NANOTECHNOLOGIES FOR PURIFICATION OF CONTAMINATED WATER

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ABSTRACT. An overview is made of the nanotechnologies and nanomaterials that are consistent with traditional water purification methods. The possible nanomaterials that can be applied through traditional water purification technologies are discussed. The adsorption of impurities is possible through the introduction of nanoparticles that have a highly developed specific surface, which, in turn, determines the discovery of new sorption layers that accelerate diffusion and chemical processes. Membrane processes whereby nanomaterials are employed make it possible to manage nano-level properties. Thus, not only a large area for purification processes is provided, but also permeability is improved, as well as the mechanical and the thermal stability, the decomposition of the deposits built up in the process of membrane operation, and the self-cleaning of the membranes. Nanomaterials are also used in the treatment of industrial waste water from toxic heavy metals by the application of modified zeolites. The creation of systems of nanomaterials for possible re-use is a key element in the implementation of nanotechnology, the outcome of which will be easy applicability, low costs, and last but not least, the protection of human health.

Keywords: Nanotechnology, nanomaterials, water purification, re-use of water, membrane processes.

НАНОТЕХНОЛОГИИ ЗА ПРЕЧИСТВАНЕ НА ЗАМЪРСЕНИ ВОДИ

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РЕЗЮМЕ. Направен е обзор на нанотехнонологиите и наноматериалите, съвместими с традиционните методите за пречистване на води. Обсъдени са възможните нанаматериали, които могат да бъдат приложени чрез традиционите технологии за пречистване на води. Адсорбцията на онечиствания е възможна чрез внедряване на наночастиците, които притежават силно развита специфична повърхност, което от своя страна обуславя откриване на нови сорбционни слоеве центрове, ускоряващи дифузията и химичните процеси. Мембранните процеси при които се използват наноматериали дават възможност за управление на свойства на нано-ниво, при което се осигурява не само голяма площ за протичане на процеси по пречистване, но и подобряване на пропускливостта, механичната, термичната стабилност, разграждането на налепите, формирани в процеса на работа на мембраната и самопочистването на мембраните. Наноматериали се използват и при пречистването на промишлени отпадъчни води от токсични тежки метали, чрез прилагането на модифицирани зеолити. Създаването на системи от наноматериали с възможна повторна употреба е ключов елемент при внедряването на нанотехнологиите, което да включва лесна приложимост, нисък разход на средства и не на последно място - опазване на човешкото здраве.

Ключови думи: Нанотехнология, наноматериали, пречистване на води, повторно използване на вода, мембранни процеси

Introduction

Water is the most valuable element on the Earth. In many parts of the world, access to pure water is a luxury that few could afford. Water purification and the full and rational use of water is a challenge for both water supply companies and industry. On a world scale, access to clean sources of water is a problem that is on the agenda in each country. This problem is related to global climatic changes, the still rapidly developing industries, and the population growth. This requires the need for technological innovations to create opportunities for an integrated water management policy.

The accelerated consumption of water supplies leads to the use of unconventional sources such as rain water, polluted freshwater, sewage and waste water, and sea water. Current purification technologies have reached the limit for providing adequate supplies of water so vital for human needs.

Nanotechnologies have the potential to contribute to the sensible management of water resources and to create the conditions for the efficient use of every drop of water. Progress in the field of nanotechnology offers opportunities for the development of next-generation water supply systems. This review aims at presenting the new highly efficient, modular and multifunctional nanotechnology-based processes that ensure high-performance water treatment at affordable pricess without being linked to major infrastructure projects (Qu et al, 2013).

Nanotechnologies are focused on the production of nanomaterials based on manipulation, control and integration of atoms and molecules of nanometric size, whereby the change in size leads to a change of properties. In the metric system, the prefix "nano" refers to one billionth (0.000 000 001 = 10^{-9}). In nanoparticles, at least one particle size should be less than 100 nm. At this level, both chemical activity due to reduced particle size and physical properties change. Owing to the increase in the surface-to-volume ratio at the nano level, the properties of the material become highly dependent on the surface of the materials. Nanomaterials can be classified in terms of particle size, surface morphology, crystalline forms, chemical nature, chemical composition, magnetic behavior, functional properties. They exist in hybrid compilations of these classifications.

Adsorption

Nanoparticles have an extremely high specific surface, which in turn leads to the discovery of new sorption centers that give opportunities for diffusion and chemical processes. A study of the adsorption of various organic substances (Pan and Xing, 2008) shows higher performance of carbon nanotubes (CNT's) compared to monolithic particles of activated carbon. The high adsorption capacity is mainly due to the large specific surface area and the possibility of interaction between carbon nanotubes and the polluting agent. According to Pan and co-authors (Pan et al., 2008), activated carbon has a lower adsorption affinity for polar organic compounds with low molecular weight than CNT's (carbon nanotubes) that easily adsorb polar organic compounds. Carbon nanotubes have been found to interact hydrophobically with the pollutant, whereby interaction between π-π-electrons is observed, as well as hydrogen, covalent bonding, and electrostatic interactions (Yang and Xing, 2010). Organic compounds with -COOH, -OH, $-NH_2$ can form a hydrogen bond to the surface of nano-sized carbon tubes, yielding electrons (Yang et al., 2008).

The effective adsorbents for heavy metals are iron oxide, titanium dioxide and alumina (dialuminium trioxide), where sorption occurs through complexation between dissolved metals and oxygen in the metal oxide (Koeppenkastrop and Decarlo, 1993). Theoretically, surface diffusivities can be predicted from site activation theory, which is based on the random walk model where atoms or molecules vibrate at localized sites along the surface. And for given oxide, the associated activation energy was observed to be equivalent for all three oxides, and for each oxide, the Polanyi constant (α) That relates adsorption enthalpy and activation energy was equivalent to the transition metals studied (Trivedi and Ax, 2000). Compounds with higher adsorption capacity have a higher rate of adsorption reaction, as well as a shorter diffusion process due to a higher number of surface reaction centers (Yean et al., 2005). Auffan and co-authors (Auffan et al., 2009) report that when the particle size drops below 20 nm, the specific surface thus formed accelerates the adsorption process due to the new adsorption sites created and the change in the surface structure.

Membranes

The main purpose of water purification is to remove undesirable organic, inorganic and biological pollutants. Membranes provide a physical barrier for these substances, allowing them to be used for purification of water from unregulated sources. In the design of membranes, the material from which they will be built is of great importance. Nanomaterial deployment makes it possible to manage nano-level properties, providing not only a large surface area for purification processes but also improved permeability, mechanical stability, thermal stability, as well as decomposition and self-cleaning of membranes (XiaoleiQu at all, 2013).

Electrospinning is an effective way of producing superfine fibers of different materials (e.g. polymers, ceramics, or even metals) (Cloete et al., 2010). The resulting nanofibers have a high specific surface and porosity. Membranes made of nanofibres can remove particle the size of up to a micron (Ramakrishna et al., 2006). Managing functional properties on the nano level can be achieved at the stage of electrospinning or during the final processing with impregnating solutions to supplement the purifying properties of matter (Li and Xia, 2004). Recently, many research groups have focused on creating multifunctional polymer and/or inorganic membranes to reduce contamination by increasing membrane hydrophilicity. The addition of nanoparticulate metal oxides Al_2O_3 (Maximus et al., 2010), silicon nanoparticles (Bottino et al., 2001), zeolite (Pendergast et al., 2010), and TiO_2 (Bae and Tak, 2005) to polymer ultrafiltration membranes increases the resistance of the membranes themselves to contamination. (Ebert et al., 2004; Pendergast et al., 2010).

The development of TFN (thin-film composite nanomembers) mainly focuses on the inclusion of nanomaterials in the active layer of thin-film composite (TFC) membranes by adding substances that modify the surface. Nanomaterials that have been tested for such applications include nano-zeolites, nano-Ag, nano-TiO_2, and CNTs. Membrane permeability and selectivity depends on the type, size and amount of added nanoparticles (XiaoleiQu at all, 2013).

Removal of heavy metals

Heavy metals are dangerous to living organisms, because due to their stability, toxicity, and persistent compounds formed, they easily accumulate in the environment. With the rapid development of such industrial activites as galvanising, exploitation of mines, tanning, manufacturing of batteries and pesticides, heavy metals in the industrial wastewater that is released into the environment are a threat to every living creature (F. Fu, Q. Wang, 2011, W. Yang et al., 2013). The heavy metals that recognised as bioaccumulative in the food chain are Pb, Hg and Cd. The removal of toxic heavy metals, such as Zn, Cu, Ni, Hg, Cd, Pb, and Cr, is of particular importance in the treatment of industrial waste water. Water purification usually involves mechanical purification, coagulation and flocculation, chemical precipitation, adsorption, solvent extraction, ultrafiltration, and ion exchange. Nanoparticles display unique characteristics due to their small sizes and large surface area compared to monolithic materials. A wide range of nanoparticles obtained by various methods have been investigated for the purposes of the removal of metallic contaminants, such as Cr (VI), Cu (II), Co (II), Cd (II), As (V), As (III), and Hg (II). Sharma and co-authors (Sharma et al., 2009) found that in most cases nanoparticles show better efficiency for removing these metallic contaminants. Separation from aqueous solutions is possible by specific methods depending on the selected nano-adsorbent.Their small size and large surface area compared to the monolithic ones. A wide range of nanoparticles obtained by various methods have been investigated for the removal of metallic contaminants such as Cr (VI), Cu (II), Co (II), Cd (II), As (V) And Hg (II), Sharma and co-authors (Sharma et al., 2009) have established that, in most cases, nanoparticles show better effectiveness in the removal of these metallic contaminants. The latter are removed from aqueous solutions by specific methods that depend on the selected nano-adsorbent.

Research by Hristovski and co-authors (Hristovski et al., 2009) found that nanoparticles of metal (hydro-) oxides could be incorporated into the micropores of activated charcoal or other porous materials. The nanocomposites thus produced can simultaneously remove organic pollutants and arsenic.

Zeolites are natural materials with a highly selective capacity and cation exchange activity. The most common among the natural zeolites, as well as the one that is used most often, is clinoptilolite. Replaceable cations in the zeolite structure, such as K, Na, Ca, Mg, are not toxic, so zeolite is particularly suitable for final treatment in sewage treatment (M. Trgo et al., 2006).

Milan Kragovića and associates (Kragovića et all, 2013) conducted studies with zeolite modified with Fe (III). The results of their research have shown that significantly higher sorption of lead is achieved by modifying the natural zeolite with Fe (III) ions under normal conditions. The characterisation of the sorption processes in both natural zeolite and Fe (III)-zeolite before and after the sorption of lead confirms a complex lead sorption mechanism involving ion exchange, as well as hemisorption and precipitation of lead on the zeolite surface. Researchers have confirmed that in zeolite modified with Fe (III) ions there is an increased sorption of lead, which makes it a reliable water purifier.

Lv Guocheng and co-authors (Lv Guocheng. et all, 2014), reported that they used zeolite modified with Fe (II) with a concentration of 55 mmol/kg or 0.3% Fe in their research work. The zeolite employed by them showed good Cr (VI) sorption. Immobilization of Cr (VI) was increased by decreasing the pH of the solution and increasing the ionic strength. In an input sample with a Cr (VI) content and a concentration of 100 mg/l, Fe (II) modified zeolite removes Cr (VI) more efficiently than unmodified zeolite. Greater particle size and well-maintained conductivity of the modified zeolite make it an appropriate permeable barrier material for restoring groundwater.

Chromium and its compounds are widely used in many industries such as metallurgy, metal finishing, and production of chemicals. Wastewater from these industries contains hexavalent chromium, Cr(VI), at concentrations ranging from tens to hundreds of mg/l. Zeolites are an appropriate material for removing heavy metal ions from wastewater because of their relatively low price coupled with the harmlessness of their exchangeable ions. Natural Bulgarian zeolite and zeolite modified with metal, Cu (II), Fe (II), Fe (III), and Pb(II), i.e. Bulgarian clinoptilolite from the region of the East Rhodopes, have been studied for their ability to remove chromium oxyanions from model wastewater. It has been found that natural and Cu (II)-modified zeolite display negligible ability to uptake Cr (VI) from soft neutral model industrial wastewater. The modification of zeolite, by its pre-treatment with Fe (II), Fe (III) and Pb (II) solutions, increases its uptake capacity. Pb-modified zeolite removes over 95 % of the available Cr(VI) in one step for 30 min at initial Cr (VI) concentration of 30 mg/l and pH=6. Over 45 % of the available Cr (VI) was removed in one step for 30 min at initial Cr (VI) concentration of 10 mg/l and pH=6 by Fe (III)-modified zeolite. These facts could be a basis for using this natural clinoptilolitic rock to remove in consecutive steps firstly Pb (II) or Fe (III) ions, and then Cr (VI) can be removed by the already loaded zeolite. Panayotova (Marinella Panayotova, 2015) establishes, that chromium removal decreases with the increase of the pH value of the wastewater subjected to treatment. The zeolite uptake capacity increases with the increase in the pollutant's initial concentration. The kinetics of Cr uptake by Fe (II) and Fe (III)-modified zeolite obeys the pseudo-first order kinetic equation for adsorption. This fact, together with the correlation that was found between Cr uptake and Na+ and K+ release into the solution, shows the importance of ion-exchange processes in Cr immobilisation by iron-modified zeolite.The kinetics of Cr uptake by Pb-modified zeolite is described by the equation for the first order irreversible reactions. The findings support the idea for the mechanism of the surface chemical precipitation of $PbCrO_4$. (Marinela Panayotova, 2015).

Osmosis

Osmosis is the process of purification by means of fine-pored membranes that permeate water molecules and retain the larger molecules of dissolved substances. Permeable membranes retain all dissolved salts, organic substances, viruses and bacteria. Liu and associates (Liu et al., 2011) describe a pollutant removal system by "destabilization" using superparamagnetic nanoparticles, thereby removing drinking water without hydraulic pressure or heat. The process of producing drinking water is environmentally sustainable and without any waste.

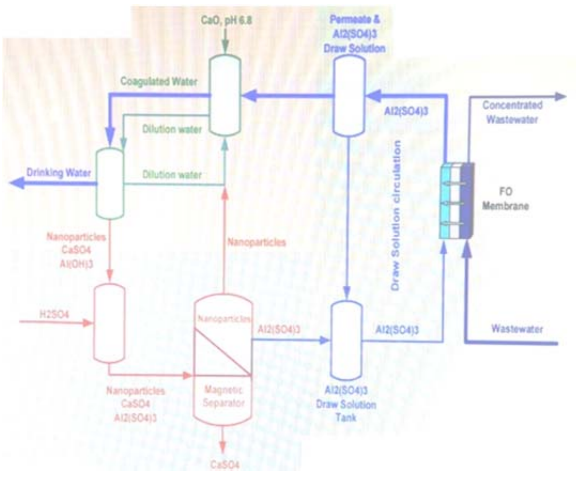

Fig.1. A detailed diagram of the release process through a $Al_2(SO_4)_3$ solution and using nanoparticles (Liu et all, 2011).

Figure 1 shows a multistage process comprising controlled osmosis, whereby a solution of 250 ml, 0.5 M $Al_2(SO_4)_3$ diffuses through the semipermeable membrane, then passes through a separating portion to separate the dissolved $Al_2(SO_4)_3$, and to produce drinking water. The $Al_2(SO_4)_3$ solution is diluted with de-ionized water and can be used repeatedly during the process. The addition of CaO to the diluted solution results in the formation of a gel-like mixture containing gel and $CaSO_4$ crystals which are stably suspended in the solution and can not be precipitated from the solution. Negatively charged nanoparticles of $Fe_3O_4@SiO_2$ are added to the solution. Upon application of an external magnetic field, the particles of the solution are separated within minutes, leaving clean water behind. The separated particles of $Al(OH)_3$, $CaCO_4$, and $Fe_3O_3SiO_2$ nanoparticles are sent for re-use by adding sulfuric acid (H_2SO_4), whereby $Fe_3O_4@SiO_2$ nanoparticles are collected by an external magnetic field and $CaSO_4$ precipitates to the bottom and is removed. The regenerated $Al_2(SO_4)_3$ solution is returned back to the process of controlled osmosis.

In the process of osmosis, it is necessary to create a hydrophilic coating on the permeable membranes, which helps dissolve the impurities that have been formed on the membrane during the process.

Conclusion

Nanotechnology for water purification is a topic that affects the entire world community. The unique properties of nanomaterials and their implementation in the familiar water purification technologies is a challenge for many researchers. Nanotechnologies for water purification are important, but it should be pointed out that not all of those could be used in modern purification systems, because, in addition to technical hurdles and high cost, there is also the risk of potential threat to the environment and human health.

Creating systems of nanomaterials with possible re-use is a key element in the implementation of nanotechnology, which includes easy applicability, low costs, and, last but not least, the protection of human health. The introduction of nanoparticles into a single monolith system would result in better property management and control over matter. It is necessary to combine technologies that allow nanoparticles to manifest their specific properties, while at the same time firmly seizing the nanoparticles in a reinforced matrix to prevent further separation of the particles from the matrix. Nanomaterials that release metal ions should be carefully controlled by laying a coating or by optimising the size and shape. The detection and release of the nanomaterial is a challenge and a major technical barrier to risk assessment (B.F. da Silva, 2011; Tiede et al., 2008).

The adoption of innovative technologies strongly depends on work efficiency, on cost, and on the management of potential risk. The production of nanomaterials and the creation of nanotechnologies that manage to purify water without allowing the nano particles involved in the purification process to leave the system is a challenge for many researchers. The use of nanofilters to capture the particles that have escapedis a possible solution to this problem but is also bound to the high value of the end product. The use of nanosystems designed to prevent potential hazards associated with the use of nanomaterials in water and in waste water treatment will lead to a wider public support, which is crucial for the spread of new technologies.

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