https://doi.org/10.1070/RCR4955

Sorbents for water purification based on conjugated polymers

Irina Yu. Sapurina,[a] Mikhail A. Shishov,[a, b] Valeria T. Ivanova [c]

[a] Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoi prosp. 31, 199004 Saint Petersburg, Russian Federation
[b] Peter the Great St. Petersburg Polytechnic University, ul. Politekhnicheskaya 29, 195251 Saint Petersburg, Russian Federation
[c] Gamaleya Research Institute of Epidemiology and Microbiology, Ministry of Health of the Russian Federation, ul. Gamalei 18, 123098 Moscow, Russian Federation

The sorption properties of polymers with a polyconjugated chain structure (polyaniline and polypyrrole) are considered. The molecular mechanism of sorption by these polymers of various compounds such as heavy metal ions, toxic organic compounds and micropathogens, which are the most hazardous and stubborn contaminants in water, is discussed. The use of such sorbents to purify water from micropathogens, including bacteria and viruses, is addressed for the first time. The adsorption capacity of polyconjugated polymers for these types of contaminants, the efficiency of water treatment by these sorbents and characteristics of the currently used sorbents are analyzed. The applicability of polyaniline and polypyrrole and composites based on them as high-performance versatile sorbents for water treatment is discussed, taking into account the sorbent properties such as high stability, lack of solubility, lack of toxicity and ability to be regenerated and reused.
The bibliography includes 194 references.

Contents

1. Introduction 1115
2. The most hazardous and stubborn water contaminants 1116
2.1. Heavy metal ions 1116
2.2. Toxic organic compounds 1116
2.3. Micropathogens 1117
3. Methods for the removal of hazardous types of contaminants from water 1117
4. Polyaniline and polypyrrole 1117
4.1. Causes behind the high adsorption activity of polyaniline and polypyrrole 1118
4.2. Interaction with heavy metal ions 1118
4.3. Binding of toxic organic compounds 1119
4.4. Interaction with biological objects 1119
5. Supramolecular structure and surface properties of electrically conductive polymers 1120
6. Efficiency of adsorption of various types of water contaminants by polyconjugated polymers and polymer-based composites 1121
6.1. Adsorption of heavy metal ions 1121
6.2. Adsorption of synthetic dyes 1123
6.3. Adsorption of bacteria and viruses 1124
7. Sorbent regeneration 1127
8. Conclusion 1128

1. Introduction

The industrial development and the growth of Earth's population lead to increasing fresh water consumption. According to World Bank research, the world consumption of fresh water tripled from 1950 to 2010 and, according to forecasts, it will further grow by 40% during the subsequent 20 years (see https://obrazovaka.ru/geografiya/vodnye-resursy-rossii.html). Meanwhile, the fresh water volume accounts for only $<3\%$ of the volume of the Global Ocean.[1] Theoretically, fresh water is a renewable natural resource; however, it is being gradually contaminated by industrial and domestic sewage and this becomes unusable. The modern treatment systems cannot cope with the growing amount of sewage. The problem is complicated by the high diversity of contaminants, which include water-insoluble particulate matter, stubborn water-soluble toxic organic and inorganic wastes of modern industrial plants and domestic and agricultural wastes, which are hazardous due to the presence of pathogenic bacteria and viruses. A relevant goal is to develop new sorbents for water treatment that would possess not only increased performance, but also

I.Yu.Sapurina. Doctor of Chemical Sciences, Leading Researcher at the Laboratory of Anisotropic and Structured Polymer Systems, IMC RAS. Telephone: +7(812)323 – 7407, e-mail: sapurina@mail.ru
M.A.Shishov. Candidate of Engineering Sciences, Senior Researcher at the Laboratory of Polymer Materials for Tissue Engineering and Transplantology, SPbPU; Researcher at the IMC RAS. Telephone: +7(812)323 – 7407, e-mail: shv_misha@mail.ru
Current research interests of the authors: synthesis and study of polyconjugated polymers (polyaniline and polypyrroles), production of composite materials based on them.
V.T.Ivanova. Doctor of Biological Sciences, Leading Researcher at the Laboratory of Etiology and Epidemiology of Influenza, RIEM MH RF. Telephone: +7(499)193 – 7171, e-mail: valivanova1946@mail.ru
Current research interests: studies of molecular-biological properties of influenza viruses, occurrence of influenza viruses and interaction with polyaniline- and polypyrrole-based polymer materials.

Translation: Z.P.Svitanko

Received 2 February 2020

© 2020 Uspekhi Khimii, ZIOC RAS, Russian Academy of Sciences and IOP Publishing Limited

versatility for binding different types of stubborn soluble contaminants.

The review is devoted to the representatives of polyconjugated polymers — polyaniline (PANI), polypyrrole (PPy) and composite materials derived from these polymers — as promising sorbents for purification of drinking water. The interaction of PANI and PPy with the most hazardous and stubborn contaminants of various classes such as heavy metal ions, organic dyes and micropathogens (bacteria and viruses) is considered. The versatility of these polymers for drinking water treatment is demonstrated. The mechanism of particle binding by polymers is discussed and higher efficiency of adsorption of contaminants by these materials compared with other sorbent classes is shown. The possibility of regeneration and multiple reuse of polymeric sorbents is proved.

The following abbreviations are used in the review:

CNTs — carbon nanotubes;

HA — haemagglutination,

MAC — maximum acceptable concentration of a contaminant in water according to WHO data;

MO — Methyl Orange;

PANI — polyaniline;

PPy — polypyrrole;

SEM — scanning electron microscopy;

TEM — transmission electron microscopy;

WHO — World Health Organization.

2. The most hazardous and stubborn water contaminants

The current requirements of the World Health Organization (WHO) to the purity of drinking water are very stringent. Removal of particulate matter is not a challenging problem; this is done using settling tanks, after which water is pumped through porous rock and then filtered through inert fine-porous materials. There are three main types of contaminants generated by human activity that are most difficult to remove from water. These stubborn and simultaneously the most hazardous types of contaminants are as follows:

— heavy metal ions,

— toxic organic compounds,

— micropathogens (bacteria and viruses).

2.1. Heavy metal ions

Heavy metal ions such as mercury (Hg^{2+}), chromium (Cr^{6+}), lead (Pb^{2+}) and cadmium (Cd^{2+}), which are present in metal working, instrument and mechanical engineering waste, are especially hazardous.[2,3] They all belong to hazard category 1 (highly dangerous chemicals) and have a cumulative effect, *i.e.*, they are accumulated in the body. While getting into the human tissues, the ions penetrate the cells and bind to certain cellular components, which disturbs functioning of nucleic acids, enzymes and proteins.[4]

For example, after being absorbed into blood, Cd^{2+} ions damage the central nervous system, cause degenerative changes in the liver and kidneys, and suppress the enzyme system activity. Chronic poisoning brings about anaemia and bone degradation.[5]

Mercury has a toxic effect on the nervous, digestive and immune systems and also on lungs, kidneys, skin and eyes. It is especially threatening to the embryonic and early children development. Water-soluble mercury species are more hazardous than the vapour, since they are able to interact more efficiently with elements of enzyme systems in the body.

Water-soluble lead species disturb the metabolism. Lead, which is mainly accumulated in bones, replaces calcium and becomes a continuous source of poisoning. The absorbed lead enters the bloodstream and is distributed in bone (up to 90%) and soft (liver, kidneys, brain) tissues and also in hair, nails and teeth. Lead inhibits the function of enzymes, causing mental deficiency and brain diseases.[6]

Soluble compounds of hexavalent chromium are very strong carcinogens among inorganic substances. According to the data of the International Agency for Research on Cancer, chromium belongs to the group of compounds that have an epidemiological carcinogenic effect; it easily overcomes cell membrane channels and interacts with DNA. Cleavage of DNA and formation of new cross-links cause the risk of genotoxicity.[7] Chromium poisoning is manifested as allergic skin reactions, destruction of nasal cartilages and oral cavity, inflammatory processes in lungs, while the major consequences of poisoning are cancer diseases.[8]

2.2. Toxic organic compounds

The major toxic organic compounds that contaminate water are waste from chemical, textile and tanning industries and from the manufacture of pharmaceuticals and dyes. The universally used synthetic dyes are most abundant among these compounds. Currently, 10 000 sorts of synthetic dyes are commercially available. Synthetic dyes are used more and more often in all of the listed industrial branches and also in the perfume industry and even in the food industry. Synthetic dyes are characterized by higher diversity of colours, higher stability and lower cost in comparison with natural dyes. However, serious problems are caused by the lack of biodegradation of many synthetic dyes, which have a complex aromatic molecular structure, and their accumulation in soil, plants and living organisms.[9,10]

Some of the dyes and/or their metabolites are toxic, mutagenic and carcinogenic compounds.[11] For example, Malachite Green, which was widely used earlier for the treatment of purulent and fungal diseases in humans, in the textile and paint-and-varnish industries and for fish farming, is a mutagenic and carcinogenic agent. The accumulated dye damages the internal organs of fish and mammals, disrupts their development and can get into the human body through the food chain.[12]

In some cases, intoxication is caused not by the proper organic dye, but by toxic impurities or metabolites, resulting from dye degradation in the body. For example, mercury salts used in the synthesis of anthraquinone are partially retained in many anthraquinone dyes; for the same reasons, some dyes may contain traces of arsenic. Toxic carcinogenic metabolites may be formed from azo dyes; metabolites of benzidine derivatives and benzidine homologues (diaminobenzanilide, *etc.*) are especially hazardous.[10] Even completely non-toxic dyes may be detrimental to the environment: having dissolved in a water area, they reduce water permeability for sunlight; this accounts, for example, for the decrease in the fish population and for algae blooming.[11] Due to the extensive use of synthetic dyes and to the multitude of known problems brought about by dyes getting into the environment, strict control is required over the removal of these contaminants from waste water.

2.3. Micropathogens

Micropathogens, that is, bacteria and viruses that are spread by water, present a severe problem for human health. The causative agents of viral diseases that were detected in natural water areas, waste water and water supply systems include various strains of influenza viruses and enteroviruses.[13] Influenza A strains can overcome interspecies barriers, they can infect not only humans, but also warm-blooded animals including pigs, horses, ferrets, birds, *etc*. This results in mixing of the viral genetic material giving new strains more hazardous to humans.[14] New strains are transferred from one continent to another by migrating swimming birds and cause epidemics and pandemics.[15] In the 20th century, there were three influenza pandemics associated with extremely high morbidity and mortality and severe social and economic consequences: in 1918–1919, 20 to 50 million of people died due of influenza A/H1N1 (Spanish flu); the A/H2N2 (Asian flu) pandemics in 1957–1958 killed 70 thousand people in the USA alone; and in 1968–1969, influenza A/H3N2 (Hong Kong flu) caused 34 thousand lethal outcomes there.[16] The scientists noted that the circulating A/H5N1 strains, which caused avian flu pandemics in 2004, have not yet adapted to be transmitted from human to human. However, if this takes place, a pandemic will be quite probable and the consequences are difficult to predict.

Enteroviruses include poliomyelitis and Coxsackie viruses, which retain the viability in small water areas or wet soil for long periods of time and are transmitted to humans through water. Enteroviruses are often isolated from sewage water and are detected in tap water. The infection enters the human body through the mucous membrane of the digestive tract and damages the gastrointestinal tract, lungs and brain. Enteroviruses can cause complications such as meningitis, encephalitis, pulmonary edema and paralysis, which may be fatal in severe cases.

Water is the most favourable habitat for the bacteria. Most of bacteria are harmless for humans; however, about 250 species are pathogenic.[17] Bacteria cause dreadful infectious diseases such as cholera, syphilis, anthrax, leprosy and bubonic plague, which threatened the mankind in the Middle Ages. Now the most abundant pathogens are gram-positive bacteria such as Staphylococcus aureus and enterococcus, while among gram-negative bacteria, Escherichia, Klebsiella, Salmonella and other enterobacteria are most abundant. The water route for transmission of the infection is especially typical of these enteric bacteria, since they are concentrated in water areas that are contaminated by domestic wastes.[18]

3. Methods for the removal of hazardous types of contaminants from water

The above types of contaminants cannot be removed by using settling tanks or filters, because they are dissolved and/or finely dispersed in water.[19,20] Heavy metals exist in water as ions several Angström in size, organic molecules have a size of the order of nanometres, while the size of micropathogens ranges from 50 nm to tens of micrometres. Filters with 1 μm pore size, which can keep only the largest bacteria, would develop too high resistance to water flow and would have a very low productivity. Certainly, complete purification of water can be attained by distillation or reverse osmosis, but these methods are very expensive (energy demanding) and have low productivity. Furthermore, in this case, all useful mineral salts are also removed and artificial mineralization of water is required.

The only economically feasible method for the removal of the listed types of contaminants is to use sorbents that actively trap these impurities.[3,21] Apart from the efficient uptake of contaminants, the key requirements to the sorbents include high stability, lack of solubility and lack of toxicity, moderate cost and the possibility for regeneration for reuse and disposal. The sorbents currently used for this purpose include zeolites, clays (montmorillonite), sand (silicon oxide), synthetic polymers, biosorbents based on plant products (wood, rice hulls, cotton, *etc*.) and carbon materials (activated carbons) and so on.[22–28]

In terms of the cumulative efficiency of removal of all three types of contaminants, activated carbons hold the first place.[29] However, their key function is to remove organic and biological contaminants. Carbons have a highly porous structure, which traps the contaminants due to the cage effect, *i.e*., a bacterium (or a large organic molecule) is retained in exceptionally small carbon pores, comparable in size with the size of retained objects. Nevertheless, a carbon cage can be considered to be open, because the entrapped species can be washed out. Heavy metal ions pass most easily through carbon sorbents, since there are no sufficiently small pores corresponding to the size of ions.

Heavy metal ions are better absorbed by inorganic sorbents and polymers with specific ion exchange groups. Only a combination of carbons with materials possessing specific adsorption — zeolites or ion exchange resins — enables the removal of some heavy metal ions from water. These sorbents contain polar and/or so-called chelating groups, which specifically bind to a particular ion *via* chemical (*e.g*., ionic) interaction. The carbon materials themselves are inert and do not provide for a specific interaction with an impurity. For example, cartridges packed with a carbon sorbent and an ion exchange resin serve for the removal of iron and lead ions from water. However, other hazardous and widely encountered types of contaminants such as mercury, chromium and cadmium ions pass through these sorbent without any hindrance (see https://www.aquaphor.ru/aqualen). Another type of cartridges packed with a carbon sorbent in combination with an ion exchange resin containing silver ions was proposed for eliminating the bacterial contamination of water (see https://blog.aquaphor.ru/serebro-v-filtrah-dlya-vody).
However, silver itself is a heavy metal, and increased concentration of silver ions in water is unhealthy for living organisms. Furthermore, silver and ion exchange resins are expensive, which markedly increases the cost of sorbents.

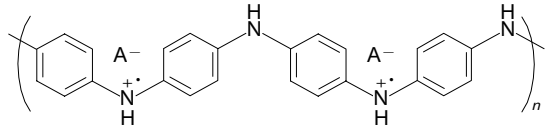
4. Polyaniline and polypyrrole

This necessitates the use of new types of sorbents with enhanced performance and versatility, *i.e*., sorbents that would ensure the removal of all three types of contaminants. This condition is fulfilled for polyaniline and polypyrrole, representatives of a new class of polymers with a polyconjugated structure. These polymers are called smart materials;[30] they possess semiconducting properties, such as electronic and ionic conductivity and redox behaviour, and intensely absorb electromagnetic radiation.[31] The properties of polymers reversibly change under the action of electrical potential, on contact with oxidants or reductants, acids or bases, *etc*. These polymers are already commonly used in a number of fields such as power engineering, electronics and

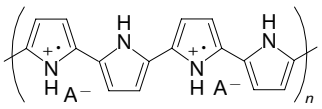
medicine and for the manufacture of protective and conductive coatings.[32–37]

However, recent studies demonstrated that PANI and PPy can be used as sorbents, in particular, for water treatment, because they possess pronounced ion exchange and sorption properties and react with various types of organic and inorganic compounds.[38–40] Apart from the excellent adsorption ability, PANI and PPy meet all the necessary requirements for sorbents meant for water treatment: they are highly stable, virtually insoluble in any solvent and do not degrade in aqueous media either under ambient conditions or at elevated temperatures, *i.e.*, they do not themselves act as a source of water pollution.[40] The polymers are non-toxic and, moreover, biocompatible (they are used in medical design both *in vivo* and *in vitro*).[41–44] Polyaniline (structure **1**) and polypyrrole (structure **2**)† can be obtained as highly porous permeable nanostructures with a high specific surface area; they are hydrophilic and readily wetted by water, which improves the sorbent performance.[45] For industrial manufacture, the prime cost of polymers should not be high. The sorption properties of PANI and PPy towards the three above-listed types of contaminants are considered below.

Structures 1, 2



1



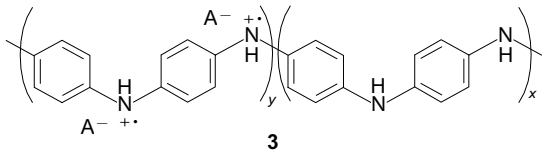
2

4.1. Causes behind the high adsorption activity of polyaniline and polypyrrole

High adsorption capacity of the title polymers is caused not only by the large specific surface area, porosity (cage effect) and hydrophilicity (good wettability) of materials based on them, but also by the possibility of specific chemical interactions with the three types of contaminants.

The PANI and PPy polymer chains contain nitrogen atoms, which are highly potent in binding both organic and inorganic compounds. Nitrogen atoms provide for various types of interaction: ionic, acid–base and donor–acceptor interactions; the proximate positions of nitrogen-containing groups imply the possibility of chelation in which a contaminant molecule (or metal ion) interacts simultaneously with several nitrogen-containing groups.[40,45] The nitrogen atoms incorporated into the polymer can undergo reversible oxidation or reduction in the potential range from -0.2 to $+1.0$ V (against the hydrogen scale).[45] The structural formula of PANI can be conventionally represented as a combination of two types of structures: oxidized monomer units with the content y and reduced units with the content x (structure **3**); in reality, the oxidized and reduced units are uniformly distributed along the polymer chain.

Structure 3



3

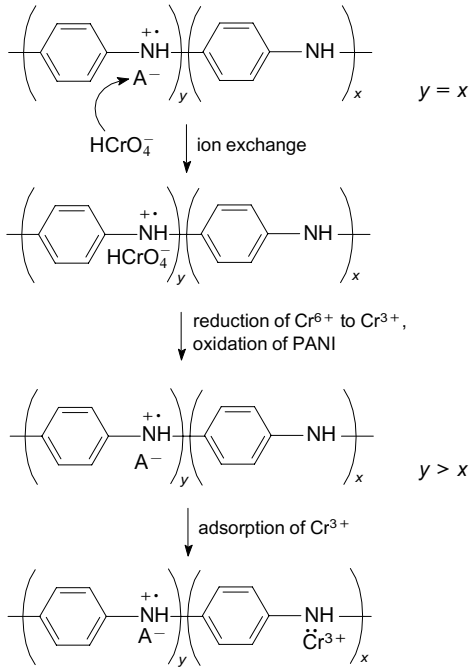
In the equilibrium state, the contents of the oxidized and reduced forms of nitrogen are approximately equal: $y = x$. However, under the action of oxidants or reductants, this equilibrium reversibly shifts, *i.e.*, one of the forms predominates. Polyaniline and polypyrrole can undergo redox reactions with many organic compounds (hydrazine, formic acid, formaldehyde and so on).[46] The polymers reduce noble metal ions (silver, gold, platinum, palladium, *etc.*) to the metallic state, while ions of more active metals are reduced to lower oxidation states.[47,48] Thus, PANI and PPy can also react with contaminants as redox agents.

4.2. Interaction with heavy metal ions

As an example, consider the chain of reactions that take place between PANI and hexavalent chromium compounds dissolved in water; chromium(VI) has a very high toxicity and mutagenicity, caused primarily by its high oxidative capacity (Scheme 1).[49]

Hexavalent chromium exists in water as $HCrO_4^-$ or $Cr_2O_7^{2-}$ anions. Initially, chromium anions electrostatically interact with positively charged nitrogen groups located along the PANI chain. The reaction is accompanied by ion exchange: the $HCrO_4^-$ anion displaces the A^- anion, which counterbalanced the positive charge of PANI. Apparently, capture of the anion and establishment of the ion exchange equilibrium are faster in electrically conductive polymers than in typical ion exchange systems owing to high mobility

Scheme 1



† Polymer structures are presented in the thermodynamically stable oxidized form in which half of the nitrogen atoms are oxidized and occur as positively charged radical cation centres counterbalanced by anions (A^-).

of a positive charge along the chain. The ion exchange interaction in PANI and PPy is supported by high ionic conductivity of the polymers. In this case, not only the $HCrO_4^-$ ion does diffuse towards the positive charge, but the positive charge can migrate towards the anion at a much higher rate.[50,51] Then the contact between the hexavalent chromium and the polymer results in chromium reduction to the trivalent state ($Cr^{6+} \rightarrow Cr^{3+}$). Chromium(III) is much less toxic than chromium(VI) and exists as a cation.[52] Binding of the Cr^{3+} cationic species is performed by reduced and uncharged amino groups of PANI. The Cr^{3+} cation binds to the lone pair of the amino group nitrogen; this donor–acceptor binding to the sorbent results in Cr^{3+} removal from the aqueous medium.

The interaction with the nitrogen lone pair also accounts for binding of cationic species of other heavy metals (Hg^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+}, *etc.*) by electrically conductive polymers.[53,54] Spectral studies reveal the interaction between positively charged metal cations and polymer amino groups.[51,55] The capacity of polymeric sorbents increases with increasing content of the reduced monomer units ($x > y$). Below we will show that heavy metal cations are adsorbed most efficiently by composite adsorbents in which the second component induces reduction of the polymer (at least, to a low extent). This effect is caused by the contact of PANI and PPy with metal oxides (Fe_2O_3, Al_2O_3).

The redox transitions for PANI and PPy are reversible; the polymer returns to the thermodynamically stable equilibrium state in which $x = y$. It was shown that the reduced form is regenerated *via* the reaction with air oxygen.[56] When the over-oxidation is significant, for example, upon the reaction with Cr^{6+} cations in a high concentration, regeneration takes place *via* minor irreversible changes — intermolecular cross-links the formation of which has little effect on the sorption properties of the polymer.[57] Thus, by being involved in redox reactions with the contaminant, the polymer can be self-regenerated over a relatively short period of time (minutes).[49] It repeatedly returns to the most active and functional equilibrium form with an average oxidation state and is ready for new interactions.

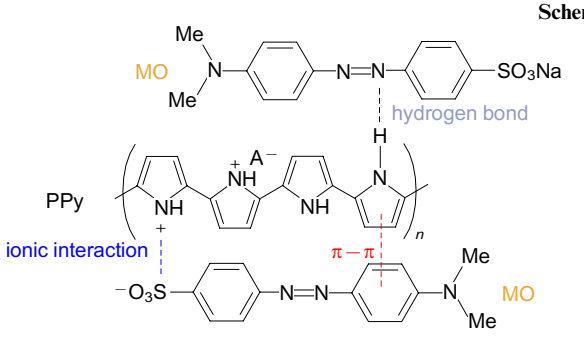
4.3. Binding of toxic organic compounds

The toxic organic compounds that pollute water usually contain acid–base groups, which facilitate their water solubility. Owing to the presence of nitrogen-containing moieties, PANI and PPy are bases and can participate in the acid–base interactions with organic compounds. The acid–base properties of the polymers differ, depending on the oxidation state. In the case of PANI, these properties vary over an especially wide range.[58] In the equilibrium form (average oxidation state), PANI has the acid–base equilibrium constant pK 3–4 (medium-strength base), whereas in the reduced form and in the highest oxidation state, the polymer has pK < 1, which corresponds to a weak base.[59]

One more widely encountered type of interaction between organic compounds is hydrogen bonding. The energy of hydrogen bonds amounts to a few tens of kilocalories per mole, which is several times lower than the energy of conventional chemical bonds, but markedly higher than the energy of van der Waals contacts. Under the action of thermal motion, hydrogen bonds are easily cleaved and reversibly formed again. Apparently, these bonds are among the driving forces that provide for self-healing and coalescence processes in living and non-living nature.[60] Studies showed that PANI and PPy are pierced by a network of hydrogen bonds.[61,62] On contact with a water-soluble organic molecule, the hydrogen bonds occurring in the polymer are replaced by intermolecular (inter-entity) hydrogen bonds, thus providing linking of the entities. Hydrogen bonds are formed between the amino groups of PANI or PPy and the oxygen, sulfur and nitrogen heteroatoms, which are present most often in organic contaminants.

Apart from the listed types of interaction, PANI and PPy can specifically interact with aromatic molecules formed by π-electrons. The vast majority of synthetic dyes and some antibiotics and other drugs that may get into water during their production and application are aromatic. The PANI and PPy polymer chains are extended conjugated chains. This is a huge reservoir of π-electrons and a potent source of π–π-electron interactions with aromatic organic compounds.[63] According to rough calculations, the energy of π–π-interactions is not lower than the energy of hydrogen bonds, and they should be necessarily considered among the interactions with organic and biological contaminants.[64,65] The possible types of interaction between Methyl Orange (MO) dye and PPy, including the ionic interaction between the dye sulfo groups and PPy imino groups, hydrogen bonding between the polymer amino groups and the azo structure of the dye and π–π-electron contacts between the polymer and the dye, are depicted in Scheme 2.[63]

Scheme 2



4.4. Interaction with biological objects

The interaction of electrically conductive polymers with biological materials is extensively studied, because PANI and PPy are biocompatible and start to be used in medicine for the hyperthermia treatment of malignant neoplasms, for targeted drug delivery, as subcutaneously implanted bioelectrodes and sensors,[66] and in the cell engineering as electrically conductive supports for the growth of living tissues — epidermal, bone, nervous and cardiac muscle tissues. Numerous studies confirmed the lack of toxicity and the biocompatibility of PANI and PPy.[42,43,67,68]

It was found that, unlike the one-stage adsorption of simple organic molecules by polyaniline and polypyrrole, adsorption of DNA by these polymers occurs in two stages.[69] Presumably, in the first stage, negatively charged DNA approaches the positively charged polymer because of long-range electrostatic forces, and then DNA is adsorbed on the surface of a polymer particle. This is accompanied by ion exchange: some of the anions that counterbalance the positive charge are displaced by DNA from the polymer

surface and migrate to the solution. The higher the polymer positive charge, the stronger the DNA adsorption. This process has a low activation energy; however, the type of the displaced anion is very significant. In the second stage of binding to the polymer, the DNA double strand undergoes conformational changes. This is a result of spatial adjustment of DNA to the polymer particle and formation of common hydrogen bonds and specific hydrophobic and π–π-electron interactions. The presence of a network of $-NH\cdots S-$ and $-NH\cdots O-$ hydrogen bonds between the polymer and DNA was confirmed experimentally. These forces are considered to be crucial for binding and, furthermore, for activation and deactivation of biological objects.[70, 71]

Thus, the results of numerous studies of polyconjugated polymers attest to the presence of chemisorption and to the possibility of adsorption *via* various types of chemical interactions: ion exchange, redox, donor–acceptor, acid–base and π–π-electron interactions and hydrogen bonding. Therefore, PANI and PPy can serve as, first, efficient and, second, versatile sorbents for water treatment, as they are able to bind large amounts of various types of contaminants.

5. Supramolecular structure and surface properties of electrically conductive polymers

Polyaniline and polypyrrole are finely dispersed black powders, usually consisting of spherical nanoparticles several tens of nanometres in size. These particles are aggregated to an, at least, two-level hierarchical structure.[72] The initial nanospheres are strongly bound into quasi-spherical particles (granules) 200–300 nm in diameter, which represent the first aggregation level (Fig. 1). The granules are, in turn, aggregated due to weak physical contacts into micrometre-scale particles, which correspond to the second level of aggregation. This is the granular structure of the polymer.

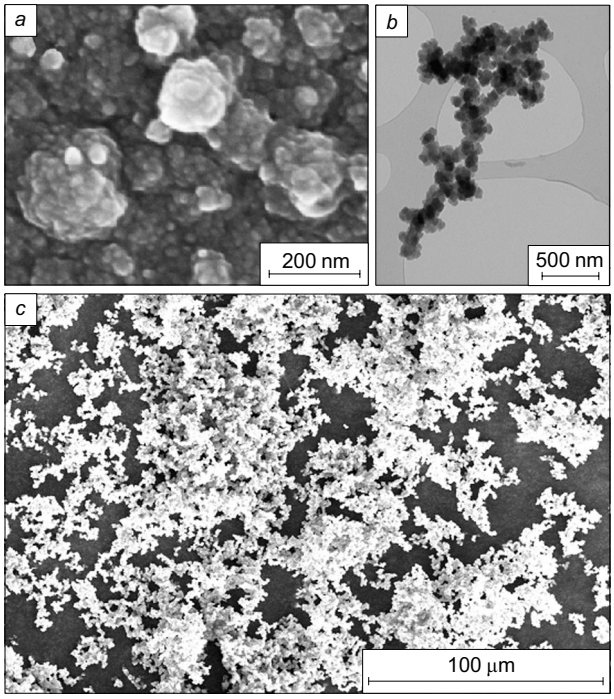


Figure 1. Granular structure typical of PANI and PPy (unpublished results of the authors). Scanning electron microscopy (SEM) images of PANI and PPy (*a*, *c*), transmission electron microscopy (TEM) image of PANI (*b*).

Second-level aggregates are permeable for contaminants, whereas granules are permeable only for ions and are virtually impermeable for large organic molecules and, the more so, for micropathogens. The smaller the granules, the greater the effective surface area of the powders and, hence, the higher their performance. The specific surface area of the granular PANI and PPy powders, determined by the Brunauer–Emmett–Teller method, is 10–30 $m^2\ g^{-1}$ (Ref. 73).

For increasing the specific surface area and the permeability, nanostructured PANI and PPy are fabricated.[74, 75] Most often, they form one-dimensional fibres or nanotubes (Fig. 2 *a*), but two-dimensional graphene-like structures are also present (Fig. 2 *b*).[75] The specific surface area of these materials is of the order of several hundreds of square metres per gram, which is much greater than that for zeolites or ion exchange resins and is comparable with the specific surface area of activated carbon.[76]

Unlike hydrophobic carbon materials, polymeric sorbents are hydrophilic and are readily wetted by aqueous media. The contact angles of carbon materials are $>90^\circ$, whereas the contact angles of polymers doped with inorganic acids are $<30^\circ$ and, in some cases, it even tends to zero (in order to eliminate the capillary effect, the contact angle is measured for polymers compacted at high pressure).[77] This means that in the case of a polymer, the polluted water penetrates into markedly smaller pores and the true effective surface area of PANI and PPy may be higher than that for carbon materials.[78]

One more way for increasing the specific surface area of PANI and PPy is to immobilize the polymer as a submicrometre- or a nanoscale-thick layer on a support. The possible supports include finely dispersed inorganic materials (SiO_2, MnO_2, Fe_3O_4), carbon allotropes, synthetic polymers and natural materials as powders, films, sponges, cloths (see Fig. 2 *c*,*d*).[79–82] When immobilized on a non-loose material (cloth, sponge), the sorbent is converted to a filtration membrane and is more convenient for handling than a powder. The immobilization of PANI and PPy on active materials possessing semiconductor and redox properties (*e.g.*, Fe_3O_4) can change the polymer oxidation state and adsorption capacity towards particular type of contaminants. For example, contact with the oxides of active metals (aluminium, zinc, iron) results in partial reduction of the polymer, *i.e.*, the content of amino groups increases and the efficiency of binding of positively charged contaminants such as Hg^{2+}, Pb^{2+} and Cd^{2+} is enhanced.[49, 52]

Methods for PANI and PPy immobilization differ from the traditional methods for polymer processing and moulding, because conductive polymers are unprocessable materials: they do not dissolve or melt.[83] The polymers are deposited on a support using preliminarily prepared dispersions containing submicrometre- and nanometre-scale polymer particles stabilized by special additives and dispersed in a particular solvent.[84] However, most often, *in situ* polymerization is used, that is, the polymer is synthesized in the presence of a support in the reaction medium. It is important to select the conditions of synthesis under which the polymer chains grow heterogeneously on the support surface.[85] In this case, a polymer layer covers the support and the adhesion to the support is usually high. Figure 3 presents the SEM images of various materials before and after they are coated by polyconjugated polymers by means of *in situ* polymerization.

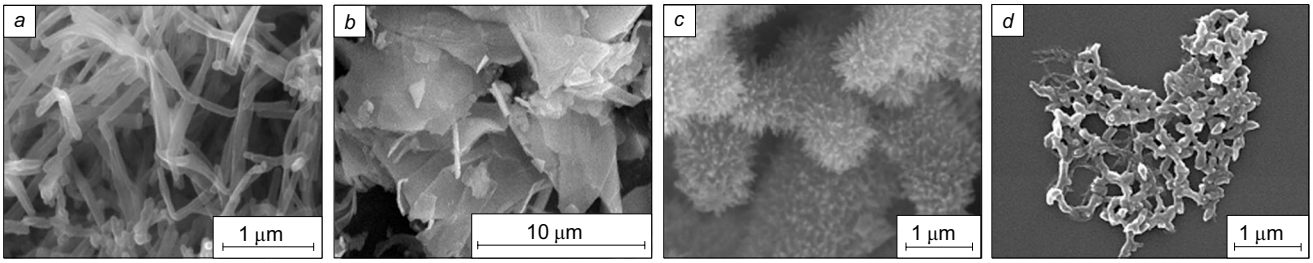


Figure 2. SEM images of PANI and PPy particles. PPy nanotubes (*a*); PANI particles with a flat two-dimensional structure (unpublished results of the authors) (*b*); Ref. 79 (*c*) and Ref. 80 (*d*) are hierarchical PANI nanostructures with a large specific surface area.

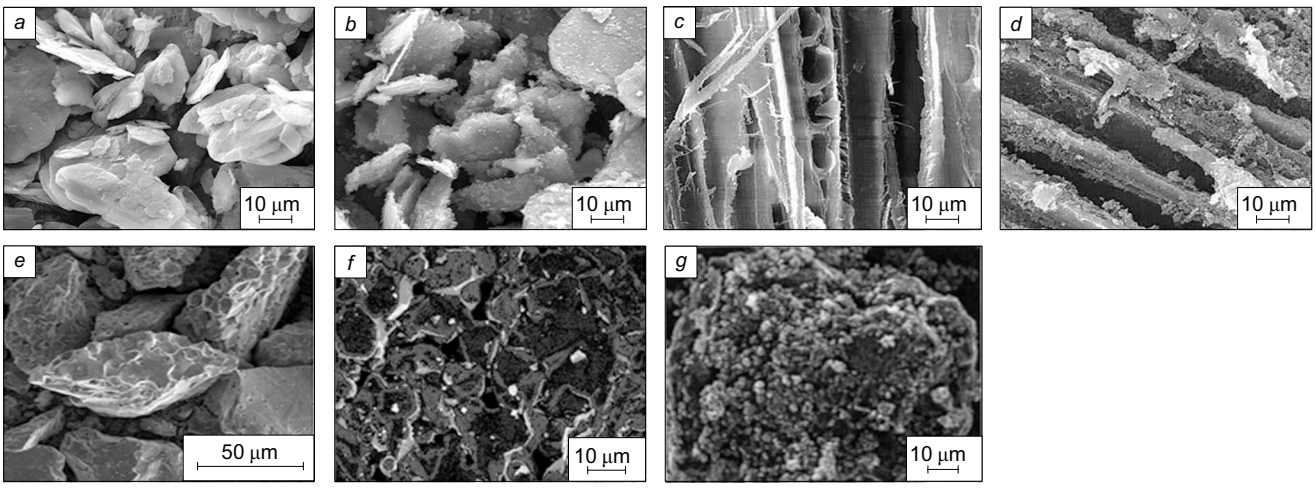


Figure 3. SEM images of composite materials based on polyconjugated polymers obtained by *in situ* polymerization. Graphite particles before (*a*) and after (*b*) PANI modification of the surface;[86] uncoated (*c*) and PPy-coated (*d*) wood fibres;[87] manganese zinc ferrite particles at different magnifications (*e*, *f*) and after coating by PANI (*g*).[88]

6. Efficiency of adsorption of various types of water contaminants by polyconjugated polymers and polymer-based composites

This Section gives particular data on the adsorption capacity‡ of PANI and PPy towards each of the three types of contaminants and on the efficiency of water purification. The results are presented in comparison with characteristics of other types of sorbents that are traditionally used for this purpose.

6.1. Adsorption of heavy metal ions

Due to the high risk of environmental pollution by heavy metal ions, the greatest number of publications are devoted to the removal of exactly this type of contaminants. Data on the adsorption of chromium ions by electrically conductive polymers are presented in reviews;[49,52] the adsorption of mercury, lead and cadmium was addressed in several studies.[89–91]

The results of studying the sorption properties of various types of sorbents, including PANI and PPy, for the removal of heavy metal ions from water are given in Table 1.[92–134] This is only a small part of data available from the literature. It is noteworthy that the given values of adsorption capacity cannot be directly compared, since the authors used different initial concentrations of heavy metal ions and different amounts of sorbents, which influenced the results. The conditions in which sorption was conducted, such as temperature, acidity of the medium, contact time between the sorbent and the contaminant, *etc.*, were also different. Finally, the sorbents and their manufacture and processing methods were different. Indeed, granular PANI can be prepared in different ways and can have different sizes of granules. For this reason, one cannot expect that the adsorption capacity values for similar sorbents would coincide.[3] Nevertheless, analysis of the results presented in Table 1 reveals the following general trends:

— natural organic sorbents (cellulose derivatives) weakly bind heavy metal ions, but the dsorption capacity somewhat increases after sorbent carbonization, *i.e.*, conversion to carbon;

— inorganic sorbents (zeolites, silicates) adsorb heavy metal ions, on average, an order of magnitude more efficiently than natural organic sorbents;

— the adsorption capacity values of PANI and PPy are higher than those of traditionally used natural organic and inorganic sorbents; the capacity increases on going from polymers with close packing of particles (granules) to nanostructured materials and composites, in which a thin polymer layer is deposited on a finely dispersed or porous material.

‡ The amount of contaminants in milligrams removed by 1 gram of the sorbent (mg g^{-1}).

Table 1. Adsorption capacities of various sorbents towards heavy metal ions and degrees of water purification by these sorbents.

Sorbent	Capacity /mg g^{-1}	Degree of water purification (%)	Ref.
Cr^{6+} *ions, MAC = 0.005 mg L*$^{-1}$			
Sorbents based on PANI			
PANI (granules)	98–180	>90	92–94
PANI (nanotubes)	248–263	97–100	92, 95
PANI/montmorillonite	308	–	96
PANI/silica gel	193	–	97
PANI/magnetite	200	90	98
PANI/graphene	1149	>90	99
Sorbents based on PPy			
PPy/magnetite	170–240	–	100, 101
PPy/PANI	227	99.8	102
PPy/Co_3O_4	70	–	111
Other sorbents			
Halloysite nanotubes ($AlSiO_n$)	63	–	103
Activated carbon	4.26	–	104
CNT	9.0	–	105
Cellulose	65	–	106, 107
Chitosan	9.42	70	108, 109
Starch	12	–	110
Cd^{2+} *ions, MAC = 0.003 mg L*$^{-1}$			
Sorbents based on PANI			
PANI (granules)	130	–	54
PANI/cellulose	138	89.6	54, 112
PANI/wood	430	–	113
PANI/magnetite	500	99	114
PANI/manganese oxide	480	89	115
Sorbents based on PPy			
PPy (granules)	50–180	85–90	55, 116
PPy/CNT	390	–	117
PPy/silica gel	120	–	118
Other sorbents			
Silica gel	18.25	–	119
Walnut sawdust	4.39	–	120
Wood sawdust	5.4	–	113
Chitosan	80	–	121
Cellulose	200	–	107
Hg^{2+} *ions, MAC = 0.001 mg L*$^{-1}$			
Sorbents based on PANI			
PANI (granules)	103	92.7	122
PANI (nanotubes)	335–206	100	122, 123
PANI /manganese oxide	437	96	115
PANI/sulfonic acid	497	98.8	124
PANI/silica gel	843	100	125
PANI/graphene	81	–	126
PANI/graphene	515–1000	94	127
Sorbents based on PPy			
PPy/polyurethane	200	–	122
PPy/zeolite	157	–	128
PPy/silica gel	680	–	129

Table 1 (continued).

Sorbent	Capacity /mg g^{-1}	Degree of water purification (%)	Ref.
Pb^{2+} *ions, MAC = 0.01 mg L*$^{-1}$			
Sorbents based on PANI			
PANI (granules)	130	–	54
PANI/ alginate	251	90	130
PANI/cellulose	217	–	54
PANI/graphene	1400	–	131
Sorbents based on PPy			
PPy (granules)	64	93	55
PPy/CNT	408	–	132
Other sorbents			
Halloysite nanotubes ($AlSiO_n$)	84	–	133
Silica gel	50	–	134
Walnut sawdust	6.54	–	120

Note. The following designations are used: MAC is the maximum concentration level, CNTs are carbon nanotubes.

The effect of adsorption conditions on the efficiency of water purification by conjugated polymers has been studied. The adsorption capacity is considerably affected by pH of the aqueous medium. This is primarily due to the pH-active nature of the polymeric sorbents. The Cr^{6+} ions are removed more intensely in acidified solutions with pH 1–3, since the redox activity of polymers is maximized under these conditions, which facilitates the reduction of Cr^{6+} to Cr^{3+}. Meanwhile, cationic species of heavy metals, including Cr^{3+} cations, are adsorbed more easily by poly-conjugated polymers in neutral media, because adsorption involves uncharged amino groups.[54, 55, 135]

Data on the microextraction of various metal cations by the PPy/CNT sorbent as a function of pH of the aqueous medium are presented in Fig. 4.[136] It can be seen that for most metals, the optimal adsorption conditions are neutral media with pH 6–8, which is important for purification of tap water.

The influence of other parameters on sorption is less pronounced.[3] Sorption characteristics virtually do not depend on temperature. As the contaminant concentration increases, the rate of adsorption and the contaminant

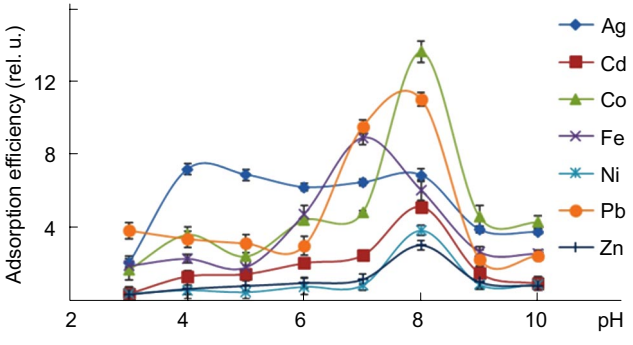


Figure 4. Efficiency of adsorption of various metal ions from an aqueous medium by the PPy/CNT sorbent as a function of pH.[136]

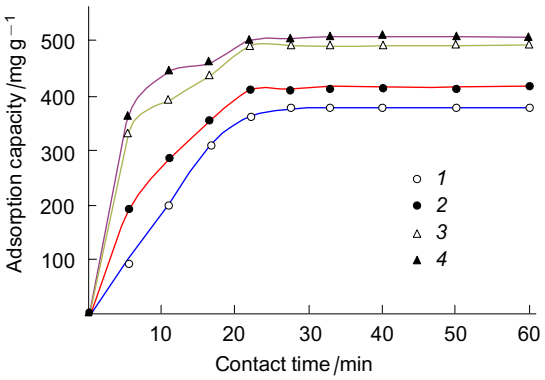


Figure 5. Effect of the initial concentration of Cd^{2+} ions and the contact time with the PANI/sawdust sorbent on the adsorption capacity.[53] Initial concentration of the Cd^{2+} ions /ppm: (*1*) 20, (*2*) 25, (*3*) 35, (*4*) 40.

uptake increase until the adsorption capacity limit for the sorbent is reached. This is shown in Fig. 5 in relation to adsorption of Cd^{2+} ion by the PANI/wood sawdust composite. After the adsorption capacity limit is reached, *i.e.*, the sorbent is saturated by the contaminant, the efficiency of water purification decreases.[53]

An important characteristic is the necessary contact time of the sorbent with the polluted medium. Many authors point out an increased rate of adsorption of contaminants on PANI and PPy in comparison with conventional sorbents.[113] The sorption equilibrium for polymeric sorbents is established within several tens of minutes or a few hours, whereas for zeolites and carbon sorbents, this time can reach tends of hours.[137, 138] An important factor for fast establishment of sorption equilibrium is the accessibility of the sorbent surface. The transport of molecules and particles in extended narrow pores substantially retards this process. Large specific surface area with shallow accessible pores, readily wetted by water, is required for the sorbent. As a rule, in the case of PANI and PPy composites in which a polymer nanolayer is immobilized on the surface of a highly porous material, the rate of equilibration is higher than that for granular PANI and PPy.[54] For example, PANI deposition on conventional sorbents used for water treatment, such as cellulose derivatives (ethylcellulose) and carbon fibres, leads to a considerable increase in the efficiency of adsorption of hexavalent chromium and to increasing rate of adsorption (Fig. 6). When a relatively small amount (10 mass %–20 mass %) of PANI is introduced into a conventional sorbent, the efficiency of Cr^{6+} removal doubles and the rate of adsorption increases by a large factor.

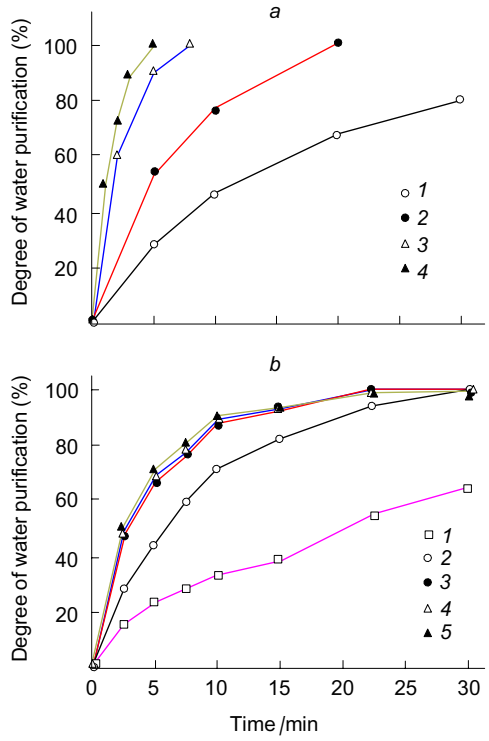


Figure 6. Removal of Cr^{6+} ions from water by composite sorbents based on PANI. Sorbent: (*a*) PANI/ethylcellulose,[139] (*b*) PANI/carbon fibres.[140] PANI content in the sorbents (mass %): *a*: (*1*) 0, (*2*) 5, (*3*) 10, (*4*) 20; *b*: (*1*) 0, (*2*) 5, (*3*) 10, (*4*) 15, (*5*) 20.

The thermodynamic parameters of adsorption of heavy metal ions by conjugated polymers have been studied. The standard Gibbs free energies for the adsorption of Pb^{2+} and Cd^{2+} by polyaniline at 30 °C are −6.38 and −5.83 kJ mol^{-1}, respectively.[54] The negative Gibbs energies attest to the spontaneous character of adsorption of metal ions by the polymer and to the possibility of retention of the contaminant by the sorbent.

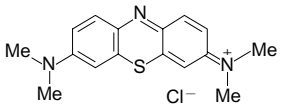
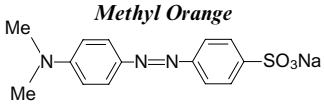
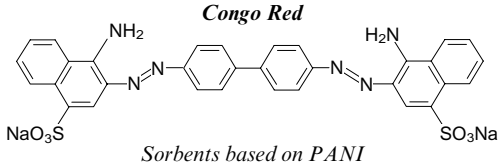
6.2. Adsorption of synthetic dyes

Different characteristics can be used to classify synthetic dyes: engineers use the field of application and solubility; chemists use the chemical structure (there are two main groups: azo dyes and anthraquinone dyes) or the sign of the charge generated on the molecule upon dissolution in water, that is, cationic (positive charge), anionic (negative charge) and neutral (zero charge) dyes. It is the chemical structure and the charge that determine the sorption interactions and the intensity of dye binding to the sorbent. The adsorption of dyes by polyconjugated polymers is the subject of several reviews.[3, 141, 142]

Data on the adsorption of chemically different dyes possessing either cationic or anionic properties by conjugated polymers are summarized in Table 2. For comparison, data on the adsorption of the same dyes by conventional sorbents are also presented. It can be seen that, despite considerable scatter of the results, the adsorption capacity is, most often, higher for materials based on PANI or PPy than for conventional natural sorbents. There are no noticeable difference between the adsorption of dyes with different chemical structure or different charge.

In a number of studies, the sorption of anionic and cationic dyes was studied under identical conditions (equal dye concentrations and contact conditions between the sorbent and the dye). In these cases, direct comparison of the results was possible. It was found that the adsorption capacities of polymers for cationic and anionic dyes are approximately equal. The adsorption capacities of PANI towards the cationic Crystal Violet and anionic Methyl Organge dyes are 245 and 220 mg g^{-1}, respectively.[168] The PANI composite can bind 467 mg g^{1} of the cationic Methylene Blue and 440 mg g^{-1} of anionic Rose Bengal dyes under the same conditions.[169] PANI nanotubes equally efficiently take up anionic Acid Green 25[170] and cationic

Table 2. Adsorption capacities of various sorbents towards synthetic dyes and degrees of water purification by these sorbents.

Sorbent	Capacity /mg g^{-1}	Degree of water purification (%)	Ref.
Methylene Blue			
			
Sorbents based on PANI			
PANI (granules)	73	–	143, 144
PANI (nanotubes)	192	–	145
PANI/MoO_3	–	96	145
Sorbents based on PPy			
PPy (granules)	19.3	–	63
PPy/poly(vinylidene fluoride)	385	–	146
PPy/TiO_2	323	–	147
Other sorbents			
Silica gel	50	–	148
Graphene	17.3	–	149
CNT	35–65	–	150
Hydroxyapatite	14.3	–	151
Sawdust	5.8	–	152
Alginate	572	–	153
Methyl Orange			
			
Sorbents based on PANI			
PANI (hollow nanospheres)	154	–	9
PANI/sawdust	137	89	154
PANI/polyamide	82	85	155
PANI/$ZrPO_4$	377	94	156
Sorbents based on PPy			
PPy (granules)	232	–	157
PPy/carbon	110–140	–	158
PPy / halloysite	215	–	159
Other sorbents			
Activated carbon	9.5	–	149
Banana husk	21	–	160
Congo Red			
			
Sorbents based on PANI			
PANI/lignin	1672	99.8	161
PANI/chitosan	323	95.4	162
PANI/Fe	244	–	163
PANI/MoS_2	71	–	164
Sorbents based on PPy			
PPy (granules)	122	–	165
PPy/ferrite	120	–	166
Biosorbent			
Rice hulls	103	–	167

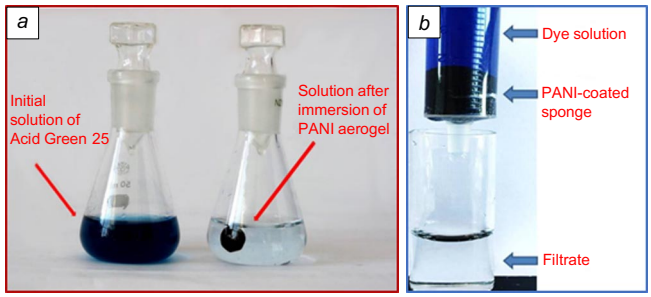


Figure 7. Removal of Acid Green 25 (*a*) and Reactive Black 5 (*b*) dyes from water.[63] (*a*) treatment by PANI-based aerogel by immersion of the sorbent; (*b*) treatment by PANI-coated polyurethane sponge by filtering a dye solution through the sponge.

Methylene Blue.[171] These results indicate that ionic interactions with the dyes do not play a crucial role in the sorption. Apparently, in the case of PANI and PPy, an important role belongs to hydrogen bonds and π–π-electron interactions between the sorbent and the dye.

Fast and efficient binding of dyes to polyconjugated polymers is evidenced by a large body of published data. Figure 7 shows examples of removal of Acid Green 25 by a PANI-based gel and Reactive Black 5 by PANI deposited on polyurethane sponge.

The rate of dye adsorption by conjugated polymers is rather high. The necessary contact time between the sorbent and a dye solution is several tens of minutes. The time dependence of the adsorption of Orange-II dye by nanostructured PANI for various dye contents in water is shown in Fig. 8. It can be seen that the adsorption curve comes to saturation within a period of not more than an hour.

Like adsorption of heavy metal ions, adsorption of dyes by conjugated polymers is a thermodynamically favourable process. The standard Gibbs free energies for the adsorption of Reactive Red 194, Acid Blue 62, Direct Blue 199 [172] and Orange-II [73] dyes by the PANI/γ-Al_2O_3 composite from aqueous solutions at 25 °C are negative, amounting to −2.27, −4.72, −7.12 and −6.83 kJ mol^{-1}, respectively.

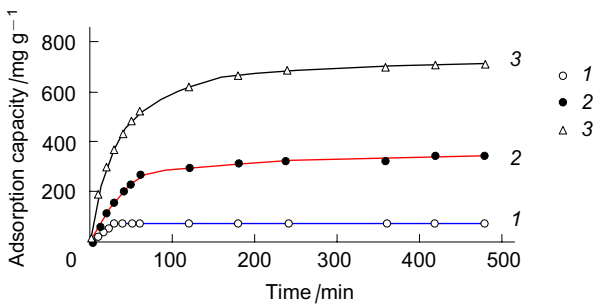


Figure 8. Adsorption capacity of nanostructured PANI *vs.* contact time with Orange-II for dye content in water of 100 (*1*), 500 (*2*) and 1000 mg L^{-1} (*3*).[73]

6.3. Adsorption of bacteria and viruses

Currently, studies of PANI- and PPy-based sorbents for the removal of micropathogens, including bacteria and viruses, from water are carried out virtually in one scientific institution, that is, Gamaleya Research Institute of Epidemiology and Microbiology.[173] Nevertheless, a large body of experimental data has been accumulated on the adsorption

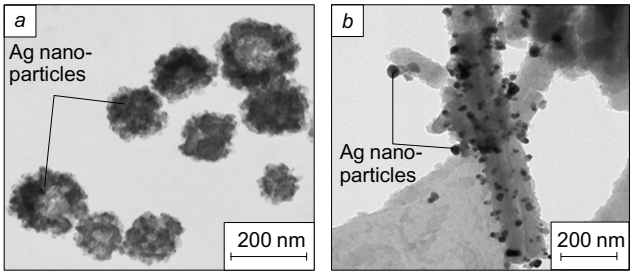


Figure 9. TEM images of PANI/Ag composites with various PANI nanostructures. Silver nanoparticles are deposited on PANI granules (*a*) [175] and nanotubes (*b*).[47]

of various types of viruses, namely, non-enveloped poliomyelitis virus and a wide range of influenza viruses as representatives of enveloped viruses, the DNA of which is surrounded by a protein membrane.[174, 175]

Adsorption of the most widespread gram-positive and gram-negative bacteria was studied. The study was performed using PANI and PPy powders, which had different nanoscale structures and contained different counterions, and also using composites of these polymers with CNT and silver nanoparticles (Fig. 9).

A series of publications [174 – 187] deal with studying the adsorption of micropathogens on PANI and PPy by a specially developed protocol using WHO-approved methods for determination of micropathogen concentrations and toxicity. For comparison, adsorption of the micropathogens was also carried out by carbon sorbents: nanodiamonds and carbon nanotubes. The results were obtained under identical conditions and, hence, they can be directly compared.

Data on adsorption of the most common types of gram-positive and gram-negative bacteria by polyconjugated polymers and their composites with silver are summarized in Table 3.[179, 180] It can be seen that all of the sorbents decrease the content of bacteria of any type in water, but the efficiency of water purification is different. The top position in the binding of bacteria is held by granular PPy and the PPy/Ag composite, which remove all types of tested bacteria almost completely. In the case of nanotubular PPy, the adsorption efficiency is lower. The adsorption capacities of PANI and PANI/Ag are markedly lower than that of PPy; the presence of silver does not always improve the adsorption performance of the material.

Data on the adsorption of poliomyelitis virus, a broad range of influenza A, B, C viruses, and avian and swine influenza viruses (from the collection of the Gamaleya Research Institute of Epidemiology and Microbiology) by PANI and PPy polymers were reported by Sapurina and coworkers.[175, 180] The results of studying the adsorption of the most dangerous strains of influenza A virus are summarized in Table 4. The polymeric sorbents take up virtually all of the considered viral strains; however, the adsorption capacity depends both on the type of polymeric sorbent and polymer oxidation state and on the type of micropathogen.[181]

It can be seen from the data of Table 4 that the use of polymeric sorbents reduces the concentration of the virus in an aqueous medium (physiological saline) by a factor of 4 – 1024, while the infectious activity of the aqueous solution decreases by at least several orders of magnitude and, in the case of PPy or PPy/Ag, it is completely suppressed. Under the same conditions, a carbon sorbent reduces the

Table 3. Adsorption of bacteria most abundant in aqueous medium by PANI and PPy polymers with different nanostructures and their composites with silver.[179, 180]

Sorbent	Infectious titer after adsorption /CFU mL^{-1}	
	aqueous phase	sorbent
Gram-positive bacteria		
Staphylococcus Aureus Cowan		
PPy	0	0
Py (nanotubes)	20×10^1	15×10^2
PPy/Ag	0	0
PANI	15×10^2	50
PANI/Ag	10×10^2	$< 10^4$
Gram-negative bacteria		
Shigella flexneri 2a		
PPy	0	0
PPy (nanotubes)	17×10^1	30×10^2
PPy/Ag	0	0
PANI	35×10^1	0
PANI/Ag	18×10^2	80×10^3
Klebsiella		
PPy	0	0
PPy (nanotubes)	20×10^2	40×10^2
PPy/Ag	0	0
PANI	80×10^2	80×10^2
PANI/Ag	$< 10^5$	$< 10^5$

Note. The infectious titer of the aqueous phase before adsorption in all experiments was 2×10^5 CFU mL^{-1} (CFU is colony-forming unit).

virus concentration by a factor of 2 – 128. On average, PANI and PPy in the oxidized form bearing a positive charge are more efficient (the adsorption capacity depends also on the type of anion counterbalancing the positive charge).[175] These results are in line with the trends identified in the study of the interaction between PPy and DNA.[69] These trends can be explained by ionic interactions between a positively charged polymer and a negatively charged micropathogen and by ion exchange, *i.e.*, replacement of the anion present in the polymer by the pathogen.[182]

The adsorption of viruses by polymeric sorbents is fairly fast. Over the 4 – 30 °C temperature range, adsorption took place equally intensely and was completed within 15 min of the sorbent contact with the polluted medium.[184] The PPy and PPy/Ag sorbents removed concentrated influenza virus from the aqueous medium almost completely and did not release the virus on attempted desorption by dilution of the sorbent – virus complex with a fresh portion of physiological saline (Fig. 10).

The nanostructural organization of the sorbent does not affect considerably its sorption properties; in some cases, one-dimensional structures of PPy and PANI had even an adverse influence on the adsorption performance. In the case of PANI and PPy composites with silver, no clear trends were revealed either.[177] In the presence of silver nanoparticles, adsorption was improved only in some cases for some micropathogens and for PANI-based sorbents, while adsorption performance of PPy most often did not change.[185] There is no need to introduce silver into PPy-based bactericidal filters.

Table 4. Adsorption of various influenza A virus strains by PANI and PPy polymers, their composites with silver and carbon nanotubes in comparison with carbon nanotubes.

Sorbent	Virus concentration (HA unit) before (I) and after (II) adsorption		*X*	Infectious activity of the aqueous phase before (I) and after (II) adsorption		Infectious activity of the sorbent after adsorption	Ref.
	I	II		I	II		
			Virus A/Wisconsin/67/05 (H3N2)				
PANI	256	< 2	< 128	–	–	–	181
CNT	256	2	128	–	–	–	175
			Virus A/Victoria/37/11 (H3N2)				
PANI	512	128	4	–	–	–	180
PANI/Ag	512	8	64	$10^{6.5}$	–	$10^{1.5}$	181
PPy	2048	8	256	$10^{6.5}$	–	$10^{2.5}$	183
PPy/Ag	2048	2	1024	$10^{6.5}$	–	0	181
CNT	512	256	2	–	–	–	181
			Virus A/IIV-Moscow/01/2009 (H1N1)swl				
PANI	64	2	32	–	–	–	187
PANI/CNT	64	8	8	–	–	–	187
CNT	64	16	4	–	–	–	187
			Virus A/California/07/09 (H1N1)pdm09				
PPy	128	8	16	–	–	–	180
PPy/Ag	128	4	32	–	–	–	180
PPy (nanotubes)	128	16	8	–	–	–	180
			Virus A/Switzerland/9715293/13 (H3N2)				
PPy	512	2	256	$10^{4.75}$	0	0	184
PANI	512	8	64	$10^{4.75}$	$10^{2.5}$	$10^{1.5}$	184
PPy/Ag	512	2	256	$10^{4.75}$	0	0	184
			Virus A/South Carolina/02/2010				
PPy	512	0	–	–	0	–	185
PPy/Ag	512	0	–	–	0	–	185

Note. Concentration of the virus in the aqueous medium was determined by the WHO-recommended haemagglutination (HA) protocol using a 0.75% suspension of human blood type O-red blood cells. The method is based on the fact that the viral protein envelope agglutinates RBCs. The HA unit is defined as the amount of the virus needed for agglutination of an equal volume of a standardized RBC suspension. *X* is the factor of decreasing concentration of the virus in aqueous medium: ratio of the virus concentrations before and after adsorption. The infectious titers were determined by treatment of a monolayer of MDCK cell culture with the virus. The dilution of a solution of the virus that kills 50% of MDCK cells was taken as the infectious titer (log $TCID_{50}$).

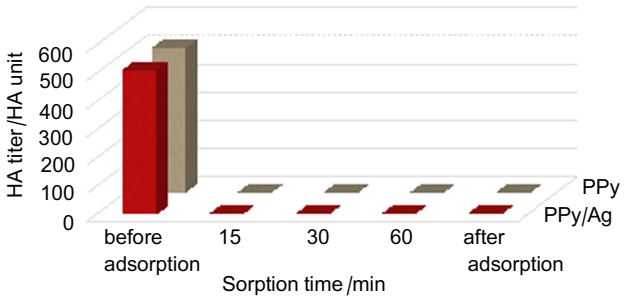


Figure 10. Haemagglutinating titers of influenza A virus/Victoria/361/11 (H3N2) in aqueous medium before and after adsorption by PPy and PPy/Ag depending on the contact time with the sorbent.[184]

A special study showed that PANI and PPy provide for cross-sorption of bacteria and viruses from aqueous media containing both types of micropathogens.[159] It was also found that viruses stripped of accompanying proteins bind more efficiently than viruses in the presence of nonviral proteins. This attests to competitive adsorption of various types of proteins by the polymers. Analysis of the set of results showed that under the same experimental conditions, the adsorption of viruses by polymers is much more efficient than adsorption by carbon sorbents, despite the greater specific surface area of the latter. A comparable adsorption capacity was found only for nanodiamonds modified by amino groups.[174, 183]

Interesting results were obtained in a study of the infectious activity of the precipitate isolated after adsorption, which represented a complex of the sorbent with the bound micropathogen. It was found that the infectious activity is considerably reduced in the case of PANI and is completely suppressed in the case of PPy and PPy/Ag.[184–186] The micropathogen is strongly held by the sorbent and is not desorbed upon dilution with fresh portions of physiological saline at either ambient or elevated temperature. Ultrasonic treatment of the sorbent–micropathogen complex releases the major portion of the virus into the aqueous phase. However, the virus extracted

from the complex proved to be non-viable and did not exhibit infectious activity. Similar results were also obtained for the isolated sorbent complexes with bacteria. These results were confirmed by literature data on the clear-cut bactericidal properties of PANI and PPy, which inhibit the vital activity of various types of bacteria and fungi.[169, 188, 189] Thus, the sorbent not only binds but also deactivates the micropathogens. This conclusion is consistent with the reported data[69] on strong binding of PPy to DNA molecules *via* hydrogen bonding, salt bridges and π–π-electron interactions. These results are highly important regarding safe disposal and also regeneration and reuse of polymeric sorbents.

To conclude this Section, we would like to note high interest in the studies of sorption properties of PANI and PPy. The high adsorption activity of the polymers can be used both for biomedical purposes and for water treatment. Here, especially important is the versatile character of adsorption of various types of contaminants by polymers, which is due to the following features of the sorbents:

— broad range of interaction types suitable for binding the contaminant,

— highly porous permeable structure comparable with carbon sorbents in the specific surface area,

— hydrophilicity of the polymers and good contact with the contaminated aqueous medium.

7. Sorbent regeneration

From the practical point of view, the possibility of repeated use and safe disposal of the sorbents are very important. In the case of PANI and PPy, reactivation makes use of the ability of polymers to change the oxidation state and doping of the polymer chains. Under the action of a small negative potential ($\leqslant -0.5$ V), polymer is reduced and its physical parameters change, in particular, the concentration of the positively charged nitrogen-containing groups sharply decreases. As this takes place, the anions that previously counterbalanced the positive charge and the water molecules that solvate the anions migrate from the polymer matrix to the aqueous phase. Analogous changes also take place when polymers are treated with aqueous solutions with pH >7; in this case, the acid anion is bound by alkali (this procedure is called dedoping). During the reduction and/or dedoping, PANI and PPy lose a considerable part of their mass and shrink in the volume; this is accompanied by decreasing hydrophilicity, decreasing concentration of hydrogen bonds and disruption of the conjugation. These changes lead to the release of contaminants bound to the polymer; furthermore, not only contaminants with anionic type of binding, but also neutral compounds are removed from the polymer matrix.[40, 45, 74, 189]

The action of the positive potential on PANI and PPy leads to the release of excess positive ions, *e.g.*, heavy metal cations or cationic dyes, from the polymer matrix.[172] Thus, by charge–discharge cycles in the potential range from -0.2 to 0.5 V against a hydrogen scale (or by changing the pH), it is possible to release various types of contaminants and regenerate the sorbent. This treatment does not damage the sorbent: no irreversible changes in PANI and PPy or degradation of sorption properties take place.

It was shown[52] that minor pH changes of PANI/TiO_2 in the range of 3–8 induce adsorption–desorption of Methylene Blue; the sorbent maintains high performance even after ten regeneration cycles: the adsorption activity amounts to 99% of the initial level. The efficiency of removal of Acid Red G, an anionic azo dye, from water by the PANI/sawdust composite and the possibility of sorbent regeneration over 45 cycles was demonstrated by Wang *et al.*,[65] while the efficiency of the removal of Methylene Blue and Acid Red G by PPy/TiO_2 nanoparticles (regeneration for six adsorption–desorption cycles) was reported by Li *et al.*[190] The results of these studies are depicted in Fig. 11.

A reversible adsorption–desorption mechanism was also observed for binding of mercury ions by polyaniline.[191] The procedure for the removal of other heavy metal ions is also rather simple and the degree of sorbent regeneration is high: $>90\%$ after 5–10 adsorption–desorption cycles.[192, 193] In the case of Cr^{6+}, a beneficial effect of decreasing the toxicity of the sorbent–metal complex appears even as chromium is reduced to the trivalent state. Nevertheless, sorbent regeneration for the reuse is attained *via* Cr^{3+} desorption under the action of weak alkali.[194]

After the adsorption of micropathogens, PPy can be reactivated under the action of ultrasound.[184, 185] Treatment in an ultrasonic bath for 15 min leads to the removal of most of infectionally inactive influenza viruses; the degree of regeneration of polypyrrole is 85%–90%.

The above examples demonstrate the possibility of regeneration and repeated use of sorbents based on PANI and PPy. Regeneration methods used after adsorption of all

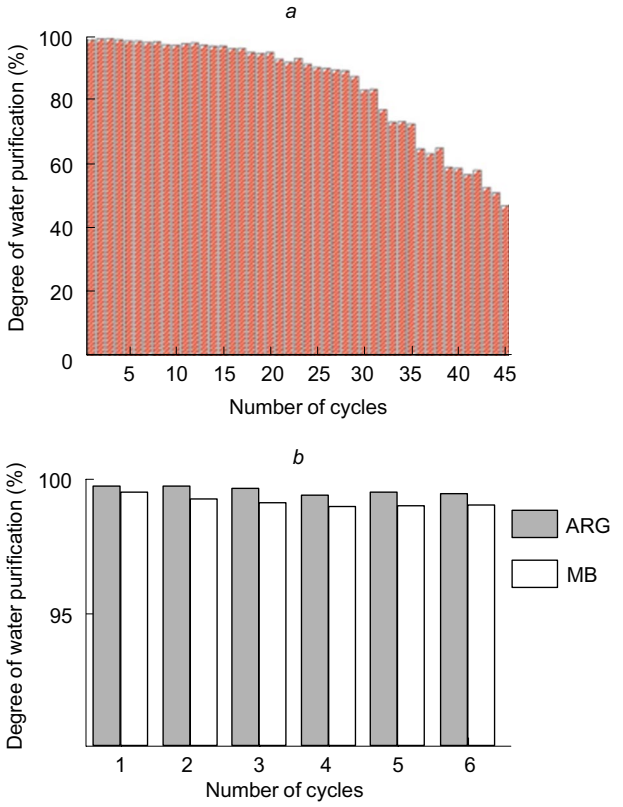


Figure 11. Diagrams of dye adsorption by sorbents based on PANI and PPy depending on the number of sorbent regeneration cycles. (*a*) Adsorption of the anionic zo dye Acid Red G (initial concentration of 180 mg L^{1}) by the PANI/sawdust composite;[65] (*b*) purification of water contaminated by MB and ARG cationic dyes using the PPy/TiO_2 sorbent.[190]

three types of contaminants are quite simple and inexpensive.

8. Conclusion

The body of experimental data that appeared in the scientific literature in recent years indicates that representatives of polyconjugated polymers, polyaniline and polypyrrole, possess excellent sorption properties, which are implemented *via* various types of chemical interactions: ion exchange, redox, donor–acceptor and acid–base interactions, hydrogen bonding and π–π-electron interactions. For this reason, PANI and PPy can bind various types of contaminants and remove the most hazardous and stubborn contaminants — heavy metal ions, toxic organic compounds and micropathogens (bacteria and viruses) — from aqueous media. The efficiency of adsorption of contaminants by PANI- and PPy-based sorbents is, most often, higher compared with currently used conventional sorbents. In view of the high stability and low cost of PANI and PPy, and also the lack of toxicity and the possibility of regeneration and reuse, one can expect that in the future, polyconjugated polymers would become versatile sorbents for the treatment of drinking water.

This work was prepared with the financial support of the Russian Science Foundation (Project No. 19-73-30003).

References

1. A.M.K.El-Ghonemy. *Renew. Sust. Energy Rev.*, **16**, 1537 (2012)
2. M.J.K.Ahmed, M.Ahmaruzzaman. *J. Water Proc. Eng.*, **10**, 39 (2016)
3. M.A.Zarea, H.Moazed, M.Ahmadmoazzam, S.Malekghasemi, N.Jaafarzadeh. *Environ. Monit. Asses.*, **191** (3), 131 (2019)
4. M.S.Bernardo, N.Lapa, R.Barbosa, M. Goncalves, B.Mendes, F.Pinto, I.Gulyurtlu. *J. Hazard. Mater.*, **166**, 309 (2009)
5. F.Fu, Q.Wang. *J. Environ. Manag.*, **92**, 407 (2011)
6. G.Macchi, D.Marani, M.Pagano, G.Bagnuolo. *Water Res.*, **30**, 3032 (1996)
7. *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*. Vol. 1. (Lyon: International Agency for Research on Cancer, 1972)
8. M.K.Aroua, F.M.Zuki, N.M.Sulaiman. *J. Hazard. Mater.*, **147**, 752 (2007)
9. M.Ajaz, S.Shakeel, A.Rehman. *Int. Microbiol.*, **23**, 149 (2020)
10. L.K.Wang, Y.Hung, H.H.Lo, C.Yapijakis. In *Handbook of Industrial and Hazardous. Wastes Treatment*. (2nd Edn). (Boca Raton, FL: Mercel Dekker, 2004). P. 65
11. H.Zollinger. *Properties and Applications of Organic Dyes and Pigments Colour Chemistry-synthesis*. (New York: VCH, 1987)
12. S.Srivastava, R.Sinha, D.Roy. *Aquat. Toxicol.*, **66**, 319 (2004)
13. V.S.Hinshaw, R.G.Webster. In *Beare AS Basic and Applied Influenza Research*. (Boca Raton, FL: CRC Press, 1982)
14. S.Borland, P.Gracieux, M.Jones, F.Mallet, J.Yugueros-Marcos. *Front. Publ. Health*, **8**, 83 (2020)
15. V.S.Hinshaw, R.G.Webster, B.Turner, P.J.Zwank. *Intervirology*, **11**, 66 (1979)
16. S.J.Lycett, F.Duchatel, P.Digard. *Philos. Trans. R. Soc. B*, **374**, 20180257 (2019)
17. K.P.Talaro, B.Chess. In *Foundations in Microbiology*. (New York: McGraw-Hill Education, 2018). P. 111
18. C.M.Hogan. *Bacteria. Encyclopedia of Earth*. (Eds S.Draggan, C.J.Cleveland). (Washington, DC: National Council for Science and the Environment, 2010)
19. A.Anantharaman, Y.Chun, T.Hua, J.W.Chew, R.Wang. *Water Res.*, **173**, 115558 (2020)
20. A.Demirbas. *J. Hazard. Mater*, **157**, 220 (2008)
21. M.M.Lakouraj, R.-S.Norouzian, S.Balo. *J. Chem. Eng. Data*, **60**, 2262 (2015)
22. A.Walcarius, L.Mercier. *J. Mater. Chem.*, **20**, 4478 (2010)
23. N.Sivarajasekar, N.Mohanraj, S.Sivamani, J.P.Maran, I.G.Moorthy, K.Balasubramani. *Mater. Today: Proc.*, **5**, 7264 (2018)
24. N.Sivarajasekar, N.Mohanraj, K.Balasubramani, J.P.Maran, I.G.Moorthy, V. Karthik, K.Karthikeyan. *Desalin. Water Treat.*, **84**, 48 (2017)
25. Y.L.Kobzar, I.M.Tkachenko, V.V.Shevchenko. *Mendeleev Commun.*, **29**, 307 (2019)
26. V.M.Akhmedov, A.M.Maharramov, A.A.Azizov, R.M.Alosmanov, I.A.Bunyad-Zadeh, S.B.Aliyeva. *Russ. Chem. Bull., Int. Ed.*, **68**, 514 (2019)
27. J.-S.M.Lee, A.I.Cooper. *Chem. Rev.*, **120**, 2171 (2020)
28. M.Yu.Koroleva, S.A.Shirokikh, L.Kh.Khasanova, E.S.Babusenko, E.V.Yurtov. *Mendeleev Commun.*, **29**, 176 (2019)
29. K.P.Singh, D.Mohan, S.Sinha, G.S.Tondon, D.Gosh. *Ind. Eng. Chem. Res.*, **42**, 1965 (2003)
30. A.G.MacDiarmid. *Angew. Chem., Int. Ed.*, **40**, 2581 (2001)
31. M.Lindorf, K.A.Mazzio, J.Pflaum, KNielsch, W.Brutting, M.Albrecht. *J. Mater. Chem. A*, **8**, 7495 (2020)
32. X.D.Hong, Y.Liu, Y.Li, X.Wang, J.W.Fu, X.L.Wang. *Polymers*, **12**, 331 (2020)
33. Z.H.Li, L.J.Gong. *Matherials*, **13**, 548 (2020)
34. B.I.Podlovchenko, V.N.Andreev. *Russ. Chem. Rev.*, **71**, 837 (2002)
35. T.F.Otero, J.G.Martinez, J.A.Pardilla. *Electrochim. Acta*, **84**, 112 (2012)
36. B.Wessling. *Synth. Met.*, **3**, 143 (1998)
37. V.E.Bochenkov, G.B.Sergeev. *Russ. Chem. Rev.*, **76**, 1013 (2007)
38. K.M.Emran, S.M.Ali, A.L.L.Al-Oufi. *Molecules*, **22**, 772 (2017)
39. N.Maity, A.Dawn. *Polymers*, **12**, 709 (2020)
40. D.C.Trivedi. In *Polyanilines. Handbook of Organic Conductive Molecules and Polymers. Vol. 2*. (Chichester: Wiley, 1997). P. 505
41. Y.Arteshia, A.Aghanejad, S.Davarana, Y.Omidia. *Eur. Polym. J.*, **108**, 150 (2018)
42. P.Humpoliček, V.Kašparkova, J.Pachernik, J.Stejskal, P.Bober, Z.Capakova, K.A.Radaszkiewicz, I.Junkar, M.Lehockya. *Mater. Sci. Eng. C*, **91**, 303 (2018)
43. E.N.Zare, P.Makvandi, B.Ashtari, F.Rossi, A.G.Perale. *J. Med. Chem.*, **63**, 1 (2020)
44. Y.Liu, P.F.Yin, J.R.Chen, B.Cui, C.Zhang, F.Wu. *Int. J. Polym. Sci.*, **2020**, 5659682 (2020)
45. *Conducting Polymers. Conjugated Polymers: Theory, Synthesis, Properties and Characterization*. (Eds T.A.Skotheim, J.R.Reynolds). (Boca Raton, FL: CRC Press, 2007)

46. A.G.Zabrodskii, M.E.Kompan, V.G.Malyshkin, I.Yu.Sapurina. *Techn. Phys. Lett*., **32**, 758 (2006)
47. J.Stejskal, J.Prokeš, I.Sapurina. *Mater. Lett*., **63**, 709 (2009)
48. I.Sapurina, J.Stejskal. *Chem. Pap*., **63**, 579 (2009)
49. B.Qiu, C.Xu, D.Sun, Q.Wang, H.Gu, X.Zhang, B.L.Weeks, J.Hopper, T.C.Ho, Z.Guo, S.Wei. *Appl. Surface Sci*., **334**, 7 (2015)
50. K.D.Kreuer. *Chem. Mater*., **8**, 610 (1996)
51. R.Karthik, S.Meenakshi. *Chem. Eng. J*., **263**,168 (2015)
52. Y.L.Jiang, Z.F.Liu, G.M.Zeng, Y.J.Liu, B.B.Zhao, Z.G.Li, Y.Liu, W.Zhang, Q.Y.He. *Environment. Sci. Pollut. Res*., **25**, 6158 (2018)
53. R.Ansari, A.F.Delavar. *J. Iran. Chem.. Soc*., **5**, 675 (2008)
54. P.T.Binh, P.T.Tot, M.T.T.Thuy, M.T.Xuan, B.M.Quy, N.T.Duyen. *Asian J. Chem*., **25**, 8163 (2013)
55. M.L.Sall, A.K.D.Diaw, D.Gningue-Sall, A.Chevillot-Biraud, N.Oturan, M.A.Oturan, C.Fourdrin, D.Huguenot, J.-J.Aaron. *Environment. Sci. Pollut. Res*., **25**, 8581 (2018)
56. A.Cook, A.Gabriel, A.Laycock. *J. Electrochem. Soc*., **151**, 529 (2004)
57. E.T.Kang, K.G.Neoh, K.L.Tan. *Surface Int. Anal*., **20**, 883 (1993)
58. I.Yu.Sapurina, J.Stejskal. *Russ. Chem. Rev*., **79**, 1123 (2010)
59. M.Vijayan, D.C.Trivedi. *Synth. Met*., **107**, 57 (1999)
60. Z.-H.Wu, J.-Y.Yang, B.Yu, B.-M.Shi, C.-R.Zhao, Z.-L.Yu. *Rare Met*., **38**, 832 (2019)
61. Ph.Colomban, J.Tomkinson. *Solid State Ionics*, **97**, 123 (1997)
62. I.Sapurina, A.Yu.Osadchev, B.Z.Volchek, M.Trchová, A.Riede, J.Stejskal. *Synth. Met*., **129**, 29 (2002)
63. J.Stejskal. *Chem. Pap*., **74**, 1 (2020)
64. F.J.M.Hoeben, P.Jonkheijm, E.W.Meijer, A.P.H.J.Schenning. *Chem. Rev*., **105**, 1491 (2005)
65. N.Wang, J.Chen, J.Wang. *Powder Technol*., **347**, 93 (2019)
66. N.Shoaie, M.Daneshpour, M.Azimzadeh, S.Mahshid, S.M.Khoshfetrat. *Microchim. Acta*, **186**, 465 (2019)
67. A.C.da Silva, S.I.Córdoba de Torresi. *Front. Mater*., **6**, 98 (2019)
68. M.Li, B.L.Guo. *Chin. Sci. Bull.-Chin*., **64**, 2410 (2019)
69. M.J.Higgins, G.G.Wallace. *Polym. Rev*., **53**, 506 (2013)
70. J.Preat, B.Teixeira-Dias, C.Michaux, E.A.Perpèete, C.Alemáan. *J. Phys. Chem. A*, **115**, 13642 (2011)
71. J.Preat, D.Zanuy, E.A.Perpèete, C.Alemáan. *Biomacromolecules*, **12**, 1298 (2011)
72. M.A.Shishov, V.A.Moshnikov, I.Yu.Sapurina. *Chem. Pap*., **67**, 909 (2013)
73. Y.Chen, W.C.Long, H.Xu. *J. Mol. Liq*., **287**, 110888 (2019)
74. I.Sapurina, J.Stejskal. *Polym. Int*., **57**, 1295 (2008)
75. I.Sapurina, M.Shishov. In *New Polymers for Special Applications*. Vol. 9. (Ed. A.S.Gomes). (INTECH, 2012). P. 251
76. I.Sapurina, M.E.Kompan, M.Shishov. *Russ. J. Electrochem*., **51**, 528 (2015)
77. J.Stejskal, J.Prokes, M.Trchova. *React. Funct. Polym*., **68**, 1355 (2008)
78. E.Konyushenko, J.Stejskal, M.Trchova, J.Hradil, J.Kovarova, J.Prokes, M.Cieslar, J.-Y.Hwang, K.-H.Chen, I.Sapurina. *Polymer*, **47**, 5715 (2006)
79. N.V.Blinova, J.Stejskal, M.Trchova, J.Prokes, I.Sapurina, G.Ciric-Marjanovic. *Polym. Int*., **50**, 50 (2009)
80. I.Sapurina, J.Stejskal, M.Spirkova, J.Kotek, J.Prokes. *Synth. Met*., **151**, 93 (2005)
81. J.Stejskal, O.Quadrat, I.Sapurina, J.Zemek, A.Drelinkiewicz, M.Hasik, I.Krivka, J.Prokes. *Eur. Polym. J*., **38**, 631 (2002)
82. P.Singh, S.K.Shukla. *J. Mater. Sci*.. **55**, 1331 (2020)
83. M.J.Dunlop, R.Bissessur. *J. Mater. Sci*., **55**, 6721 (2020)
84. M.A.Abshinova, N.E.Kazantseva, P.Sáha, I.Yu.Sapurina, J.Stejskal. *Polym. Degrad. Stab*., **93**,1826 (2008)
85. M.A.Shishov, V.A.Moshnikov, I.Yu.Sapurina. *Russ. J. Appl. Chem*., **86**, 51 (2013)
86. J.Stejskal, I.Sapurina, M.Trchová. *Prog. Polym. Sci*., **35**, 1420 (2010)
87. I.Sapurina, N.E.Kazantseva, N.G.Ryvkina, J.Prokes, P.Saha, J.Stejskal. *J. Appl. Polym. Sci*., **95**, 807 (2005)
88. N.E.Kazantseva, Yu.I.Bespyatykh, I.Sapurina, J.Stejskal, J.Vilčáková, P.Sáha. *J. Magn. Magn. Mater*., **301**, 155 (2006)
89. E.N.Zare, A.Motahari, M.Sillanpaa. *Environ. Res*., **162**, 173 (2018)
90. H.N.M.E.Mahmud, A.K.O.Huq, R.B.Yahya. *RSC Adv*., **6**, 14778 (2016)
91. K.Dutta, S.De. *Environ. Sci.: Water Res. Technol*., **3**, 793 (2017)
92. J.Wang, K.K.Zhang, L.Zhao. *Chem. Eng. J*., **239**, 123 (2014)
93. S.M.Riahi, S.M.Borghei, A.Olad, M.J.Chaichi. *Iran. J. Chem. Chem. Eng*., **30**, 97 (2011)
94. Q.Li, Y.Qian, H.Cui, Q.Zhang, R.Tang, J.P.Zhai. *Chem. Eng. J*., **173**, 715 (2011)
95. Y.X.Tian, H.Z.Li, Y.Liu, G.J.Cui, Z.B.Sun, S.Q.Yan. *RSC Adv*., **6**, 10478 (2016)
96. J.Chen, X.Q.Hong, Y.T.Zhao, Q.F.Zhang. *Water Sci. Technol*., **70**, 678 (2014).
97. L.Tang, Y.Fang, Y.Pang, G.M.Zeng, J.J.Wang, Y.Y.Zhou, Y.C.Deng, G.D.Yang, Y.Cai. *J. Chen. Chem. Eng. J*., **254**, 302 (2014)
98. X.Han, L.Gai, H.Jiang, L.Zhao, H.Liu, W.Zhang. *Synth. Met*., **171**, 1 (2013)
99. S.Zhang, M.Zeng, W.Xu, J.Li, J.Li, J.Xu, X.Wang. *Dalton Trans*., **42**, 7854 (2013)
100. M.Bhaumik, S.Agarwal, V.K.Gupta, A.Maity. *J. Colloid Interface Sci*., **470**, 257 (2016)
101. M.Bhaumik, T.Y.Leswifi, A.Maity, V.V.Srinivasu, M.S.Onyango. *J. Hazard. Mater*., **186**, 150 (2011)
102. M.Bhaumik, A.Maity, V.V.Srinivasu, M.S.Onyango. *Chem. Eng. J*., **181**, 323 (2012)
103. T.Zhou, C.Li, H.Jin, Y.Lian, W.Han. *ACS Appl. Mater. Interfaces*, **9**, 6030 (2017)
104. Y.Y.Sun, Q.Y.Yue, Y.P.Mao, B.Y.Gao, Y.Gao, L.H.Huang. *J. Hazard. Mater*., **265**, 191 (2014)
105. M.A.Atieh. *Proc. Environ. Sci*., **4**, 281(2011)
106. D.Sud, G.Mahajan, M.P.Kaur. *Biores. Technol*., **99**, 6017 (2008)
107. W.Yu, L.Y.Chai, L.Y.Zhang, H.Y.Wang. *Trans. Nonferrous Met. Soc. China*, **23**, 3490 (2013)
108. S.Perumal, R.Atchudan, D.H.Yoon, J.Joo, I.W.Cheong. *J. Mater. Sci*., **55**, 9354 (2020); DOI: 10.1007/s10853-020-04651-1
109. S.Srinivasan, P.Chelliah, V.Srinivasan, A.B.Stantley, K.Subramani. *Oriental J. Chem*., **32**, 2231 (2016)
110. M.Mosaferi, S.Nemati, A.Khataee, S.Nasseri, A.A.Hashemi. *J. Environ. Health Sci. Eng*., **12**, 1 (2014)

111. Y.Q.Zhou, W.H.Sun. *Polym. Compos.*, **39**, 4416 (2018)
112. M.Ghorbani, H.Eisazadeh. *Composites, Part B*, **45**, 1 (2013)
113. M.S.Mansour, M.E.Ossman, H.A.Farag. *Desalination*, **272**, 301 (2011)
114. R.S.Norouzian, M.M.Lakouraj. *Polym. Adv. Technol.*, **26**, 9 (2015)
115. K.Rajakumar, S.D.Kirupha, S.Sivanesan, R.L.Sai. *J. Nanosci. Nanotechnol.*, **14**, 2937 (2014)
116. M.F.Siddiqui, E.A.Khan, T.A.Khan. *Environ. Prog. Sust. Energy*, **38**, e13249 (2019)
117. R.Kanthapazham, C.Ayyavu, D.Mahendiradas. *Desalinat. Water Treat.*, **5**, 36, 16871 (2016)
118. A.Heidari, H.Younesi, Z.Mehraban. *Chem. Eng. J.*, **153**, 70 (2009)
119. W.T.Tsai, K.J.Hsien, J.M.Yang. *J. Colloid Interface Sci.*, **275**, 428 (2004)
120. Y.Bulut, Z.Tez. *J. Environ. Sci.*, **19**, 160 (2007)
121. S.Srinivasan, P.Chelliah, V.Srinivasan, A.B.Stantley, K.Subramani. *Orient. J. Chem.*, **32**, 671 (2016)
122. A.V.Seyed, B.Majid, A.A.Mohammad. *J. Environ. Chem. Eng.*, **6**, 6612 (2018)
123. X.G.Li, H.Feng, M.R.Huang. *Chem.–Eur. J.*, **15**, 4573 (2009)
124. Q.F.Lü, M.R.Huang, X.G.Li. *Chem.–Eur. J.*, **13**, 6009 (2007)
125. H.Javadian, M.Ghaemy, M.Taghavi. *J. Mater. Sci.*, **49**, 232 (2014)
126. Q.Fan, Y.Yang, Y.K.Hao, X.Zhao, Y.Feng. *J. Mol. Liq.*, **212**, 557 (2015)
127. R.Li, L.Liu, F.Yang. *Chem. Eng. J.*, **229**, 460 (2013)
128. H.Javadian, M.Taghavi. *Appl. Surface Sci.*, **289**, 487 (2014)
129. Y.Zhao, K.Xia, Z.Zhang, Z.Zhu, Y.Guo, Z.Qu. *Nanomaterials*, **9**, 455 (2019)
130. N.Jiang, Y.Xu, Y.Dai, W.Luo, L.Dai. *J. Hazard. Mater.*, **215–216**, 17 (2012)
131. Y.Yang, W.Wang, M.Li, H.Wang, M.Zhao, C.Wang. *Polym. Compos.*, **39**, 1663 (2018)
132. R.Kanthapazham, C.Ayyavu, D.Mahendiradas. *Desalinat. Water Treat.*, **57**, 1687 (2016)
133. C.S.C.Chiew, H.K.Yeoh, P.Pasbakhsh, K.Krishnaiah, P.E.Poh, B.T.Tey, E.S.Chan. *Appl. Clay Sci.*, **119**, 301 (2016)
134. Y.Y.Zhang, X.Cao, J.Y.Sun, G.H.Wu, J.Wang, D.G.Zhang. *J. Sol–Gel Sci. Technol.*, **94**, 658 (2020)
135. H.N.M.E.Mahmud, A.K. O.Huq, R.Yahya. *Mater. Sci. Eng.*, **206**, 012100 (2017)
136. A.Rohanifar, L.B.Rodriguez, A.M.Devasurendra, N.Alipourasiabi, J.L.Anderson, J.R.Kirchhoffa. *Talanta*, **188**, 570 (2018)
137. M.E.Mahmoud, N.A.Fekry, M.M.A.El-Latif. *Chem. Eng. J.*, **304**, 679 (2016)
138. L.Ai, J.Jiang, R.Zhang. *Synth. Met.*, **160**, 762 (2010)
139. B.Qiu, C.Xu, D.Sun, H.Qu, M.Guerrero, H.Yi, J.Guo, X.Zhang, Z.Luo, N.Noel, X.Wang, Z.Guo, S.Wei. *ACS Sust. Chem. Eng.*, **2**, 2070 (2014)
140. B.Qiu, C.Xu, D.Sun, H.Wei, X.Zhang, J.Guo, Q.Wang, D.Rutman, S.Wei, Z.Guo. *RSC Adv.*, **4**, 29855 (2014)
141. I.Anastopoulos, A.Mittal, M.Usman, J.Mittal, G.Yu, A.Núñez-Delgado, M.Kornaros. *J. Mol. Liq.*, **269**, 855 (2018)
142. S.-W.Lv, J.-M.Liu, Z.-H.Wang, H.Ma, C.-Y.Li, N.Zhao, S.Wang. *J. Environ. Sci.*, **80**, 169 (2019)
143. B.Yan, Z.H.Chen, L.Cai, Z.M.Chen, J.W.Fu, Q.Xu. *Appl. Surface Sci.*, **356**, 39 (2015)
144. M.Maruthapandi, V.B.Kumar, J.H.T.Luong. *ACS Omega*, **3**, 7196 (2018)
145. S.Agarwal, I.Tyagi, V.K.Gupta, F.Golbaz, A.N.Golikand, O.Moradi. *J. Mol. Liq.*, **218**, 494 (2016)
146. F.F.Ma, D.Zhang, N.Zhang, T.Huang, Y.Wang. *Chem. Eng. J.*, **354**, 432 (2018)
147. J.J.Li, J.T.Feng, W.Yan. *Appl. Surface Sci.*, **279**, 400 (2013)
148. H.Heidari, J.Moghimi, J.Rashidiani, R.A.Taheri. *Phys. Chem. Res.*, **6**, 857 (2018)
149. G.K.Ramesha, K.Vijaya, H.B Muralidhara, S.Sampath. *J. Colloid Interface Sci.*, **361**, 270 (2011)
150. C.Lu, H.Chiu. *Chem. Eng. Sci.*, **61**, 1138 (2006)
151. D.Lucaci, A.Duta. *Environ. Eng. Manag.*, **10**,1255 (2011)
152. M.Abbas, M.Trari. *Fibers Polym.*, **21**, 810 (2020)
153. T.Lu, T.Xiang, X.L.Huang, C.Li, W.F.Zhao, Q.Zhang, C.S.Zhao. *Carbohydr. Polym.*, **133**, 587 (2015)
154. R.Ansari, Z.Mosayebzadeh. *Chem. Pap.*, **65**, 1 (2011)
155. Y.Xia, T.Li, J.Chen, C.Cai. *Synth. Met.*, **175**, 163 (2013)
156. L.Wang, X.-L.Wu, W.-H.Xu, X.-J.Huang, J.-H.Liu, A.-W.Xu. *ACS Appl. Mater. Interfaces*, **4**, 2686 (2012)
157. X.Ye, Q.C.Xu, J.Xu. *RSC Adv.*, **9**, 5895 (2019)
158. X.L.Li, H.J.Lu, Y. Zhang. *Chem. Eng. J.*, **316**, 893 (2017)
159. M.M.Zhang, LL.Chang, Z.H.Yu. *Desalin. Water Treat.*, **110**, 209 (2018)
160. G.Annadurai, R.S.Juang, D.Lee. *Water Sci. Technol.*, **47**, 185 (2015)
161. S.Debnath, N.Ballav, A.Maity, K.Pillay. *Int. J. Biol. Macromol.*, **72**, 732 (2015)
162. V.Janaki, B.T.Oh, K.Shanthi, K.J.Lee, A.M.Ramasamy, S.Kamala-Kannan. *Synth. Met.*, **162**, 974 (2012)
163. M.Bhaumik, H.J.Choi, R.I.McCrindle, A.Maity. *J. Colloid. Interface Sci.*, **425**, 75 (2014)
164. R.Kumar, S.A.Ansari, M.A.Barakat, A.Aljaafari, M.H.Cho. *New J. Chem.*, **42**, 18802 (2018)
165. H.Chafai, M.Laabd, M.Elamine, A.Albourine. *Desalin. Water Treat.*, **83**, 314 (2017)
166. A.Karamipour, N.Rasouli, M.Movahedi, H.Salavati. *Phys. Chem. Res.*, **4**, 291 (2016)
167. M.Ajmal, K.R.R.Ali, S.Anwar, J.Ahmad, R.Ahmad. *Bioresours. Technol.*, **86**, 147 (2003)
168. V.Sharma, P.Rekha, P.Mohanty. *J. Mol. Liq.*, **222**, 1091 (2016)
169. J.J.Shen, S.Shahid, I.Amura, A.Sarihan, M.Tian. *Synth. Met.*, **245**, 151 (2018)
170. W.A.Amer, M.M.Omran, A.F.Rehab, M.M.Ayad. *RSC Adv.*, **8**, 22536 (2018)
171. W.A.Amer, M.M.Omran, M.M.Ayad. *Colloid Surface, A*, **562**, 203 (2019)
172. H.Javadian, M. T.Angaji, M.Naushad. *J. Ind. Eng. Chem.*, **20**, 3890 (2014)
173. V.T.Ivanova, V.F.Ivanov, Ya.E.Kurichkina, O.L.Gribkova, M.V.Il'ina, A.A.Manykin. *Vopr. Virusol.*, **54** (3), 21 (2009)
174. V.T.Ivanova, M.V.Ivanova, N.N.Nosik, E.I.Burtseva, N.G.Kondrashina, N.G.Kondrashina, M.V.Polkovnikova, A.A.Isakova, B.V.Spitsyn, I.Yu. Sapurina. *Biotechnology* (*Ecology*), **30** (3), 67 (2014)
175. I.Yu.Sapurina, M.V.Ivanova, V.T.Ivanova, E.I.Burtseva, S.V.Trushakova, E.I.Isaeva, Yu.E.Kurochkina, A.A.Manykin, L.V.Uryvaev. *Polym. Sci., Ser. A*, **56**, 450 (2014)

176. V.T.Ivanova, M.V.Ivanova, B.V.Spitsyn, K.O.Garina, S.V.Trushakova, A.A.Manykin, A.P.Korzhenevsky, E.I.Burseva. *J. Phys. Conf. Series*, **345**, 012019 (2012)
177. V.T.Ivanova, M.V.Ivanova, E.I.Burtseva, E.O.Garina, S.V.Trushakova, E.S.Shevchenko, A.A.Manykin, A.A.Isakova, A.P.Korzhenevsky, B.V.Spitsyn. *Vopr. Virusol.*, **57** (2), 9 (2012)
178. V.T.Ivanova, M.V.Ivanova, I.Yu.Sapurina, E.I.Burtseva, S.V.Trushakova, E.I.Isaeva, E.S.Kirillova, H.V.Stepanova, T.A.Oscerco, A.A.Manykin. *Vopr. Virusol.*, **60** (3), 25 (2015)
179. V.T.Ivanova, E.O.Morozova, T.N.Nikolaeva, E.I.Burtseva, I.Yu.Sapurina, A.V.Pronin. *Sorbtsionnye i Khromatograficheskie Protsessy*, **18**, 248 (2018)
180. V.T.Ivanova, E.O.Garina, T.N.Nikolaeva, I.A.Suetina, S.V.Trushakova, M.V.Mezentseva, E.I.Burtseva, I.Yu.Sapurina, I.Steiskal, A.V.Pronin. *Water: Chem. Ecol.*, **10**, 71 (2016)
181. T.V.Ivanova, E.O.Garina, E.I.Burtseva, E.S.Kirillova, M.V.Ivanova, J.Stejskal, I.Yu.Sapurina. *Chem. Pap.*, **71**, 503 (2017)
182. V.F.Ivanov, E.O.Garina, I.Yu.Sapurina, O.L.Gribkova, E.I.Burtseva, V.T.Ivanova, A.V.Vannikov. *Protect. Met. Phys. Chem. Surfaces*, **52**, 291 (2016)
183. V.F.Ivanov, V.T.Ivanova, Yu.E.Kurochkina, O.L.Gribkova, M.V.Ilyina, A.A.Manykin, A.A. Isakova, I.Yu.Sapurina. *Mater. Phys. Applic.*, **1255**, 46 (2010)
184. V.T.Ivanova, E.O.Garina, I.Yu.Sapurina, J.Stejskal, O.L.Gribkova, E.S.Kirillova, V.F.Ivanov, E.I.Burtseva. *Sorbtsionnye i Khromatograficheskie Protsessy*, **17**, 592 (2017)
185. E.O.Morozova, E.A.Kulik, I.Yu.Sapurina, T.N.Nikolaeva, E.I.Burtseva, A.V.Pronin, V.T.Ivanova. *Sorbtsionnye i Khromatograficheskie Protsessy*, **19**, 390 (2019)
186. E.O.Garina, V.T.Ivanova, N.N.Nosik, N.G.Kondrashina, I.A.Suetina, M.V.Mezentseva, E.I.Burtseva, I.Yu.Sapurina, J.Stejskal. *Nanotekhnologii: Razrabotka, Primenenie — XXI vek*, **8** (2), 3 (2016)
187. V.T.Ivanova, Ya.E.Kurochkina, V.F.Ivanov, M.V.Il'ina, S.V.Trushakova, E.S.Shevchenko, E.I.Burtseva, A.A.Simakov, A.A.Manykin, N.N.Nosik, M.M.Shneider, A.V.Timofeeva, I.Yu.Sapurina. *Vopr. Virusol.,* **56** (4), 19 (2011)
188. D.O.S.Ramirez, A.Varesano, R.A.Carletto, C.Vineis, I.Perelshtein, M.Natan, N.Perkas, E.Banin, A.Gedanken. *Mater. Sci. Eng., C: Mater. Biolog. Appl.*, **102**, 164 (2019)
189. N.Mikušová, K.Nechvilová, A.Kalendová, T.Hájková, Z.Capáková, I.Junkar, M.Lehocký, M.Mozetič, P.Humpolíček. *Int. J. Polym. Mater. Polym. Biomater.*, **68**, 152 (2019)
190. Q.Li, Q.Zhang, J.Feng, W.Yan. *Chem. Eng. J.*, **225**, 766 (2013)
191. D.Majhi, B.N.Patra. *J. Chem. Eng. Data*, **63**, 3427 (2018)
192. W.Lyu, M.Yu, J.Feng, W.Yan. *Appl. Surface Sci.*, **458**, 413 (2018)
193. Y.Kim, Z.Lin, I.J.T.Van Voorhis, T.M.Swager. *J. Am. Chem. Soc.*, **140**, 14413 (2018)
194. Q.Li, C.M.Hao, H.L.Liu. *Appl. Mech. Mater.*, **130** – **134**, 3773 (2012)