REMOVAL OF HEAVY METAL IONS FROM WASTEWATER USING CONVENTIONAL AND NANOSORBENTS: A REVIEW

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ABSTRACT

Wastewater that contains heavy metal ions is considered as the serious threat for environmental pollution. Most of the heavy metals are toxic and their ions are not biodegradable with the tendency to accumulate in the soil and in the living organisms, and hence they are significant environmental pollutants. Therefore, the treatment of the heavy metal ions and their elimination from water and wastewater is very important for environmental protection, and thus the public health. Adsorption is the most commonly used method for removal of the heavy metal ions from large volumes of aqueous solutions. There are a number of materials that can be applied as adsorbents for heavy metals. The clay minerals (bentonite), zeolites, activated carbon, metal oxides, are widely used as conventional adsorbents in the removal of different heavy metal ions, such as Zn(II), Pb(II), Ni(II), Cd(II), Cu(II) from wastewater. The development of nanotechnology enabled nanomaterials, such as graphene and carbon nanotubes, to be widely used as the effective sorbents for the heavy metal elimination from wastewater.

Keywords: heavy metal ions, adsorption, conventional adsorbents, graphene, carbon nanotubes.

INTRODUCTION

Environmental pollution is one of the main problems nowadays. The rapid development of industries and the drastic increase of population are responsible for the destruction and damaging of the environment and adversely affecting the health of the people. Different contaminants are released to wastewater, including heavy metal ions, organics, bacteria, viruses and so on. Heavy metal ions are non-degradable and persistent, hence, they are significant environmental pollutants, and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons [1]. Most of heavy metals such as Pb, Cr, As, Cd, Ni, Hg, Mn, Co, Zn, Fe are toxic inorganic pollutants in soil, surface and groundwater, and by their properties, threaten all living organisms and humans in the polluted environment. Various regulatory bodies have set the maximum prescribed limits for the discharge of toxic heavy metals in the aquatic systems. However the metal ions are being added to the water stream, by industrial activities, at a much higher concentration than the prescribed limits, thus leading to health hazards and environmental degradation. Consumption of the food or water contaminated with heavy metals above the limited values can cause metabolic problems because heavy metals accumulate in the organism and they are hardly processed and disposed of it. The most common health problems that occur in humans when they are acute or chronic exposed to the effect of heavy metals, are presented in Table 1 [2].

Therefore, the removal or reduction of the quantities of heavy metal ions from the wastewater is very important for public health protection.
Table 1. Human diseases that occur while acute or chronic exposure to the impact of heavy metals.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Acute exposure</th>
<th>Chronic exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>Nausea, vomiting, &quot;rice-water&quot; diarrhea, encephalopathy, painful neuropathy</td>
<td>Diabetes, hypopigmentation/ hyperkeratosis, cancer: lung, bladder, skin, encephalopathy</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Pneumonitis (oxide fumes)</td>
<td>Proteinuria, lung cancer, osteomalacia</td>
</tr>
<tr>
<td>Chromium</td>
<td>GI hemorrhage, hemolysis, acute renal failure ($Cr^{6+}$ ingestion)</td>
<td>Pulmonary fibrosis, lung cancer (inhalation)</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Beer drinker’s (dilated) cardiomyopathy</td>
<td>Pneumoconiosis (inhaled); goiter</td>
</tr>
<tr>
<td>Copper</td>
<td>Blue vomitus, GI irritation/ hemorrhage, hemolysis, MODS (ingested); MFF (inhaled)</td>
<td>Vineyard sprayer’s lung (inhaled); Wilson disease (hepatic and basal ganglia degeneration)</td>
</tr>
<tr>
<td>Iron</td>
<td>Vomiting, GI hemorrhage, cardiac depression, metabolic acidosis</td>
<td>Hepatic cirrhosis</td>
</tr>
<tr>
<td>Manganese</td>
<td>MFF (inhaled)</td>
<td>Parkinson-like syndrome respiratory, neuropsychiatric</td>
</tr>
<tr>
<td>Mercury</td>
<td>Lemental (inhaled): fever, vomiting, diarrhea, ALI; Inorganic salts (ingestion): caustic gastroenteritis</td>
<td>Nausea, metallic taste, gingivo-stomatitis, tremor, neurasthenia, nephrotic syndrome; hypersensitivity (Pink disease)</td>
</tr>
<tr>
<td>Nickel</td>
<td>Dermatitis; nickel carbonyl: myocarditis, ALI, encephalopathy</td>
<td>Occupational (inhaled): pulmonary fibrosis, reduced sperm count, nasopharyngeal tumors</td>
</tr>
<tr>
<td>Zinc</td>
<td>MFF (oxide fumes); vomiting, diarrhea, abdominal pain (ingestion)</td>
<td>Copper deficiency: anemia, neurologic degeneration, osteoporosis</td>
</tr>
</tbody>
</table>
Heavy metal ions could be eliminated from wastewater by several traditional techniques, including chemical precipitation [3], ion exchange [4], reverse osmosis [5], electrolysis [6], membrane filtration [7], adsorption [8-11]. Most of these methods may be extremely expensive or ineffective when the metals are dissolved in large volumes of a solution at a relatively low concentration. Among all the approaches proposed, adsorption is one of the most popular methods and it is considered as an effective, efficient and economic method for wastewater purification and it is widely used in effluent treatment processes.

Various materials, such as, clays minerals, zeolites, activated carbon, metal oxides, are used as conventional adsorbents for the removal of heavy metals from wastewater [12]. In recent years, the development of nanoscience and nanotechnology has shown remarkable potential for the remediation of environmental problems [13,14]. Compared with traditional materials, nanostructured adsorbents, such as graphene and carbon nanotubes, have exhibited much higher efficiency and faster rates in water treatment [15].

**KIND OF ADSORBENTS**

**Conventional adsorbents**

High specific surface area, high ion exchange capacity, low cost and their presence in nature in large quantities, are the main characteristic of the materials that are widely used as conventional adsorbents for heavy metal removal from wastewater. Some of the most commonly used adsorbents, such as clay minerals (special emphasis of bentonite), zeolites, activated carbon and metal oxides, are reviewed in this paper.

**Clay minerals (bentonite)**

Clay minerals have typical characteristics, high specific surface area, high ion exchange capacity, chemical and mechanical stability and layered structure, which make them good adsorbents. They are widely used to adsorb various kinds of pollutants from large volumes of aqueous solutions. Clays are those aluminosilicate minerals which make up the colloid fraction (<2 µm) of soils and act as natural scavengers for heavy metal ions. Their tetrahedral and octahedral layers are seen to incorporate different ions which develop a range of properties with different responses to experimental conditions such as contact time, temperature, pH, adsorbent dosage, concentration of adsorbate etc.

Numerous studies relating to heavy metal adsorption using clays are presented. Hamdy studied the adsorption of Zn(II) and Pb(II) on natural clay mineral and saw the impact of pH and on the adsorption efficiency [16]. The best removal of Zn and Pb occur at pH 5. Zinc ions were 98.5 % removed by applied clay mineral, whereas the lead ions were 100 %, completely adsorbed from the contaminated water. Sdiri et al. examined natural clay from Tunis as adsorbent for elimination of copper and zinc from single and binary aqueous systems [17]. The results showed that good adsorption capacities can be achieved under the following working conditions: contact time of 60 minutes, pH of the solution 6, and the concentration of the adsorbent 1g/L at 25°C. The clay indicated better adsorption potential for Zn(II) ions removal than Cu(II) ions. The same conclusion, that the natural clay mineral can be applied as an effective adsorbent for removal of the Zn(II) and Cu(II) ions from aqueous solutions, gave Veli et al. [18]. Al-Degs et al. found that Jordanian natural clay, consisting of silicate and carbonate minerals is efficient adsorbent for removal of the Zn(II), Pb(II) and Co(II) ions from aqueous solutions [10].

Despite the researches that were performed on natural minerals, many studies were focused on modified minerals. Attempting to improve the quality and the characteristics of the clay minerals, many different techniques for their modification were applied. Unuabonah and his colleagues, studied the sorption of Pb(II) and Cd(II) ions on kaolinite clay modified with sodium tetraborate and found that the modified kaolinite has an increase of the adsorption capacity and affinity for metal ions compared to the natural kaolinite [19]. The effectiveness of natural and acid activated clay mineral in the removal of Pb(II) ions, was investigated by Mabrouk and Mourad [20]. They used two natural materials, marked RGC and RRC and perform their acid activation by 6M H2SO4 with mechanical stirring for 4h, at 75°C. After modification, minerals, marked AGC and ARC, showed improved adsorption properties. The adsorption capacities for Pb(II) ions, were: 25,44 mg/g and 40,75 mg/g for RGC and its modified form AGC and 17,84 mg/g and 27,15 mg/g for RRC and ARC, respectively [20].

Bentonite belongs to the group of clay minerals. It has typical layered silicate structure consisting of two silica tetrahedral sheets with a central alumina octahedral sheet. Interlayer space is easily accessible to water and other polar liquids (Fig. 1). Bentonite has a high
cation exchange capacity due to the presence of hydrated cations, Ca\(^{2+}\), Na\(^{+}\), K\(^{+}\), etc. on the interlayer surfaces, and these cations can be easily replaced with heavy metal ions. There are many studies related to the use of natural or modified bentonites in the treatments of water systems purification from heavy metal ions. Melichova and Hromada have used natural bentonite from Leiskovac (Slovakia) as an effective adsorbent for adsorption of Pb\(^{2+}\) and Cu\(^{2+}\) ions from aqueous solutions [21]. They found that the adsorbed amount of metal ions increases with increasing the pH value of the solution, by increasing of the initial concentration of the metal ions and contact time, while the amount of Pb\(^{2+}\) and Cu\(^{2+}\) ions adsorbed per unit mass of the adsorbent, decreases at equilibrium conditions by increasing the amount of used bentonite.

Experimental data better fit with Langmuir than Freundlich isotherm. The adsorption capacity was higher for Pb\(^{2+}\) than Cu\(^{2+}\) ions and is 32.7 mg/g and 11.3 mg/g, respectively. Inglezakis et al., who investigated the ability of the natural zeolite - klinoptiolit and of the natural bentonite for removal of lead ions from aqeous solutions [22]. They found that the adsorbed amount of metal ions increases with increasing the pH value of the solution, by increasing of the initial concentration of the metal ions and contact time, while the amount of Pb\(^{2+}\) and Cu\(^{2+}\) ions adsorbed per unit mass of the adsorbent, decreases at equilibrium conditions by increasing the amount of used bentonite.

Studies about the retention of metals Cu, Co, Ni, and Zn in two types of Peruvian bentonite have been accomplished for monometallic, bimetallic, trimetallic and tetrametallic solutions [24]. On the effect of initial metallic concentrations they have considered that for each one of the metals a quickly diminution of the adsorption percentage of the different studied metals (Cu, Co, Ni, Zn) comes, when there is an increase of the solution concentration. The effect of ionic competence between metal ions has low signification at low concentration of the solutions. It is as well to emphasis that with 0.001 M solutions the competence ionic effect has a low signification and the adsorption percentage of each metal (even in a tetrametallic solution such as Cu-Co-Ni-Zn) has the values higher than 90% for each one of them. The diminution of the adsorption rate of metals by bentonites occurs with the decreasing of the pH of solutions. This, probably, happens because at lower pH, the concentration of the H\(^{+}\) ions in the solution is higher and they compete with metal ions for the sorption sites in bentonite. Using natural bentonite from Morocco as adsorbent for ions of the same heavy metals (Cu\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\) and Zn\(^{2+}\)) from aqueous solutions, Ghormi et al. came to the same conclusion that at lower pH values decrease adsorbed amount of metal ions [25]. They examined the influence of contact time and the temperature of the solution on the effect of adsorption and found that the amount of adsorbed metal ions increases with increasing the temperature of the solution as well as with increasing the contact, and then remains constant when the equilibrium is achieved. At the same, optimal conditions of adsorption the following order of adsorption of heavy metals on bentonite was determined: Cu\(^{2+}\) > Zn\(^{2+}\) > Ni\(^{2+}\) > Co\(^{2+}\) with adsorption capacities of 28.88 mg/g, 20.5 mg/g, 17.05 mg/g and 13.85 mg/g, respectively [25].

We have applied natural bentonite from Republic of
Macedonia as an adsorbent for removal of Ni(II), Fe(II) and Zn(II) ions from aqueous solutions [26, 27]. Our results have shown very nice effects of application of the linearized form of Langmuir and Freundlich isotherm models (Fig. 2a and Fig. 2b) in the adsorption equilibrium data analysis [26]. Both models indicates good correspondence to the experimental results. The percentage of the removal of Ni(II) ions at different initial concentrations of 0.3, 0.4 and 0.5 mg/l were 80, 75 and 72 %, respectively (Fig. 3).

Natural bentonite from Macedonia, also show excellent results for the removal efficiency for Fe(II) and Zn(II) ions of 96 % and 99 %, respectively [27].

The main objective of Al-Jilil et al., was to remove the heavy metals Cu, Co, Zn, Pb, As, Cd and Cr from industrial wastewater by adsorption using natural local bentonite from Saudi Arabia [28]. The minimum removal efficiency of metal ions was 97 % and it has been shown that bentonite has good potential for purification of industrial wastewater from heavy metals through adsorption. The same team in another article, committed characterization of natural bentonite from Saudi Arabia and analyzed its ability for the adsorption of copper and nickel from wastewater at different temperatures [29]. Showed that the adsorption capacity of bentonite increases with temperature and is 13.22 mg/g for Cu²⁺ and 9.29 mg/g for Ni²⁺ at 20°C.

Very often improving the adsorption properties of natural bentonite is carried out by modification using appropriate chemical or thermal treatments. Kaya and Oren examined adsorption properties of natural bentonite and bentonite enriched by Na for the adsorption of Zn²⁺ ions at various pH values and different initial concentrations of the metal ion [30]. Found that the rapid increase in the removal of zinc is obtained at a pH above 7. The increase of the initial concentration of the metal ions leads to increased adsorption to some extent, and then comes to a complete saturation of the material with zinc cations. Bentonite enriched with Na showed much better adsorption characteristics than natural bentonite.

Budsaereechai et al., examined adsorption of lead, cadmium and copper on natural and acid activated bentonite with HCl, showed that modified bentonite has improved adsorption characteristics compared to natural bentonite [31]. The results showed that the activation of bentonite, increases the specific surface area 57 % i.e. from 47 m²/g for natural bentonite, acid activated bentonite had a surface area of 74 m²/g. They also found that adsorption capacities of activated bentonite are higher for all three...
metal ions and are 83,02 mg/g and 92,85 mg/g for Pb\(^{2+}\), 48,20 mg/g and 57,88 mg/g for Cd\(^{2+}\), 30,99 mg/g and 36,68 mg/g for Cu\(^{2+}\) for the natural and acid activated bentonite respectively [31]. Natural bentonite from Western Algeria was impregnated in 1M NH\(_4\)Cl solution with the bentonite/NH\(_4\)Cl solution ratio of 1/1 w/w. The suspension was left overnight at the ambient temperature under constant stirring, then dried in an oven at 60\(^{\circ}\)C for several days. After that, the bentonite was thermally treated in furnace at 100\(^{\circ}\)C, 200\(^{\circ}\)C, 250\(^{\circ}\)C, 300\(^{\circ}\)C, 350\(^{\circ}\)C, 40\(^{\circ}\)C, 450\(^{\circ}\)C and 500\(^{\circ}\)C for the different exposition times of 0,5, 1, 2, 3, 4, 5 and 6 hours. Best results were obtained when treating the bentonite to 200\(^{\circ}\)C for one hour [31, 32]. Boukerroui et al., proved that under these conditions of physicochemical treatment of bentonite improves its adsorption capacity to remove copper from aqueous solutions, for about 30 %, or adsorption capacity increased from 0, 12 mmol/g for the natural bentonite to 0,18 mmol/g for activated bentonite [32]. Ahmed with his colleagues examined the adsorption ability of natural and modified bentonite from Iraq, to remove the Cr\(^{3+}\) ions from wastewater [33]. Modification of bentonite was carried out in three ways: 1) the thermal activation at different temperatures (100\(^{\circ}\)C, 200\(^{\circ}\)C, 300\(^{\circ}\)C, 400\(^{\circ}\)C, 500\(^{\circ}\)C and 700\(^{\circ}\)C) for 3 hours, 2) activated with acid solutions of H\(_2\)SO\(_4\) with different concentrations (0.5; 0.75, 1, 1.5, 1.75 and 2M) on a magnetic stirrer for 3 hours and 3) the combined acid-thermal activation by application of H\(_2\)SO\(_4\) solution with a predetermined optimal concentration (1.5M) and then heated in an oven at the obtained optimal temperature (200\(^{\circ}\)C). BET analysis showed that greatest specific surface of 109,85 m\(^2\)/g has a thermal acid-activated bentonite, compared with the specific surface of natural bentonite, acid activated and thermally treated that are 22,43 m\(^2\)/g, 32,68 m\(^2\)/g and 27,61 m\(^2\)/g, respectively. The effect on the amount of material used for adsorption was also examined. Maximal adsorption efficiency of 99.83 % was received using the 25 mg of acid- thermal treated bentonite at pH 7, mixed with 50 ml of chromium ions solution, with initial Cr\(^{3+}\) concentration of 100 mg/l.

**Zeolites**

Zeolites are microporous aluminosilicate minerals with different cavity structures consisting of a three dimensional framework and a negatively charged lattice. The negative charge is balanced by cations like Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\) and others that can be easily exchanged by other cations that are present in the solutions. High ion-exchange capacity, high specific surface areas and their relatively low cost, make zeolites attractive adsorbents for the removal of heavy metal ions from aqueous systems. Ghasemi et al. studied adsorption characteristics of a natural zeolite of clinoptiolite type using single, binary and ternary metal solutions with different initial concentrations of the Pb, Cd and Zn ions [34]. Experimental data for the three metals showed a highly significant fit with Freundlich and Lesser Langmuir adsorption isotherms. It was determined that analyzed zeolite has the biggest adsorption capacity and bonding strength for ion of lead, then zinc and smallest capacity for cadmium ion. The similar results gave Sabry and his associates, who also studied the adsorption ability of natural zeolite – clinoptilolite [35]. The zeolite adsorbed 32 %, 75 %, 28 %, 99 % and 59 % of the heavy metal ions Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II), respectively. According to the percentage of adsorption, the zeolite selectivity for the tested metals decreased in the order Pb > Cu > Zn > Cd > Ni. The effect of the removal of heavy metals of Ni (II) and Cr (VI) from aqueous solutions using the natural zeolite under the various operating parameters such as the initial concentration of heavy metals, the amount of adsorbent and the pH value is described in the article of Salunkhe and Raut [36]. In addition, they showed that the degree of adsorption for both Ni(II) and Cr(VI) ions increases with increasing of the amount of adsorbent (zeolite) as well as by increasing the pH of the solutions, and decreases with an increase in the initial concentration of metal ions. The zeolite showed better results for the adsorption of Cr(VI) ions. Silvio and Jorge in their work, made the comparation of the adsorption power of natural zeolite from Chile and activated zeolite [37]. Modification of zeolite was performed treating natural zeolite with NaCl, NaOH, Na\(_2\)CO\(_3\) and NH\(_4\)Cl. The results showed that activation of the zeolite leads to increasing its adsorption efficiency of 0,26 meq Mn\(^{2+}\)/g of natural zeolite to 0,67 meq Mn\(^{2+}\)/g upon activation with NH\(_4\)Cl, 0,72 meq Mn\(^{2+}\)/g with Na\(_2\)CO\(_3\), 0,76 meq Mn\(^{2+}\)/g with NaOH activation and to the highest 0,77 meq Mn\(^{2+}\)/g when the zeolite is activated by NaCl.

**Activated carbon**

Activated carbon is widely used in the treatment of water and wastewater purification as adsorbent for inorganic and organic contaminants. Because of the
large volumes of micropores and mesopores, leading to large specific surface area, activated carbon is often used to remove ions of heavy metals. Active carbon can be obtained from easily available materials, like coal, wood, coconut shells and a number of other agricultural wastes.

Using a series of adsorption processes, Kouakou et al., studied the application of the commercial activated carbon in terms of its ability to remove ions of zinc and iron from model solutions and from industrial wastewater [38]. It was determined that for the adsorption of zinc and iron on activated carbon can be applied Langmuir’s model and found that the degree of removal of these metals is about 70%. Bernard et al. demonstrated that activated carbon derived from orange peel and activated carbon derived from coconut husks can be applied as good adsorbents for purification of wastewater from the Pb(II), Fe(II), Cu(II) and Zn(II) ions [39, 40]. While Kongsuwan and collaborators, showed that activated carbon derived from the bark of eucalyptus has the necessary properties for copper and lead removal [41]. The active carbon obtained from oil industry wastes, proved to be a good adsorbent for Cd(II) and Ni(II) ions elimination from wastewater. Hema and Srinivasan, using the Langmuir isotherm to calculate the adsorption capacities of the activated carbon obtained the values: 54.95 mg/g for Ni(II) and 23.70 mg/g for Cd(II) ions at optimum pH 7 and 30°C [42]. There are many studies who show that to improve the adsorption and price reduction, as effective adsorbents of heavy metals can be used composites of activated carbon [43, 44].

**Metal oxides**

The main metal oxides used as adsorbent for heavy metals, are: Mn-oxide, Fe-oxide, TiO$_2$, γ-Al$_2$O$_3$, O’Reilly and Hochella determined and compared the Pb(II) adsorption on a number of natural and synthetic Mn and Fe-oxides [45]. Debnath et al., applied nanostructured hydrous titanium oxide to adsorb Ni(II) ions from natural and industrial wastewater [46]. Nano and Stathmann used colloidal TiO$_2$, γ-AlOOH and γ-Al$_2$O$_3$ as hydrated oxides to investigate Fe(II) ions adsorption to iron-free mineral surfaces, and found that iron-free soil minerals can exert a significant influence on Fe(II) sorption and speciation in heterogeneous aquatic systems [47]. Ming et al. made review research focusing on the preparation of metal oxide in nano sizes as iron oxide, manganese oxide, aluminum oxide, titanium oxide, magnesium oxide and cerium oxide, their physicochemical properties, adsorption features and mechanisms and their application in the removal of ions of heavy metals [48].

**Nanosorbents**

Besides the above mentioned conventional materials used as adsorbents for removing heavy metals from aqueous systems, in recent years, nanomaterials have found wide application for wastewater treatment, in particular those materials based on carbon, such as carbon nanotubes, and graphene. To be applicable as adsorbents for removing the ions of heavy metals from wastewater, nanomaterials should satisfy the following criteria: 1) should not be toxic; 2) should have a relatively high adsorption capacity and selectivity at low concentrations of pollutants; 3) the adsorbed pollutants need to be easily removed from the surface of the nanosorbents; 4) adsorbents should be recyclable continuously [49]. Up to now, for the removal of heavy metal ions from aqueous systems, various nanomaterials as, carbon nanotubes, composite materials based on carbon, graphene, nanometals or metal oxides, polymeric sorbents, were studied, and it was found that these materials have a high adsorption capacity. In the last decades, carbon-based nanomaterials, due to their non-toxicity and high adsorption capacity, are widely used to remove heavy metals from wastewater [50]. Development of nanotechnology, enables synthesis of carbon nanotubes and graphene, and their application as nanosorbents for heavy metals elimination. This review particularly highlighted the application of graphene in its modifications as adsorbents for heavy metals removal.

**Carbon nanotubes**

Carbon nanotubes (CNTs), discovered by Iijima, have been widely studied, because of their excellent properties and application possibilities [51]. As a relatively new adsorbents, due to the unique structural, electronic, semiconductor, mechanical, chemical and physical properties CNTs are widely utilized for heavy metals removing in wastewater treatment. Carbon nanotubes are divided into two groups, namely, single walled carbon nanotubes (SWCNTs) and multi walled carbon nanotubes (MWCNTs).

Krystyna and Michal gave the advantages and limitations of heavy metals adsorption on activated carbon, carbon nanotubes and carbon-encapsulated magnetic
The adsorption investigations were based upon adsorption of Co²⁺ and Cu²⁺ ions. The results showed that carbon nanomaterials have a significantly greater adsorption efficiency for both metal ions, compared to activated carbon.

To improve the adsorption capacity, carbon nanotubes are modified by: oxidation, combining with other metal ions or metal oxides, and merger with organic compounds [53 - 56]. The adsorption capacities of untreated CNTs for metal ions, are relatively small, but are significantly increased after oxidation with HNO₃, H₂O₂ and KMnO₄. Li et al., carried out the oxidation of CNTs with HNO₃, H₂O₂, and KMnO₄ and received increased adsorption capacities for adsorption of Cd (II) ions, compared to adsorption capacity of the untreated carbon nanotubes which was 1.1 mg/g [57]. After oxidation, adsorption capacities were 2.6, 5.1 and 11.0 mg/g for CNTs oxidized by H₂O₂, HNO₃ and KMnO₄, respectively. Similarly, Akbar and Parviz committed acid activation of multi walled carbon nanotubes with HNO₃, H₂O₂ and KMnO₄, and examined their adsorption characteristics for lead and copper ions removal from aqueous solutions [58]. The results showed that adsorption capacities of oxidized MWCNTs are significantly improved. It stems from the proliferation of the number of functional groups containing oxygen, -COOH, -OH or -C = O, on the surface of the CNTs, which can react with Pb²⁺ and Cu²⁺ and to form a salts or complexes. Di et al., in their papers showed that the oxidized carbon nanotubes have high adsorption capacities and high efficiency in the removal of Pb(II), Cd(II) and Cr(VI) ions from water [59]. Rao et al. made review of several publications that have studied the removal of divalent metal ions (Cd²⁺, Cu²⁺, Ni²⁺, Pb²⁺, Zn²⁺) from aqueous solutions, using different types of carbon nanotubes [60]. The influence of various factors over the adsorption efficiency was examined: pH of the solution, initial concentration of the metal ions, amount of adsorbent, contact time. It was concluded that the sorption capacities of metal ions to different CNTs, follow roughly the order: Pb²⁺ > Ni²⁺ > Zn²⁺ > Cu²⁺ > Cd²⁺, and that process parameters such as surface total acidity, pH and temperature, play a key role in determining sorption rate of metal ion onto CNTs. Anna and Krystyna employed the carbon nanotubes as adsorbents to remove divalent metal ions of Cu, Co, Zn, Mn and Pb [61]. For the adsorption processes were used three types of CNTs: untreated carbon nanotubes, CNTs soaked in HNO₃ for 12 hours at room temperature, and the CNTs refluxed with HNO₃ at 400K for 2 hours. At pH of the solution 9, the affinity of CNTs to the metal ions is as follows: Cu(II) > Pb(II) > Co(II) > Zn(II) > Mn(II). The article of Yan et al., have given good results and showed that MWCNTs treated with nitric acid, successfully remove metal ions from multi-component system [62]. Maximal adsorption capacities, calculated by applying the equation of Langmuir for adsorption isotherms for the individual ions were 97.08 mg/g for Pb²⁺, 24.49 mg/g for Cu²⁺ and 10.86 mg/g for Cd²⁺. Adsorption trials about the competitive, multi-component system, showed that the affinity of MWCNTs towards the three metal ions decreases in the following order: Pb²⁺ > Cu²⁺ > Cd²⁺. Adsorption characteristics of the oxidized multiwalled carbon nanotubes in the adsorption of Pb(II) ions from aqueous systems were investigated as a function of the contact time, the pH of the solution, ionic strength, presence of other ions and the amount of adsorbent [63]. The results indicate that adsorption of Pb(II) ions on the oxidized MWCNTs is highly dependent on pH, and does not depend on ionic strength and type of present ions. Oxidized multiwalled carbon nanotubes were also applied for the adsorption of Ni(II) ions from aqueous solutions. The results of Chen and Wang showed that pH of the solution and the amount of used adsorbent (oxidized MWCNTs) have great influence on the adsorption of Ni(II) and the ionic strength affects lesser [64]. Adsorption equilibrium was reached in 40 minutes.

Graphene

Graphene is another type of carbon nanomaterial which is applied as adsorbent for removing heavy metals from aqueous systems. Graphene consists of one or several atomic layers of graphite. It is two-dimensional carbon allotrope and attracts great research interest because of its unique structure and physicochemical properties. Many studies on nanomaterials based on graphene, including modified graphene, oxidized graphene, graphene/semiconductor hybrids, composites graphene/metal nanoparticles and others, are performed. All these nanomaterials inherit the unique properties of graphene with an increasing number of functional groups or composite nanoparticles on their surfaces that improve their performance. Graphene has great theoretical specific surface area and graphene oxide
(GO) has functional groups and hence their potential for application in adsorption processes. In recent years, many studies have been focused on the application of graphene and its composites in the removing of pollutants from air and water. Modification of graphene and graphene oxide with metal oxides or organic compounds, will create different nanocomposite materials with improved adsorption capacity and efficiency of the separation of pollutants from the polluted environment, including ions of heavy metals as one of the most dangerous pollutants in water systems.

Sitko et al. examined adsorption properties of graphene oxide (GO) to divalent metal ions of copper, zinc, cadmium and lead [65]. Characterization of graphene oxide, obtained by the oxidation of graphite with potassium dichromate, was performed with the following techniques: SEM, XRD, SPS and FT-IR. Maximal adsorption capacity of Cu (II), Zn (II), Cd (II) and Pb (II) ions on the GO at pH 5 are 294 mg/g, 345 mg/g, 530 mg/g, 1119 mg/g, respectively. Experiments have shown that the affinity of the graphene oxide to metal ions, follows the order: Pb(II) > Cu(II) > Cd(II) > Zn(II). Few-layered graphene oxide nanosheets were synthesized and their ability of removing various metal ions: Cd$^{2+}$ and Co$^{2+}$ [66], Pb$^{2+}$ [67] and U(VI) [68], from aqueous solutions, was tested. They found that functional groups containing oxygen, on the surface of oxidized graphene (GO), play an important role in sorption of metal ions. Adsorption of Cd$^{2+}$ and Co$^{2+}$ ions was strongly depended on the pH of the solution and less depended of ionic strength. At pH 6 and 30°C, the maximal adsorption capacities of graphene oxide for Cd$^{2+}$ and Co$^{2+}$ are 106.3 mg/g and 68.2 mg/g, respectively. For ions of lead, maximum adsorption capacities at different temperatures 20°C, 40°C and 60°C, are 842 mg/g, 1150 mg/g and 1850 mg/g, respectively, while adsorption capacity for U (VI) ions at pH 5 and 20°C has a value of 97.5 mg/g. Yang et al., investigated the interaction of Cu$^{2+}$ with the graphene oxide in the aqueous solutions and found that Cu$^{2+}$ ions cause the GO layers to form large aggregates [69]. Graphene oxide adsorption capacity for Cu$^{2+}$ ions is 46.6 mg/g and is higher than adsorption capacities of carbon nanotubes (MWCNTs) and of the activated carbon having the values 28,5 mg/g and 4 - 5 mg/g, respectively. Ren and his collaborators, came to the same conclusion, comparing adsorption capacities of the three carbon materials (graphene oxide, multiwalled carbon nanotubes and activated carbon) during adsorption of Cu (II) ions [70]. The removal of cadmium ions from solutions by applying graphene, exfoliated carbon and multiwalled carbon nanotubes, was investigated by Dana et al. [71]. They have focused their analysis on the effects of adsorption at five different times of contact 1, 3, 6, 12 and 24 hours. After interaction of one hour, it was determined that 99 % of the cadmium ions were adsorbed by graphene. The effect of adsorption of carbon nanotubes was lower and after 1 hour was 30 % and after 24 hours of contact the adsorption of 50 % was achieved. The least effect on the removal of Cd(II) ions showed expanded carbon, 10 % after 24 hours interaction. The same authors, in another paper, performed comparative studies about the adsorption efficiency of four types of adsorbents: reduced graphene oxide (RGO), expanded carbon, multiwalled carbon nanotubes and magnetic particles of iron (Fe$_3$O$_4$), for Pb(II), Cd(II) and Cu(II) adsorption [72]. All adsorption trials were performed at pH 7, and the contact time of 1 min to 24 hours. After 24 hours of interaction best results showed reduced graphene oxide and Fe$_3$O$_4$ with total (100 %) elimination of Pb(II) and Cd(II) ions, and 98 % removal of Cu(II) ions. MWCNTs and expanded carbon had less efficacy in removing the metal ions: MWCNTs - 80 %, 70 % and 98 %, and expanded carbon - 78 %, 56 % and 84 % for Pb(II), Cd(II) and Cu(II), respectively. Hou et al., synthesized graphene oxide using the modified Hummer’s method and then characterized the material by SEM, AFM, XRD and FT-IR [73]. The adsorption of Zn(II) ions on the graphene oxide, was investigated, as a function of pH, the quantity of adsorbent, contact time and temperature. The results showed that the suitable pH for adsorption of Zn(II) is about 7, and the optimum amount of graphene oxide 2 mg. Maximum adsorption capacity, determined by the Langmuir’s isotherm model, was 246 mg/g, at 20°C. Ping et al., prepared membranes from the graphene oxide with a large space between the layers, and used them as adsorbents to remove Cu$^{2+}$, Cd$^{2+}$ and Ni$^{2+}$ ions from aqueous solutions [74]. The effects of pH, ionic strength, time of contact and the concentration of metal ions, were investigated. The results showed that the adsorption of tested metals on the graphene oxide membranes largely depends on the pH and weakly of the ionic strength. Adsorption equilibrium was achieved in a short time, and adsorption isotherms fit well with Langmuir’s model. Maximal adsorption capacities for Cu$^{2+}$, Cd$^{2+}$ and Ni$^{2+}$ ions have values 72,6
mg/g; 83,8 mg/g and 62,3 mg/g, respectively. Based on the examination performed on the adsorption/desorption cycles, it was determined that membranes of graphene oxide can be regenerated more than six times, with minor losses of adsorption capacity. In the article of Zhuhong et al., a fixed-bed sand column with graphene oxide layer was used to remove heavy metals Pb(II) and Cu(II) from an aqueous solution injected under steady flow [75]. By increasing the injection flow of the solution from 1 to 5 ml/min, the removal efficiency decreased from 15,3 % to 10,3 % for copper and from 26,7 % to 19,0 % for lead ions. Provided the fixed concentration of the heavy metal ions in the injected flow, increasing the amount of graphene oxide in the column from 10 to 30 mg, resulted in a sharp increase in the removal efficiency, especially for Pb (II) ions, from 26,7 % to 40,5 %. Considering that small amount of graphene oxide is required to enable the sand columns to improve their filtration capacity and adsorption rate, the authors suggested graphene oxide to be applied as an effective adsorption medium in filters and reactive barriers to enhance filtration of heavy metals from flow-through aqueous solutions.

Modification of graphene oxide with organic compounds can change the surface functional groups, which will allow improved adsorption of different types of metals. Gao et al. modified graphene oxide with thiol groups and the amount of Hg²⁺ ions adsorbed on its surface, was six times bigger, compared with graphene oxide and activated carbon [76]. Madadrang et al. used EDTA-silane for modification of the graphene oxide and received EDTA-GO to which they found is an ideal adsorbent for Pb(II) ions removal [77]. The adsorption capacity of EDTA-GO is 479 mg/g at pH 6,8 and 25°C and under the same working conditions, adsorption capacity of GO was 367 mg/g. Similar functionalization of graphene oxide with EDTA was performed for more efficient adsorption of the Pb²⁺ and Cu²⁺ ions, and to improve the microbial properties compared with the GO [78]. The adsorption of heavy metals was investigated under various concentrations, pH and contact times. The maximum adsorption capacities of GO-EDTA was obtained and are 454,6 mg/g and 108,7 mg/g of Pb²⁺ and Cu²⁺, respectively, and these values exceed the capacities of conventional adsorbents as activated carbon. To remove toxic mercury ions from aqueous solutions, Rahmatollah and his associates, used graphene oxide-porphyrin nanocomposites as an adsorbent [79]. Characterization of synthesized nanocomposites was performed using FESEM, UV-Vis and FT-IR techniques. According to the results, the graphene oxide-porphyrin composite show more effective adsorption of Hg(II) ions, compared to the graphene oxide. It was determined that the composite with a solution of EDTA, can quickly regenerate and has a long service life. The main objective of the study of Najafi et al., was to compare and explain adsorption of Zn(II) ions by the graphene oxide and functionalized graphene oxide-glycine [80]. Amino groups of glycine were added to the surface of the graphene oxide. The results showed that by increasing the initial concentration of zinc ions adsorption capacity increases too. Adsorption equilibrium was attained after 50 minutes. Adsorption processes of Zn(II) removal by graphene oxide and graphene oxide-glycine were performed at a fixed temperature of 298K and pH 6. By applying Langmuir’s adsorption isotherm with initial Zn(II) ions concentration of 15mg/l, the following adsorption capacities of GO and GO-glycine were received: 88,12 mg/g and 95,41 mg/g, respectively. Polyvinylpyrrolidone-reduced graphene oxide (PVP-RGO) was prepared by applying the modified Hummer’s method on the natural graphite [81]. SEM and FT-IR techniques were used for the characterization of the resultant material which was used as adsorbent for Cu(II) ions removal from wastewater. The influences of the contact time and concentration of metal ions, on the effect of adsorption, were examined. Maximal adsorption capacity of 1689 mg/g was reached for 10 min. at pH of the solution 3,5. These results led to the conclusion that the PVP-RGO has a very high adsorption capacity for ions of copper, and it is 10 times higher than the maximum values that had been previously presented. Minghan et al., by the reduction of graphene oxide with acetylatedone, synthesized soluble functional graphene with improved properties for heavy metals adsorption [82]. The morphology of the resulting graphene was analyzed by SEM, TEM and AFM techniques, structural changes were characterized by Raman spectrum, functional groups were analyzed by FT-IR and UV-vis, and the thermal stability of graphene has been studied by TGA. The high surface area of graphene, allowed maximum adsorption capacity for Cd2+ ions of 49,28 mg/g, which is 4,5 times higher than that of carbon nanotubes, and adsorption capacity for elimination of Co²⁺ ions 27,78 mg/g.

Graphene and graphene oxide, can also be incor-
porated with a metals or metal oxides. The obtained composites usually have specific characteristics and are widely used as effective adsorbents for the elimination of various pollutants. Lee and Yang, using the hydrothermal procedure, have synthesized graphene oxide - TiO\textsubscript{2} hybrid, that was applied for the removal of heavy metal ions of zinc, cadmium and lead from water [83]. Adsorption capacities of GO-TiO\textsubscript{2} hybrid, after 6h and 12 h of hydrothermal treatment at 100°C and at pH 5,6 were, respectively, 44,8 mg/g and 88,9 mg/g of Zn\textsuperscript{2+}, 65,1 mg/g and 72,8 mg/g of Cd\textsuperscript{2+} and 45,0 mg/g and 65,5 mg/g of Pb\textsuperscript{2+}. For comparison, under the same operating conditions, graphene oxide had the following adsorption capacities: 30,1 mg/g; 14,9 mg/g and 35,6 mg/g for Zn\textsuperscript{2+}, Cd\textsuperscript{2+} and Pb\textsuperscript{2+} ions, respectively. In their paper, Sreeprased et al. described various simple preparation procedures of composites of reduced graphene oxide-metal/metal oxide [84]. RGO-MnO\textsubscript{2} and RGO-Ag composites were considered as adsorbents for removal of Hg(II) ions and showed excellent adsorption capacity and improved capabilities for elimination of metal ions compared to basic materials. Ren et al., synthesized graphene/δ-MnO\textsubscript{2} composite for removing of nickel ions [85]. Adsorption capacity of G/MnO\textsubscript{2} for Ni\textsuperscript{2+} was 46,6 mg/g at room temperature. It was confirmed that this adsorption capacity is 1,5 times higher of capacity of pure δ-MnO\textsubscript{2} and 15 times higher than that of pure graphene. It was determined that G/MnO\textsubscript{2} composite can be reused five times with a high degree of recovery of 91 %. Sangit et al. have performed a similar experiment, examining the G/δ-MnO\textsubscript{2} nanocomposite as adsorbent for the removal of Ni\textsuperscript{2+} ions [86]. They realized that the adsorption sharply rises in the first 60 minutes of contact, and that after 120 minutes there is almost no change in the degree of adsorption. Based on these results, they concluded that the contact time of three hours is sufficient to achieve adsorption equilibrium. Like previous authors and these confirmed that adsorption capacity of nanocomposites for Ni\textsuperscript{2+} ions removal, is higher 1,5 and 15 times, compared to the capacities of the basic materials.

We have studied graphene obtained by the method of electrolysis in molten salts, produced in our lab [87]. Characteristic morphology is shown in Fig. 4, [88]. Dependence of the concentration from time of adsorption, at initial Ni(II) ions concentration of 0.5 mg/l, for investigated graphene is given on Fig. 5. It can be seen that the adsorption equilibrium for was achieved after 50 min of adsorption. Percentage of removal was evaluated and is 33,3 %.

In the recent years, magnetic adsorbents attract great interest for their application in the treatments of water purification. The incorporation of magnetic particles in graphene and graphene oxide should provide effective approach to overcome the problems of separation associated with graphene. At the same time, the magnetic nanoparticles will reduce the possibility of agglomeration and rearrangement of layers of graphene and as a result, will provide greater available surface and improve the adsorption capacity.

Liu et al. used magnetic Fe\textsubscript{3}O\textsubscript{4}/GO composite for removal of Co\textsuperscript{2+} ions and examined adsorption kinetics, equilibrium and thermodynamics [89]. The resulting value of the composite’s adsorption capacity is 12,98 mg/g and is higher than the value of pure Fe\textsubscript{3}O\textsubscript{4} which is 6,2 mg/g. Fe\textsubscript{3}O\textsubscript{4}/GO composites have found wide application in the removal of Cr(VI) ions and U(VI) ions [90, 91]. The adsorption capacity of U(VI) ions was found to be 69,49 mg/g and has a higher value than the capacities of most studied materials and nanomaterials. Jin et al. performed comparative adsorption of Cu(II), Pb(II) and Cd(II) ions, on the magnetic graphene oxide (MGO), the multiwalled carbon nanotubes (MWCNTs) and activated carbon (AC) [92]. The values of the maximal adsorption

Fig. 4. SEM microphotograph of graphene.
capacities of utilized adsorbents were calculated using the equation of Langmuir and follows as: Pb(II) > Cu(II) > Cd(II). The adsorption for each metal was lower when working with multi-component system compared to single-metal systems. The adsorption properties of the used adsorbents follow the order: MGO > MWCNTs > AC. Adsorption capacities of MGO, MWCNTs and AC, for Pb(II) ions at pH 7 are: 81.49; 59.08 and 35.15 mg/g, respectively. To improve the properties, Zhang et al., synthesized nanocomposite polycrylic acid/graphene oxide/Fe₃O₄ (PAA)/GO/Fe₃O₄ [93]. Because of its excellent properties, this nanocomposite showed extremely good adsorption ability to remove Cu(II), Cd(II) and Pb(II) ions, with a removal efficiency of 85% even after five cycles of use.

CONCLUSIONS

Adsorption, as an effective, efficient and economic method, is the most widely used technique for removal and reduction of heavy metal ions from large volumes of aqueous solutions. A fundamentally important characteristics of a good adsorbent are: high porosity and consequent larger surface area with more specific adsorption sites, high ion exchange capacity, low cost and occurring in the nature at large quantities. Some of the materials, such as, clay minerals (bentonte), zeolites, activated carbon and metal oxides, which satisfy these requirements are widely used as conventional adsorbents in the removal of heavy metals from wastewater.

Besides this materials, the development of nanoscience and nanotechnology enabled nanomaterials, as graphene and carbon nanotubes, to be widely used for the remediation of environmental problems. Nanomaterials have a number of physicochemical properties that make them particularly attractive for wastewater purification. Recent researchers have indicated that nanomaterials as sorbents are useful tools for heavy metal removal, due to their unique structure and surface characteristics. In the future, graphene and carbon nanotubes can be produced in large scale, using appropriate methods to reduce their cost and thereby increase their application as adsorbents to protect the environment.

Compared with conventional materials, nanostructure adsorbents have exhibit much higher efficiency and faster rates in water treatment.

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