NANOMATERIALS FORHEAVY METALS REMOVAL FROM WASTEWATER

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Keywords:wastewater, heavy metals, nanotechnology, adsorbent, carbon nanotube.

ABSTRACT

Human, agricultural, industrial, and mining activities generate large quantities of wastewater contaminated with toxic and non-biodegradable heavy metals such as As, Cr, Cd, Co, Cu, Hg, Ni, Pb and Zn.To avoid the harmful effects of heavy metals on terrestrial and aquatic ecosystems and on human health, it is essential to develop and implement innovative technologies for the removal of these toxic and hazardous pollutants from wastewater.In wastewater treatment, and particularly in nanotechnology applications, many efficient, ecological and cost-effective nanomaterials have been developed, having unique functions of heavy metals removal from industrial effluents, surface waters, groundwater and drinking water.Due to their antimicrobial properties, nanoparticles are also used for wastewater disinfection and microbial control.

INTRODUCTION

Wastewater pollutants include pathogenic microorganisms (intestinal parasites, bacteria and viruses), antibiotics and steroids, cosmetics and other personal care products, nutrients (nitrogen and phosphorus), heavy metals, pesticides, insecticides, herbicides, furans and dioxins, lubricants, detergents, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, phthalates, industrialsolvents, dyes, oils, etc.

Heavy metals in wastewater effluents can come from natural sources (volcanic activities, soil erosion, weathering of rocks and minerals), respectively anthropic sources (fuel combustion, leachate from landfills, agricultural activities, and industrial activities including textile dyes, mining, metal plating, printed board manufacturing, semiconductor manufacturing, etc. Widespread industrial heavy metals include Ag, Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sn and Zn.

A variety of technologies can be applied for the removal of heavy metals from polluted wastewater, and they are based on physical, chemical, physico-chemical, electrochemical and biological methods.

Nanotechnology is the creation of materials, devices and systems using individual atoms and molecules that are 1/80000 the diameter of human hair [42].

A multidisciplinary sciencenanotechnology, has gained a great interest due to the needs and applications of nanomaterials in agriculture, food industry, molecular biotechnology, medicine, public health, computing, robotics and other industries.Nanotechnology isanefficient technology for addressing several environmental issues, including wastewater treatment [37].

Nanotechnological wastewater treatment processes can be divided into three main groups: treatment and remediation, sensing and detection, pollution prevention [47].

Nanomaterials arematerials smaller than 100 nm in at least one dimension [26]. Because of their small size, their surface to volume ratio is relatively high; so, these particles possess numerous active sites, which, in turn, significantly improve their activity [11].Ag, Au, Fe, Ce, Co, Cu, Ni, Mg, Mn, Zn and their oxides are the most frequently synthesized nanomaterials [6] by processes of microemulsion, co-precipitation and thermal decomposition.

Nanomaterials must be non-toxic, cost-effective, selective to low concentration of contaminants, highly reactive, reusable, with strong sorption capacities, and should allow the easy removal of the sorbedpollutant from their surface[34].The surface properties of nanomaterials are affected by their chemical composition and surface roughness [18].There are many available shapes of nanomaterials with superior performance: single-walled and multi-walled carbon nanotubes (CNT), carbon quantum dots (CQD), nanowires, nanocolloids, nanoparticles, nanomembranes and nanofilms [15].

Nanomaterials including carbon nanotubes (CNT), carbon based material composites, graphene, nanometals or metal oxides, metal sulphides, polymeric sorbents, zeolites and dendrimers[45]have been used in the removal and recovery, respectively in sensing and monitoringof disease causing microbes, harmful chemicals, toxic metal ions, salts, organic and inorganic solutes from wastewater.

Although the efficiency of nanomaterials is provedby many studies and nanotechnology is better than any other techology for wastewater treatment, there are environmental and ethical concerns because the high loads of nanomaterialslead to their accumulation in the environment, with impact in agriculture, ecology and human health(Fig. 1).

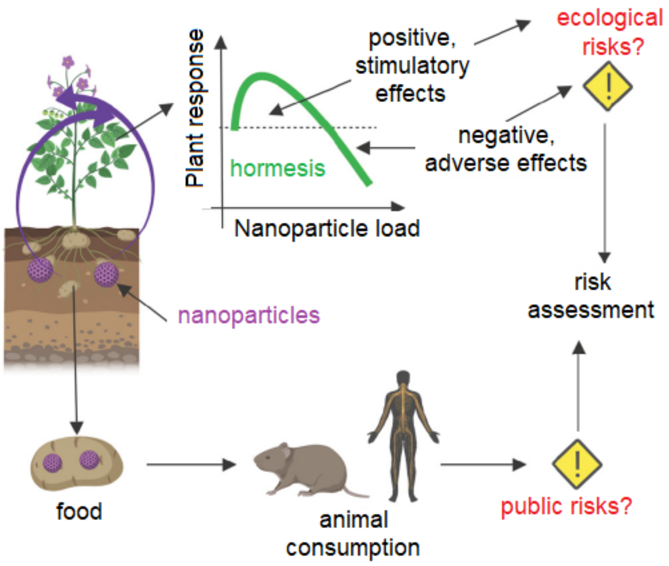

Fig. 1. Nanoparticles accumulation and potential risks [3]

Due to their small size and highly active surface, the nanoparticles can pass through cell membranesand could have harmful effects on terrestrial and aquatic ecosystems depending on the size, shape and chemical composition of the nanoparticle [39].Nanoparticles interaction with biological macromolecules within the human body could develop diseases and clinical disorders [13]. Gold is believed to be non-reactive under environmentally significant conditions, so gold nanoparticles are considered safe to use [2]. There are some limitations of nanotechnology use in wastewater treatment, mostly because the nanoparticles might be difficult to separate from the treated solution. To avoid nanoparticle loss, they can be immobilized on appropriate substrate. Another drawback is that nanotechnology is rarely adaptable to mass processes, and is not competitive with conventional treatment technologies [34].

MATERIAL AND METHOD

Nanotechnologies can be classified based on the nature of nanomaterials in three main categories: nanoadsorbents, nanocatalysts and nanomembranes [6]. Based on their morphology, size and chemical properties, there are four main categories of nanomaterials: metal based polymeric nanoparticles, carbon-based nanomaterials, polymeric nanomaterials and hybrid nanomaterials [30].

Nanoadsorbents. In nano-adsorption, the nanoadsorbent used to remove pollutants from wastewater can be produced using atoms of elements that are chemically active and have a high adsorption capacity on the surface of nanomaterials. The required characteristics of nanoadsorbents are high surface area, charge density and hydrophobicity. Effectiveness of adsorbent nanoparticles for the removal of pollutants from wastewater is given by adsorbents surface functionalization, size and shape, surface chemistry, solubility and dispersion state, chemical composition, crystallinity, sorbate initial concentration, sorbent dose, pH of the medium, reaction time, concentration, temperature, etc.

Materials used for the development of adsorbent nanoparticles include activated carbon, silica, clay, metal oxides, and modified compounds as composites.Despite the efficiency in removing biochemical oxygen demand (BOD) and chemical oxygen demand (COD), adsorption based on activated carbon is largely limited by its expensive cost [18].Among the nanoadsorbents, oxide-based nanomaterials such as ferric oxide (Fe_3O_4), titanium oxide (TiO_2), zinc oxide (ZnO), magnesium oxide (MgO), manganese oxide (MnO_2), cobalt oxide (Co_3O_4) [41] and their composites have an important role. Fe_3O_4 is an effective and economical magnetic oxide, frequently used for the removal of various toxic metal ions from wastewater, such as Cr^{3+}, Hg^{2+}, Pb^{2+} Ni^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+} and As^{3+} with the advantage of their easy separation under magnetic field for reuse.

Conventional sorbents commonly employed for removing heavy metals from wastewater effluents are clay minerals, activated carbon, zeolites, industrial by-products, agricultural waste, biomass, polymers [35]. Since many of the conventional sorbents have low metal sorption capacity, nanoadsorbents such as graphenes, fullerenes (C_{60}, wrapped graphene), and single or multi-wall carbon nanotubes (rolled graphene) presented in Figure 2, are the most used in removing the heavy metals from wastewater. These carbon-based adsorbents are nontoxic and biodegradable, and have very high strength, resistance, electrical conductivity and thermal stability [9].

Graphene is one-atom thick layer of carbon atoms (between the nearest atoms is 0.14 nm) sp^2-hybridized and linked by σ and π bonds to a honeycomb-type hexagonal two-dimensional close-packed crystal lattice [9].Graphene can be folded into a molecule of fullerene and carbon nanotubes, and it forms graphite crystals. Graphene can be oxidized to add hydrophilic groups for heavy metal removal [20] and has a strong sorption capacity.

Fullerenes are carbon allotropes, whose molecules are forming a hollow tube, sphere, or ellipsoid and represent convex closed polyhedral made up of an even number of three-coordinated carbon atoms [20]. Currently, fullerenes are mostly used for the extraction of organic compounds from water.

Carbon nanotubes are single or multi-wall long carbon cylinders as rolled graphite sheets (in which carbon forms a continuous hexagonal network). Their diameter ranges from one to several tens of nm and the length is up to severalcm [9]. Carbon nanotubes possess great potential as superior adsorbents for removing many types of heavy metals such as Pb^{+2}, Cd^{+2}, Ni^{+2}, and Cu^{+2} [24]. Multi-wall carbon nanotubes are having metal-ion sorption capacity of 3–4 times larger than the widely used powder activated carbon [7].

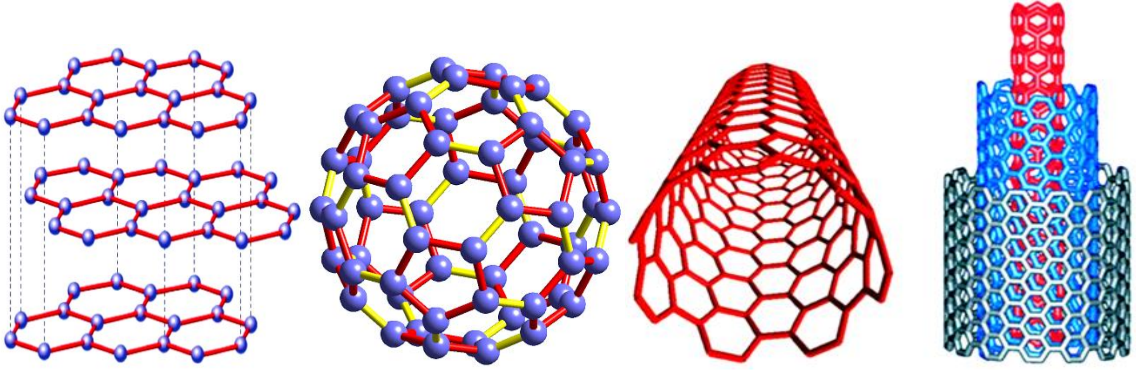

Fig. 2. Structures of mostly used nanoadsorbents
a)graphene[56], b) fullerenes [56], c) single wall carbon nanotube [38], d) multi-wallcarbon nanotube [38]

Nanocatalysts. In nanocatalyst technology, nanomaterials such as metal oxides, semiconductor materials, zero-valence metal and bimetallic nanoparticles [43] have gained considerable attention for wastewater treatment. Different types of nanocatalysis methods are used for the degradation of organic and inorganic pollutants from wastewater: electrocatalysis, photocatalysis, Fenton-based catalysis, chemical oxidation.

Photocatalysis is the most significant oxidation process in which the organic molecules are oxidized and reduced by redox reactions activated through the electron-hole pairs generated on the surface of metal oxide semiconductors upon beyond band gap light irradiation.

Catalysts such as zinc oxide (ZnO), cadmium sulphide (CdS), zinc sulphide (ZnS), gallium phosphide (GaP), titanium dioxide (TiO_2), tin dioxide (SnO_2), tungsten trioxide (WO_3), molybdenum trioxide (MoO_3), magnetite (Fe_3O_4), graphitic carbon nitride (g-C_3N_4) [48] were tested and applied in wastewater treatment. There are also catalysts with antimicrobial properties.Semiconductor metal oxides, like zinc oxide (ZnO) and titanium dioxide (TiO_2), provide an ample surface area for the adsorption of heavy metal ions from wastewater and they are often used in the photocatalytic oxidation under the irradiation of UV light of organic pollutants like dyes.

Semiconductor nanocomposites $BiVO_4/CuCr_2O_4$, $TiO_2/(ZnS)_x(CuInS_2)_{1-x}$, Bi_2WO_6, Ag_3PO_4/TiO_2, Ag_2CO_3 and $Bi_2TiO_4F_2$have excellent photocatalytic properties under visible light [41].Composite structures formed of CNT and lanthanum orthovanadate $LaVO_4$possessimproved photocatalytic activity in the degradation of organic compounds and antibiotics(Fig. 3)[50].Silver (Ag) nanocatalyst, AgCCA catalyst, N-doped TiO_2 and ZrO_2 nanoparticles catalysts are highly efficient in the degradation of microbial contaminants in water [43]. The biggest drawback of nano-photocatalysis is the high operating cost of ensuring the required light energy (UV radiation), so this technology is, so far, not considered an economically viable treatment of wastewater [53].

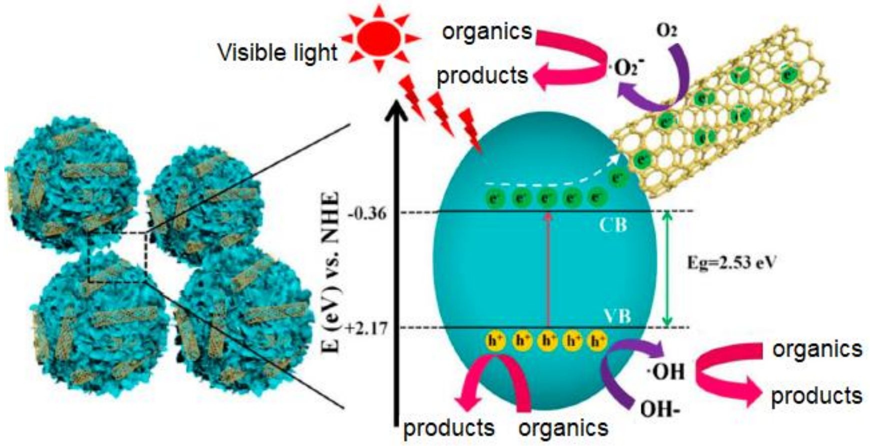

Fig. 3. Photocatalysis of CNT/LaVO$_4$ composite catalyst [50]

Nanomembranes. Among the available types of membrane-basedtechnologies that are capable of removing heavy metals from wastewater (Fig. 4), nanofiltration (NF) is widely applied due to small pore size, low cost, high efficiency and ease of use.Nanofiltration is highly efficient in the removal of organic and inorganic substances, bacteria and viruses, so the necessity for subsequent disinfection of water is minimal. Nanofiltration membranes are mostly applied for the reduction of hardness, color, odor and heavy metal ions [43] and for retaining the microorganisms from wastewater. The performance of membrane systems is decided by the membrane material [32].

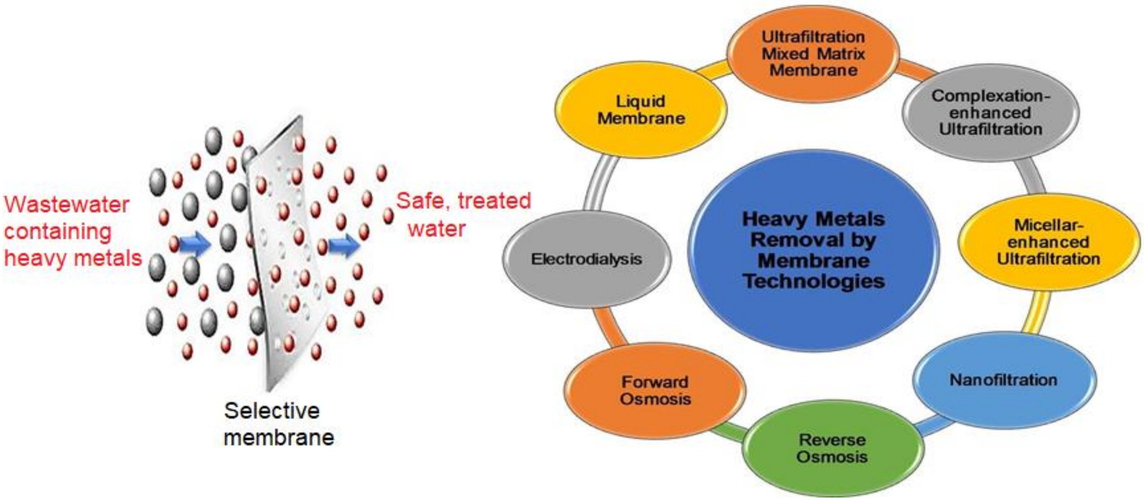

Fig. 4. Membrane technologies for heavy metals removal from wastewater [1]

One of the most difficult problems in nanomembrane processes is membrane fouling caused by the deposition of pollutants onto the membrane surfaces, which shortens membrane lifetime. Membrane fouling is influenced by the characteristics of wastewater, operating parameters and membrane properties.Also, biofouling of membranes caused by the bacterial load in wastewater can occur. To overcome this issue, new polymeric membranes with antifouling coating (organic brush-like coating, membrane impregnated with nanoparticles) were developed. Antifouling photocatalytic nanoparticles such as nano-Ag, nano-TiO$_2$, nanoalumina and CNT [33] have been integrated into polymeric membranes (reactive membranes) and they combine the physical separation and the reactivity of a catalyst toward pollutants degradation [31].

RESULTSAND DISCUSSIONS

Cr(VI) is highly toxic, very soluble and mobile in wastewater andis found as chromate CrO_4^{2-}, dichromate $Cr_2O_7^{2-}$,hydrogen chromate $HCrO_4^-$ and H_2CrO_4 , depending on pH and total chromate concentration in the solution [46]. Chitosan / alginate nanocomposite was applied to remove Cr(VI) from wastewater. Maximum adsorption capacity of Cr(VI) in batch adsorption was 108.8 mg/g and the adsorbent favored a multilayer adsorption [19]. Magnetic nanocompositesof MnO_2/Fe_3O_4/multi-wall CNTremoved a large quantity of Cr(VI). The highest adsorption capacity achieved was 186.9 mg/g in 150 min of process time [28]. Magnetic iron–nickel oxide was used as adsorbent for Cr(VI) and showed the highest adsorption capacity of 30 mg/g [48].

Nanoscale zero valent iron (nZVI), a composite consisting of Fe(0) and ferric oxide coating, achieved maximum removal capacity of Cr(VI) of 253.68 mg/g in a batch adsorption experiment [52].One-step method for the removal of Cr(VI) and Cr(III) with a mixture of TiO_2 and titanate nanotubes was proposed. The efficient transfer of Cr(III) from TiO_2 surface to titanate nanotubes interlayer greatly increased the release of photocatalytic sites of TiO_2,which led to more than doubled Cr removal efficiency comparing with the conventional two-step processes [27].

Zeolites were used in the removal of Cr(III), Ni(II), Zn(II), Cu(II) and Cd(II) from metal electroplating and acid mine wastewaters [4]. The differences between ZnO nanoparticles and calcium doped ZnO nanoparticles were compared towards adsorbtion of Cr(VI), Cd(II) and Ni(II). The results indicated that the incorporation of Ca in ZnO nanoparticles could improve the uptake effect of these heavy metals [16].Metal / metalloids such as Cr(VI) and As(V) were removed from water by magnetic Fe_3O_4NPs coated with phosphonium-silane (PPhSi-MNPs). After contact time of 50 and 70 min, the removal efficiencies of PPhSi-MNPs for As(V) and Cr(VI) were 97%and 67.8%, at at optimal pH=3 [8].

In wastewater and groundwaterpolluted with arsenic (As), the adsorption of As using TiO_2 materials in combination with filtration is a promising technology [51].Removal and recovery of As in copper smelting wastewater using TiO_2 as adsorbent were tested and an average of 3890 ± 142 mg/L As(III) at pH 1.4 in the wastewater was reduced to 59 ± 79 µg/L in the effluent with final pH at 7 in the 21 successive treatment cycles using regenerated TiO_2. Coexisting heavy metals Cd, Cu and Pb with initial concentrations of 369 mg/L, 24 mg/L, and 5 mg/L were reduced < 0.02 mg/L [28].Magnetite–graphene composite with particle size of 10 nm give a high binding capacity for As(III) and As(V), due to the increased adsorption sites in the graphene composite [6]. The removal efficiency of As^{3+} by carboxyl, amine and thiol-functionalized Fe_3O_4 was 91%, 95% respectively 97%, at pH=8 [41].

Graphene was functionalized and used as a adsorbent nanomaterial to remove Pb(II) from an water. Its maximum adsorption capacity was found to be 406.6 mg/g at the optimum pH=5.0 [14]. Hybrid adsorbent systems formed of carbon nanotubes, TiO_2 and MnO_2 were used for the removal of Pb(II). The adsorption capacity was 137 mg/g for CNT+TiO_2, respectively 78.74 mg/g for CNT+MnO_2 [54].Magnetic chitosan nanocomposites achieved 94.6% removal efficiency for Pb(II) from wastewater [26].Synthesized maghemite nanoparticles of79.35 m^2/g surface area were applied to remove Pb(II) and Cu(II) in wastewater, and adsorption capacities were 68.9 for Pb(II) and 34.0 for Cu(II) [35].

Three graphene-based composites were compared for theirPb(II) sorption capacity–suspension of graphene nanoplatelets (SGN), paste of multilayered oxidized graphene (PMOG) and paste of few-layered oxidized graphene (PFOG). The maximum Pb(II) sorption capacities were 457 mg/g for SGN, 103 mg/g for PMOG and 38 mg/g for PFOG [23]. Nanocomposites of kaolinite-nZVI and zeolite–nZVIwere very efficient (>96%) in removing Pb(II) from aqueous solutions [24].Manganese oxides-based nanomaterials have been reported to remove Pb(II), U, Cd(II), Cu(II), Zn(II), Hg(II) [22]. Synthesized magnetite nanoparticles were used to adsorb Pb(II), Cu(II), Zn(II) and Mn(II) in a batch mode. Nanosized magnetite had the best adsorption effect for Pb(II) with 0.180 mmol/g while the lowest adsorbtion was for Mn(II) with 0.140 mmol/g [17].

ZnOnanoparticles with size of 26 nm prepared by precipitation were applied in batch system for the removal of Zn(II), Cd(II) and Hg(II). At 100 ppm initial concentration of all ions, pH between 4-8, adsorbent dosage of 0.5 g/L, the adsorption capacities were 357 for Zn(II), 387 for Cd(II) and 714 for Hg(II) [40]. Crystal nanoparticles of γ-Fe_2O_3 prepared by chemical co-precipitation was applied in order to remove Zn(II), Cu(II) and Cr(VI). The nanoparticles had spherical shape and 10 nm diameter. At adsorbent amount of 1 g/L and pH=2.5, the highest adsorption capacities were 15.9 for Zn, 15 for Cu and 55 mg/g for Cr(VI) [44].

Dendrimer-conjugated magnetic nanoparticles (Gn-MNPs) combining the superior adsorbent of dendrimers with magnetic nanoparticles (MNPs) were tested for removal and recovery of Zn(II). The adsorption efficiency increased with increasing pH. At pH<3, Zn(II) was readily desorbed and the Gn-MNPs retained the original removal capacity of Zn(II) after 10 consecutive stages of adsorption–desorption [12].

Synthesized-layered graphene oxide nanosheets adsorbed Cd(II) and Co(II) in water by the batch method. The adsorption effect was strongly influenced by pH and presence of humic acid in aqueous solution could reduce the adsorption of Cd(II) and Co(II). The maximum adsorption capacities of Cd(II) and Co(II) onto GO were 106.3 and 68.2 mg/g [55].

CONCLUSIONS

Water pollution by heavy metals is a serious environmental problem.Exposure to heavy metals is known to cause toxic effects on human healthand other living organisms.

The solution to the problem of wastewater treatment from heavy metal ions is associated with the development of new technologies.Nanotechnology grants an economical, convenient and ecofriendly wastewater treatment.

Nanomaterials possess a high removal capacity of heavy metals in wastewater, so theyare a promising alternative to the traditional adsorbents used in wastewater treatment.Nanosized metals, metal oxides, graphene, carbon nanotubes and nanomembranes have proven to be very effective in the detection and removal of heavy metals from wastewater.

Nanoparticles have antimicrobial properties, so they are applied for disinfection and microbial control in wastewater treatment technologies.

Although there are many studies with very encouraging results in terms of nanomaterials efficiency, there is still a long way to use nanomaterials in large scalewastewater treatment systems. Furthermore, the impact of emerging nanomaterials on human health and the environment must be thoroughly investigated.

ACKNOLEDGEMENT

This work was supported by a grant of the Romanian Ministry of Research and Innovation CCDI - UEFISCDI, Project INNOVATIVE TECHNOLOGIES FOR IRRIGATION OF AGRICULTURAL CROPS IN ARID, SEMIARID AND SUBHUMID-DRY CLIMATE, project number PN-III-P1-1.2-PCCDI-2017-0254, Contract no. 27PCCDI/2018, within PNCDI III.

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