Adsorption of Heavy Metals (Hexavalent Chromium, Lead, Manganese and Cadmium) on Multiwall Carbon Nanotubes

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Abstract
Nanotechnology holds great potential in the sector of water/wastewater treatment since it is considered as an advanced technology for improving water quality. Carbon nanotubes is a carbonaceous material that shows exceptional adsorption capacity for the removal of heavy metals due to their novel properties. Thus their application for the treatment of industrial wastewater or contaminated groundwater exhibits high interest. In this study the efficiency of multiwall carbon nanotubes as adsorbent for hexavalent chromium, manganese, lead and cadmium removal as a function of pH and the initial concentration of heavy metal is investigated. In addition, the occurrence of any competitive effects amongst the aforementioned metals during adsorption is investigated. For this reason batch experiments are performed keeping constant the concentration of multiwall carbon nanotubes (2 g/L) and the contact time (5 h).
Keywords: multi wall carbon nanotubes, adsorption, hexavalent chromium, manganese, lead, cadmium

1. Introduction

The growth of world population and climate change are two important parameters that increase demand for fresh water. Only the 2.5% of total global water is considered to be fresh, 0.5% comes from lakes and rivers, 31% comes from groundwater whereas the rest of it consists part of glaciers as well as ice caps. Due to the fact that glaciers melt away in ocean environments, a great portion of water tends out to be saline, thus groundwater accounts for 98% of the global fresh water reserves. It is a well-known fact that groundwater is contaminated with heavy metals, such as hexavalent chromium(Cr(VI)), cadmium (Cd), lead (Pb), manganese (Mn) which are hazardous for human beings and need to be removed, in order to avoid serious health problems that can be caused. In recent years several methods have been applied for the removal of Cr(VI), Pb(II), Cd(II), Mn(II), with the adsorption technique to have many advantages such as operation simplicity, low cost, high removal efficiency, as well as the potential regeneration of the adsorbent (Borna et al., 2016). The use of nanomaterials as adsorbents results in even higher performance of the process, due to their fast kinetics, high reactivity and large specific area (Zhang et al., 2016). Carbon nanotubes (CNTs) exhibit high specific surface area and are characterized by highly tailored adsorption sites thus acting as adsorbents for heavy metals, polar and non- polar organic compounds and oils (Vilardi et al., 2018).

2. Materials

2.1. Materials

The multi wall carbon nanotubes (MWCNTs) used in the present study were provided by Glonatech S.A. (Greece). They are produced by chemical vapor deposition method (CVD) (Mpouras et al., 2018). Batch experiments were performed to investigate MWCNTs adsorption behavior towards Cr(VI), Pb(II), Cd(II) and Mn(II).Two series of batch experiments were performed in order to invsestigate a) the effect of pH on metals adsorption and b) the effect of Cr(VI) initial concentration on its adsorption for two different pH values. In both series the adsorbent concentration was kept constant at 2 g/L and the samples were kept at room temperature (23^{o}C). pH adjustment was achieved by using HCl and NaCl solutions of 0,01 M. The MWCNTs aqueous solutions were placed in an orbital shaker at 150 rpm and after equilibrium they were filtered through a 0.45μm pore membrane filter. Cr(VI) was measured applying the 7196A EPA (diphenyl-carbazide)method. The determination of Pb(II), Cd(II) and Mn(II) in the aqueous solutions was performed by ICP-MS.

3. Results

3.1 Effect of pH on heavy metals adsorption

Figure 1 presents the adsorption efficiency of MWCNTs for the tested heavy metals in the pH range 5 to 8. Adsorption of Cr(VI) was maximized at pH 5 and was equal to 88 mg/Kg. On the contrary adsorption of metal cations was maximized at pH 8 and was equal to 48 mg/kg for the three tested cations. In general adsorption efficiency was increased with increasing pH in the case of metal cations while was decreased in the case of Cr(VI). The adsorption of the tested metal ions on MWCNTs is generally attributed to electrostatic forces between metal ions and the MWCNTs surface. These forces are created due to the presence of functional groups such as –OH and –COOH which exist on the MWCNTs surface. For pH values higher than the point of zero charge (PZC) these groups are de-protonated causing attraction of the metal cations enhancing thus adsorption efficiency to the solid surface. On the contrary, in the case of Cr(VI) which is presented as an anion (chromates) adsorption efficiency is enhanced at pH values below the PZC point at which the MWCNTs surface is protonated. In addition, especially for Cr(VI), at high pH values possible reduction phenomena of chromates by the functional groups have been reported (Hu et al., 2009; Qureshi et al., 2017; Di et al., 2004).

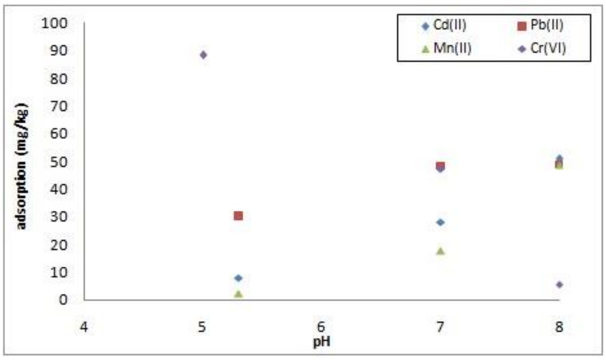

Figure 1. Effect of pH on Cr(VI), Pb(II), Cd(II), Mn(II) adsorption (initial concentration of metals = 100 ppb, equilibrium time = 5 h)

3.2 Effect of Cr(VI) initial concentration on adsorption

The effect of Cr(VI) initial concentration (100 to 5000 ppb) on its adsorption was investigated for two different pH values, 6 and 7 (Figure 2). The results showed that for pH equal to 6, the adsorption efficiency increased with increasing the Cr(VI) initial concentration up to 4500 ppb where the adsorption of Cr(VI) was maximized (1,165 mg/kg). In the case of pH equal to 7, the adsorption efficiency was significantly decreased compared to pH equal to 6. In addition, adsorption was maximized (305 mg/kg) for Cr(VI) concentration equal to 1,400 ppb. This phenomenon, is attributed to the saturation of the adsorption sites with increasing the Cr(VI) initial concentration.

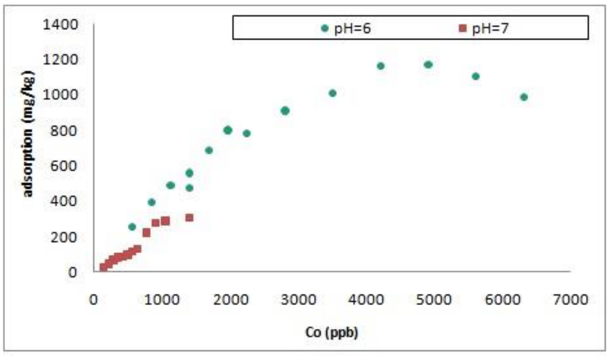

Figure 2. Effect of Cr(VI) initial concentration on Cr(VI) adsorption (equilibrium time = 24 h)

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