Nanomaterials applied for heavy metals removal from wastewater

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Abstract. In the past years, nanotechnology has been studied and it proved that is one of the advanced ways for toxic compounds removal from wastewater. In this paper we focus on nanomaterials used for treatment of wastewater containing heavy metals. Nanoparticles have very high and specific adsorption capacity being applied in water depollution, remediation and treatment process. The depollution methods based on nanomaterials could be more cost-effective, less time and energy consuming, generating no or less waste in comparison with conventional methods. The aim of this review is to summarize the applications of nanoadsorbants within heavy metals depollution methods.

1. Introduction
For the heavy metals removal process are used various conventional methods such as redox reactions, solvent extraction, chemical precipitation and filtration, reverse osmosis, electrochemical treatment methods, ion exchange and lime coagulation which are characterized by low removal yields and high cost of operation.

In the past years the adsorption process using nanomaterials was studied as an alternative solution, materials such as magnetic oxides, polymers, ceramic, silica and derivatives of carbon have been developed for wastewater treatment.

2. Nanomaterials as adsorbants
Nanotechnology has been studied since 1980 along with the introduction of scanning tunnel microscope development STM [1].

Materials that have size range between 1 and 100 nm are described as nanoparticles and have distinct properties such as high surface area, high efficiency in the magnetic separation process, increased chemical and physical surface interactions sustaining the application for pollutants removal [2]. In the past years were synthesized by different methods various nanomaterials such as: metal oxide nanoparticles, magnetic nanoparticles, carbon nanotubes (CNTs), chitosan or silica nanoparticles [3-14].

Nanoadsorbants are used in wastewater treatment because of their high capacity of adsorption of pollutants. Some of the most important parameters of wastewater treatment process using nanomaterials are the thermodynamic activity and chemical potential to reach the equilibrium concentrations (the maximum yield), constants between the phases and the efficiency of reaction on which the removal is based [15].
2.1 Metal oxide nanoparticles
The main difference between micro/macro level and nano level is the band gap of the oxide particles, when the particle size decrease also the band gap decrease with direct impact on conductivity and chemical reactivity [16].

Compared with normal sized metal oxide, nanoparticles of metal oxide have higher adsorption because of the formation of the ternary ligand or metal-ligand precipitation [17].

Adsorption mechanism of heavy metals on nanoadsorbants of oxides of Zn, Cu and Fe showed a dependence of metal removal efficiency on the pH of the wastewater solution. Removal of heavy metal ions from the solution increase with pH because of electrostatic interactions, precipitation and formation of metal complexes having ionic or covalent bonding, depending either upon the chemistry between metal and the solution or on the nature of the functional groups. At the nanoadsorbant surface the increase of solution pH leads to deprotonation, increase the negative charge resulting in a higher adsorption capacity due the attraction forces between the negative side (adsorbant) and positive side (metal ions). Contrary, lower pH, facilitate competitive adsorption between metal ions and H+ ions of solution [18].

Some studies regarding the Fe3O4 removal capacity for Pb (II) ions showed that the maximum adsorption was 36 mg/g, obtaining equilibrium in less than 30 min. The process is endothermic and was showed that the amount of Pb (II) ions absorbed increase along with the increasing of the temperature value [19].

Studies regarding the removal of copper, lead and arsenic ions using anatase nanoamaterial synthesized by sol-gel method showed that the maximum adsorption capacities was 31.25 mg/g for lead ions, 23.74 mg/g for copper ions and 16.98 mg/g for arsenic ions. The adsorption capacity was influenced by pH in cases of lead and copper ions, while in case of arsenic ions the process was not influenced by pH value [20].

In 2013 a nanoadsorbant was synthesized by doping Fe2O3 with 10% Mg2+ using a thermal process, having the average size of 3.7 nm, a specific surface area of 438.2 m2/g and specific magnetization of 32.9 emu/g making them easy to use for wastewater treatment. The As (III) ions adsorption capacity was 127.4 mg/g and for As(V) ions 83.2 mg/g at pH 7 [21].

Another nanomaterial was obtain in 2013 as an As(III) and As(V) adsorbant for the treatment of wastewater. Using coprecipitation method were synthesized nanoparticles of manganese feroxoyte (δ-Fe0.76 Mn0.24OOH). This process used a strong oxidizing agent for coprecipitation of FeSO4 and KMnO4, resulting an homogeneous distributed crystal structure. The nanoadsorbant was tested on drinking water at a pH of 7, revealing a potential removal capacity for As(III) of 6.7 μg/mg and for As(V) of 1.7 μg/mg [22].

Fe-La nanosized particles were synthesized in 2014 and tested as an adsorbant for As(III) removal from wastewater solutions. The composite present the same crystal structure as La(OH)3 and have a maximum adsorption capacity for As(III) of 58.2 mg/g in a solution with pH of 7.

Using an alumina (Al2O3) nanoadsobant with the purpose of removal of Zn(II) ions from wastewater, was obtained a maximum adsorption capacity of 1047.83 mg/g at pH 2 after 4.5 h [23].

2.2 Magnetic nanoparticles (MNPs)
Superparamagnetic nanoparticles have properties such as: are less toxic, biocompatible, chemically inert, give small diffusion resistance and, using organic molecules, inorganic ions or some functional groups, possibility of surface modification facilitating the heavy metals removal from wastewater. Because of the surface modifications MNPs will be more stable by preventing their oxidation. The interactions responsible for the adsorption process of heavy metal ions from wastewater are physical (electrostatic and Vander Waal’s interactions) and chemical (chemical binding, complex formation or modified ligand combination) [24, 25].

Mercapto-functionalized nano-Fe3O4 magnetic polymers (SH-Fe3O4-NMPS) were synthesized for the Hg(II) removal from wastewater. MNPs showed high efficiency at 35°C temperature value and pH 3.0. When the pH value increase, also the adsorption efficiency increase. The results were correlated
using Freundlich isotherm equation and the constants have been calculated [26]. Thermal decomposition of FeOOH was studied for carboxymethyl-β-Cyclodextrin (CMCD) monodisperse magnetite nanocrystals synthesis and were prepared particles of 10 nm for As (III), As (V), naphthal and naphthalene removal from wastewater. After a single stage of magnetic separation, nanocrystals were efficient for wastewater treatment [27]. Hydrothermal method was studied for synthesis of superparamagnetic nanocomposites of Fe₃O₄ coated with ascorbic acid that were used for arsenic removal from wastewater. Nanocomposites formed had dimensions less than 10 nm. For the As(III) removal the maximum adsorption capacity was 16.56 mg/g and for As(V) removal was 46.06 mg/g [28].

For Hg(II) removal were tested unmodified Fe₃O₄ magnetic nanoparticles and also a modified Fe₃O₄ with 2-mercaptobenzthiazole. The initial concentration of Hg(II) was 50 ng/mL and the yield was about 43 % for unmodified nanoparticles and 98% for modified nanoparticles [29]. Magnetic nanoparticles of MnFe₂O₄ were coated with shells of amorphous oxide of Mn-Co resulting a hybrid with strong negative charge on a wide range of pH. The maximum adsorption capacities were 481.2 mg/g for Pb(II) removal, 386.2 mg/g for Cu(II) removal and 345.5 mg/g for Cd(II) removal [30]. Co-precipitation technique was used for the synthesis of ferrite coated nanosorbant for the Eu(III) ions removal from wastewater. Resulted magnetic nanoparticles had a specific surface area of 85.11m²/g, the mean particles size was 63 nm and showed thermal resistance at more than 600°C. For obtaining the equilibrium capacity of 157.14 mg/g in less than 12h, at a pH value of 2.5 was used 5mg of adsorbant. By chemical coprecipitation technique were synthesized Fe₃O₄ nanocomposites of cellulose used for wastewater polluted with arsenic ions [31]. Composites had a surface area of 113 m²/g being easily separable because of its sensitive magnetic behavior obtaining maximum removal capacities for As(III) and As(V) of 23.16 mg/g and 32.11 mg/g [32]. On surface of Fe₃O₄ nanoparticles was immobilized thiosalicylhydrazide forming magnetic nanoparticles for heavy metal ions removal from aqueous solutions. There were obtained the following results: 188.7 mg/g for Pb(II), 107.5 mg/g for Cd(II), 76.9 mg/g for Cu(II), 51.3 mg/g for Zn(II) and 27.7 mg/g for Co(II). Modified nanoparticles also have advantages of easy reusable and are friendly environmental [33].

2.3 Carbon nanotubes (CNTs)
Carbon nanotubes present a unique structure and possess some characteristics such as optical activity, specific surface design morphologies, electrical conductivity and mechanical strength. Also, their light mass density, high surface porosity, large specific surface area, strong interactions with pollutant and hollow structure makes them the perfect candidate for a nanoabsorbant [34].

Because of their unique structure, carbon nanotubes have four different adsorption sites: outside surface, grooves, interstitial channels and internal sites, with faster equilibrium reached on external sites compared with internal sites. The main reason for their adsorption properties is the chemical interactions between the nanotubes surface and metal ions.

Carbon nanotubes can contain –COOH, –C=O and –OH groups according to the process of synthesis and purification method used. Furthermore, carbon nanotubes can be doped with more functional groups by oxidation with catalysts such as Ni, Pd, or Pt.

They have high preference for hydrophobic groups such as hexane, cyclohexane and benzene than hydrophilic groups such as alcohol. Changing the wettability of CNT surfaces, the preference can be reversed. The H - atoms of CNTs functional groups are replaced by metal ions and the pH value of the solution is decreased: when the H⁺ ions are release, the solution pH is dropping [35, 36, 37].

Using microwave irradiation method were synthesized maghemite nanotubes. They had a magnetic saturation of 68.7 emu/g and specific surface area of 321.6 m²/g. This nanotubes are coated with shells of Mn-Co resulting a hybrid [38]

A magnetite nanocomposite was synthesized as a multi-wall carbon nanotube for adsorption of Hg(II) and Pb(II) from wastewater. They have a maximum adsorption capacity of 65.52 mg/g for Hg(II) and 65.40 mg/g for Pb(II) [39]. Another application of magnetic multi-walled nanotubes is the removal of Ni(II) from wastewater. The results indicate a value of 2.11 mg/g as maximum monolayer
adsorption capacity. The process of Ni(II) adsorption is favourable thermodynamically and spontaneous [40]. Another multi-wall carbon nanotube was synthesized by treating purified multi-walled carbon nanotubes with concentrated sulphuric acid at high temperature. The synthesised carbon nanotube was tested on aqueous solutions polluted with Cu(II). The sulfonation revealed an adsorption capacity rate for Cu(II) of 58.9% [41].

CNTs were synthesized by chemical vapour deposition of cyclohexanol and ferrocene at 750°C functionalized with chitosan and HNO₃ in the presence of nitrogen. Adsorption capacity was increased from 23.32 mg/g without functionalization of CNTs to 57.34 mg/g with functionalization at an initial concentration of 800 mg/L for Cu(II) ions [42].

Magnetic multi-wall carbon nanotubes were prepared using a wet chemical process for the removal of Cr (VI) ions from wastewater. The results showed that the adsorption capacity is directly proportional with the contact time and metal ion concentration and inversely proportional with adsorbant dose. The process is spontaneous and endothermic [43].

2.4 Chitosan based nanomaterials
Chitosan is a byproduct from the waste of processed shellfish. It is a biopolymer formed by natural polysaccharides being an excellent adsorbant because is inexpensive, abundant, chemically stable, nontoxic, biodegradable, biocompatible, hydrophilic, renewable and has a good reactivity for a large range of pollutants. Because of the amine group presence (-NH₂) existing in the polymer matrix and because of partial positive charge, it has an excellent adsorption capability for the toxic metal ions. Magnetised chitosan nanoparticles showed high efficiency of adsorption. Interactions between chitosan and heavy metal ions are reversible, thus magnetised chitosan nanoparticles are easy to recover after wastewater depollution applying an external magnetic field [44, 45].

For removing As(III) from wastewater were synthesized binary oxides coated with chitosan and the adsorption capacity was 16.94 mg/g. In wastewater were found Ca(II) and Mg(II) which affected the removal process of As(III). Between the pH range from 3 to 9 the adsorption process was not efficient. The As(III) concentration was reduced from 983.7 to 7.44 g/L [46]. Chitosan coated magnetite NPs were synthesized and used for Hg(II) ions removal from wastewater following the Box-Behnken technique. It was obtained a yield of 99.91% at pH 5 and an initial concentration of 6.2 mg/L for Hg(II) ions using a quantity of 0.67 g adsorbant. Chitosan coated magnetite NPs had active sites with high density on the surface [47]. Also magnetic coated nanoparticles were studied for Cu(II), Cd(II), Zn(II) and Pb(II) ions adsorption, showing a significantly decrease for ions concentration from wastewater [45]. Deacetylation of chitin was studied for preparation of chitosan nanoparticles used in Mn(II), Zn(II), Fe(II) and Cu(II) ions removal. The quantity of adsorbant added in solution was 2 g/L with a pH value of 7 and initial pollutants concentration of 20 mg/L and the mixing time was 30 minutes. The removal efficiency for Fe(II) was 99.94%, for Mn(II) was 80.85%, for Zn(II) was 90.49% and for Cu(II) was 95.93% [48]. A composite nanofiber of chitosan and TiO₂ was synthesized by coating and entrapped method for the removal of Cu(II) and Pb(II) ions from wastewater. The study revealed a maximum adsorption capacity of 710.3 mg/g for Cu(II) ions and 579.1 mg/g for Pb(II) ions by entrapped method and 526.5 mg/g for Cu(II) ions and 475.5 mg/g for Pb(II) ions by coating method. Nanofibers from entrapped method can be reused after 5 desorption cycles with the same performance. In case of coating method, the yield of adsorption was only 60% in the first cycle [49].

2.5 Silica based nanomaterials
Silica is a material used as a shell for nanoparticles being the subject of wastewater depollution experiments. The coating process of nanoparticles with silica activates their surfaces having a variety of functional groups because of the silanol groups onto silica layer. Silica also protects nanoparticles at low pH of the solution. Polymer layered silicate nanocomposites has better properties when the content of filler is low. At pH=7, acidity of silica nanoparticles increases with the particle size
increase, thus it will result a percent of 5-20% ionisation of silanol groups. So, anionic silica surface will attract cations through ion pairing.

The adsorption method was studied for zinc, nickel, chromium, lead and cadmium ions removal from wastewater using as adsorbants silica nanoparticles, silica/graphite oxide composites and nanostructured graphite oxide. The order of heavy metals adsorption using nanostructured graphite oxide was Ni(II) > Zn(II) > Pb(II) > Cd(II) > Cr(VI). For the nickel removal the adsorbant that also showed good results was graphite oxide. For wastewater depollution the most efficient adsorbant between those three was silica/graphite oxide composite having the 2:3 ratio [50]. Adsorption of lead, nickel, cadmium, zinc and chromium from wastewater was studied using activated carbon microparticles with an average particle size of 25μm, silica nanoparticles and silica/activated carbon nanocomposite having the ratio of 2:3 with an average particle size of 12 nm. Compare with activated carbon microparticles and silica nanoparticles, silica/activated carbon nanocomposite with the ratio of 2:3 showed higher efficiency for adsorption of nickel ions from wastewater. Using a 30mg/L nickel ion concentration, the efficiency of removal by activated carbon microparticles was 99.4%, by silica nanoparticles was 70.3% and by silica/activated carbon nanocomposite in ratio of 2:3 was 92.1% [51]. Kong et al. studied industrial silica fumes treated by HNO₃ at 80°C for obtaining amino modified silica nanoparticles. This nanoparticles were used to remove zinc, cadmium, mercury, copper and lead ions from wastewater and the high efficiencies were obtained for copper, mercury and lead ions adsorption [52]. Mesoporous silica nanoparticles were synthesized by embedding silica magnetic nanoparticles by cetyltrimethylammonium bromide followed by transformation of silane coupling agent 3-aminopropyltriethoxysilane. This nanoparticles were used for Cr(VI) ions removal from wastewater. The conclusion was that the yield varied with the pH value. Mesoporous silica nanoparticles presented high removal for heavy metals, regeneration and easy separation using an external magnetic field followed by reutilization [53]. For the Hg(II) adsorption form wastewater were synthesized mesoporous silica nanoparticles MCM-41 that were grafted from poly-amide derivative applied as the supporting matrix. These nanoparticles were labelled having high surface area and large pores. Thus, Hg ions were adsorbed from wastewater within 3 minutes in a pH range between 3-11 and the adsorbant nanoparticles were not influenced by other compounds from the solution [54].

3. Conclusions

In this review we presented relevant data for six promising nanomaterials types applied for the removal of heavy metal from wastewater by adsorption: metal oxide nanoparticles, magnetic nanoparticles, carbon nanotubes, chitosan based nanomaterials and silica based nanomaterials. For every category we found different synthesize methods and different conditions with good results in adsorption capacity, easy usability, facile regeneration and environment friendly.

Unique chemical and physical properties of nanomaterials as high specific surface, size and specific structure makes them excellent adsorbsants used in wastewater depollution in comparison with conventional methods.

Furthermore, it is required more research regarding adsorbants characteristics being crucial to understand the impact on toxicity and desorption in the process of reuse and recycle of nanoadsorbants.

4. References

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