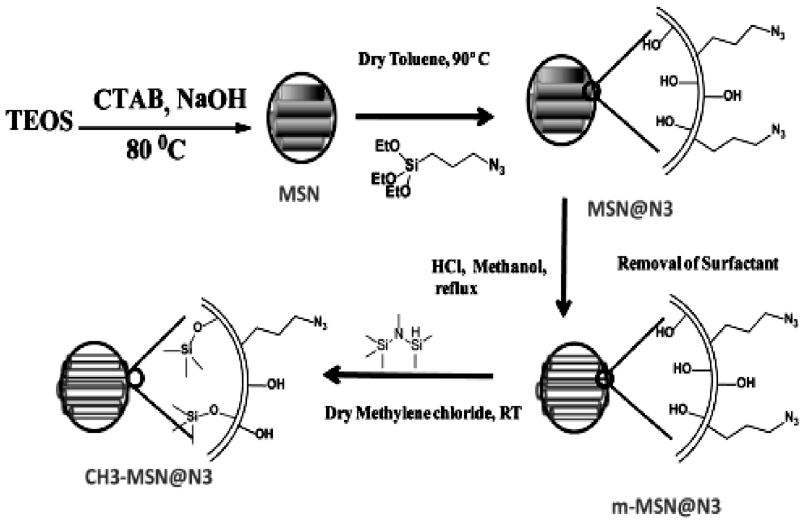
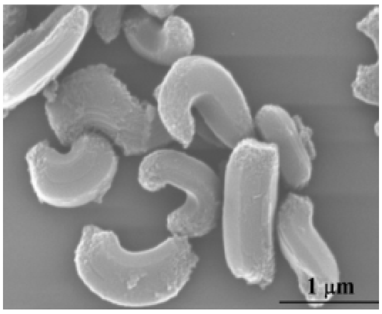


Fig. 10. Scheme of synthesis of amphifunctional silica nanoparticles by stepwise chemical modification: TEOS – tetraethyl ortho-silicate; CTAB – 3-chloropropyl triethoxySilane; MSN – mesoporous silica nanoparticle [24]

The similar one is the adsorption effect of silica-based organic-inorganic hybrid nanomaterials with surfactants. The latter, despite providing functional properties, improve porosity of hybrid gels. The authors [25] have shown the effectiveness of such adsorbents in extracting water from ions of heavy metals. For example, hybrid gels with separate functional groups have reduced adsorption, for example, in the series Pb ≥ Cr> As> Hg. This makes it possible, in addition to extracting heavy metal ions, to separate them from a mixture that is often found in real waters.

The authors [26] showed high capacity ability of phosphoryl functionalized mesoporous silica in uranium adsorption, which has ecological matter and commercial value. The proposed nanoporousbifunctional adsorbents (Fig. 11) are effective for removing U (VI) from aqueous solutions with its subsequent removal.



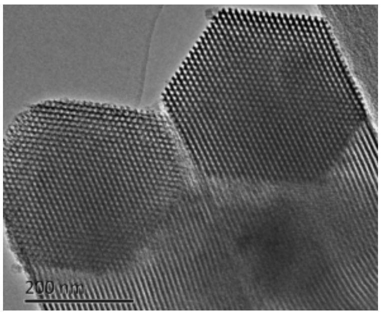
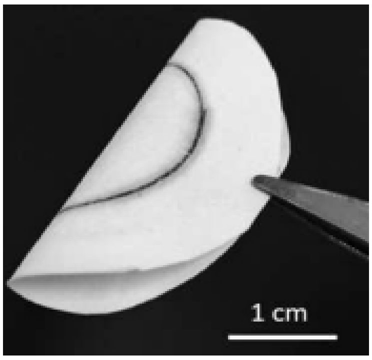


Fig. 11. SEM image of phosphoryl functionalized mesoporous silica and TEM image of normal to pore axis [26]

The bifunctionality of the adsorbent surface is also used in hybrid asymmetric polymer/ceramic nanomembranes [23], which, due to hydrophobic regions of the surface, provide an opportunity for adsorption of oil and petroleum products, fat emulsions. The ultra-long dimension of ceramic nanofibers/polymeric microfibers endows this novel membrane with mechanical flexibility and robustness, due to the integrated and intertwined structure (Fig. 12). This membrane is able to separate oil/water emulsions with high oil separation efficiency (99.9 %), thanks to its nanoporous selective layer made of ceramic nanofibers.



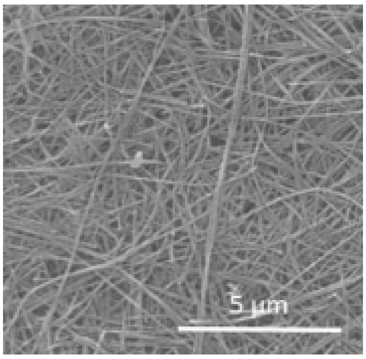


Fig. 12. Photo of the asymmetric membrane based on ultra-long sodium titanatenanofibers/cellulose microfibers and SEM image of membrane fragment [23]

It has been shown in [27] that 3D porous graphene hydrogel is a super adsorbent to remove such pollutants: antibiotics, dyes, and heavy ions. The peculiarity of such an adsorbent is based on the properties of water found in a stable hydrogel to absorb water-soluble substances.

Magnetic nanoparticles are productive water purifiers [1]. They can be modified by various functional groups to increase affinity for a specific adsorbed compound or ion. They can also provide high capacity and selectivity for the absorption of toxic metal ions, radionuclides, organic and inorganic substances due to secondary ligand-anions on the surface (Fig. 13).

The main advantage of the method [1] compared with other adsorption methods based on nanomaterials is as follows. Modified superparamagnetic materials can be introduced into large volumes, for example, in oil and oil-contaminated coastal parts of the seas and lakes. After the adsorption of the pollutants, they are easily magnetized in the presence of an external magnetic field and easily removed by magnets from the reservoirs.

Nanomaterials are also used in the separation of aqueous solutions of organic compounds. For example, nanoporous ceramics are an effective adsorbent of water used for dewatering the solutions. Thus, high performance nanoporous zeolite membranes showed a separation factor of 9.400 and a total flux of 9.8 kg·m^2·h^1 in water extraction from a water-ethanol mixture [22].

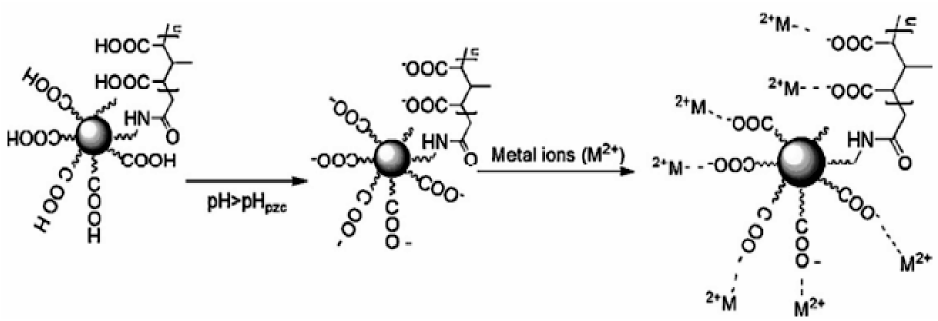


Fig. 13. Schematic representations of possible mechanism for adsorption of metal ions by Fe_3O_4 @APS@AA-co-CA [1]

3. Photocatalytic degradation

In recent years, contamination of natural waters with toxic organic substances, which present a toxicological hazard to plants, marine and animal lives, is increasing. Consifering the huge scale of such waters and, as already noted, the ineffectiveness of traditional methods of purification (chlorination, ozonization) requires new, modern approaches for decontamination. Among the nanotechnologies of water purification, the encouragement for this is water treatment using heterogeneous photocatalysis of titanium (IV) oxide [28], zinc oxide [29, 30] and other metal oxides with semiconductor properties.

Zinc oxide is the most studied material towards photocatalysis because of its quite excellent physical, chemical, and biological features, for example, wide direct bandgap (~3.37 eV), highly robust, extremely bio-friendly [29]. Photocatalytic degradation on the surface of nanoparticles ZnO, TiO_2 and other semiconductor oxides is based on the initiation of light quanta by the formation of anode and cathode regions (Fig. 14). The latter cause the course of electrochemical and chemical processes with the formation of radicals and peroxide compounds (1–10). The result is almost complete oxidation of organic compounds to CO_2 and H_2O (11).

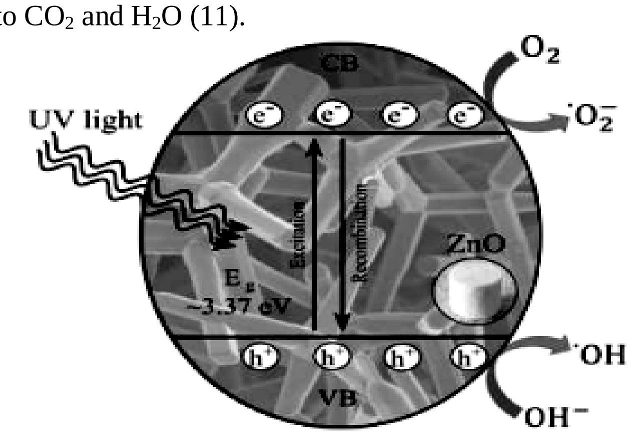


Fig. 14. Concept of photocatalysis using metal oxide ZnOnanomaterials [29]

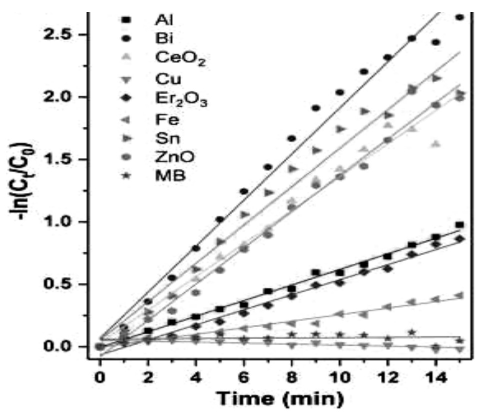


Fig. 15. Photocatalytic degradation of dye in the present of different metal oxide hybrid ZnO-T ceramic networks [29]

$ZnO + h\nu \rightarrow ZnO + e^- + h^+$ (1)

$H_2O + h_{VB}^+ \rightarrow OH^\bullet + H^+$ (2)

$OH^- + h_{VB}^+ \rightarrow OH^\bullet$ (3)

$2HO^\bullet_2 \rightarrow H_2O_2 + O_2$ (6)

$HO^\bullet_2 + O^{\bullet-}_2 \rightarrow HO^{\bullet-}_2 + O_2$ (7)

$HO^{\bullet-}_2 + H^+ \rightarrow H_2O_2$ (8)

$O_2 + e_{BC}^- \rightarrow O^{\bullet -}_2$ (4) $H_2O_2 + e_{BC}^- \rightarrow OH^\bullet + OH^-$ (9)

$O^{\bullet -}_2 + H^+ \rightarrow HO^\bullet_2$ (5) $H_2O_2 + O^{\bullet -}_2 \rightarrow OH^\bullet + OH^- + O_2$ (10)

$$OH^\bullet + \text{Pollutants} \rightarrow \text{Intermediary Products} \rightarrow CO_2, H_2O \ldots \quad (11)$$

In order to increase the action of semiconductor particles, modifications of semiconductor oxides with oxides of other metals are carried out (fig.15), putting them on the substrates [30] with the formation of photocatalytic materials, suitable for long-term operation in real conditions. Research of dimensional effect is also one of the priority directions of research. Thus, in [28] it is shown that even the length of nanowires significantly affects the rate of photo-oxidation of organic pollutant and the completeness of its chemical degradation (Fig. 16).

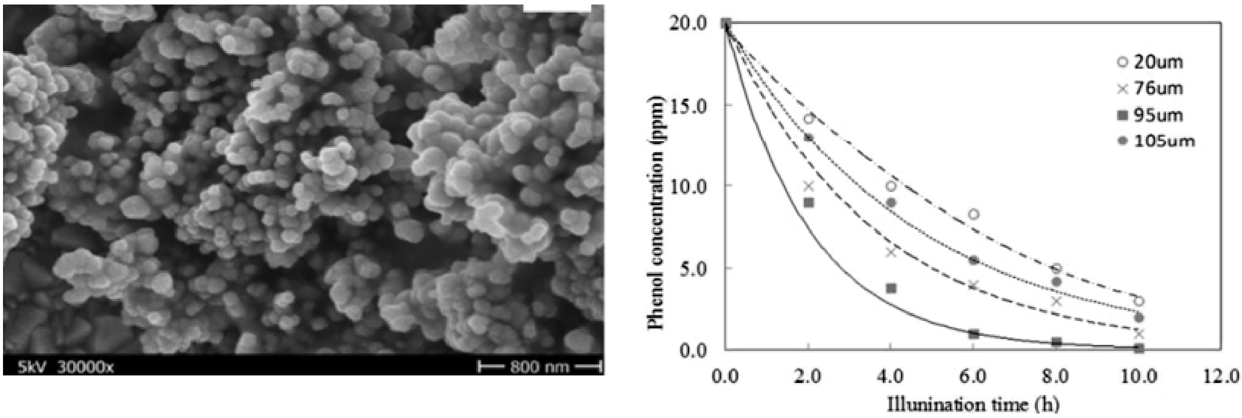


Fig. 16. SEM of TiO_2 films deposited at 30.0 V and variation of phenol concentration with illumination time on TiO_2 films of varying thicknesses [28]

4. Conclusions

Existing technologies are not typically capable of reaching the new levels of cleanliness demanded by regulations without using additional expensive chemicals for coagulation, settling and the like. This increases operating expenses and produces greater volumes of hazardous wastes. In addition, international standards require more efficient separation systems than those currently used in full. Nanotechnology can greatly influence the domain of wastewater treatment in the comingfuture. Nanotechnology focuses on improving the existing methods by increasing efficiency of the processes andenhancing the reusability of nanomaterials. Nanomaterialsare endowed with unique properties like high surface-to-volume ratio, high reactivity and sensitivity, having theproperty of self-assembling on substrates to form films,high adsorption, etc. Owing to these properties, nanomaterials are effective against various organic andinorganic pollutants, heavy metals, as well as againstseveral harmful microbes present in contaminated water.

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