



REVIEW

Technologies for the 21st century: carbon nanotubes as adsorbents of metals

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Submitted: 02 April 2014; Accepted: 14 May 2014; Available on line: 21 August 2014

ABSTRACT: Nowadays and in the recent past when the word “nano” appeared in almost anything it attracted immediate attention and interest, this is why carbon nanotubes, since its discovery nearly twenty years ago, caught the interest of a wide scientific and industrial population to apply the somewhat amazing properties of these nanomaterials in a number of applications. Among them, the removal of toxic and sometimes profitable metals from aqueous streams appeared, due to its economical and social impact, as one of the targets for their uses. This paper reviews some recent advances (2009–2013 years) in the application of carbon nanotubes materials in the removal of a variety of metals from these aqueous streams.

KEYWORDS: Adsorption; Carbon nanotubes; Environment; Metals

Citation / Cómo citar este artículo: Alguacil, F.J., Cerpa, A., Lado, I., López, F.A. (2014) “Technologies for the 21st century: carbon nanotubes as adsorbents of metals”. *Rev. Metal.* 50(3): e025. doi: <http://dx.doi.org/10.3989/revmetalm.025>.

RESUMEN: *Tecnologías para el siglo XXI: los nanotubos de carbono como adsorbentes de metales.* Tanto en el pasado como hoy en día, cuando la palabra “nano” aparece en cualquier sitio inmediatamente suscita atención e interés; por eso y desde su descubrimiento hace cerca de veinte años, los nanotubos de carbono interesaron tanto a científicos como a industriales, que utilizaron las propiedades de estos nanomateriales en una serie de aplicaciones. Entre éstas, se incluye la eliminación de metales tóxicos, y otros con un cierto valor económico, de medios acuosos, problemática que además tiene unas implicaciones económicas y sociales importantes. Este trabajo revisa los avances más recientes (años 2009–2013) de la utilización de estos nanotubos de carbono en la eliminación de una serie de metales contenidos en distintos medios acuosos.

PALABRAS CLAVE: Adsorción; Medioambiente; Metales; Nanotubos de carbono

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1. INTRODUCTION

Metals are essential for life and also they are of multiple practical uses, thus, there are many industries in relationship with these metallic elements

with the potential hazard of their discharge to the environment. It is assumed that the free discharge of metals to the environment, through different effluents, is become more and more prohibited since under given environments and concentrations, these

essential elements change their beneficial properties to hazardous and non-tolerable for living organisms.

Thus, practical, and sometimes not as clear, approaches for the removal of such metals from effluents and their safe disposal and even recycle are of interest either for the industry, the academia and the scientists.

In the case of liquid effluents, and due to the nature of many of these metal-bearing streams: diluted, multi-elemental, valuable and non-valuable elements, etc., some kind of technologies must be used for the correct treatment of such effluents, some of them adapted from well known hydrometallurgical operations, i.e. liquid-liquid extraction, ion exchange resins and carbon adsorption, and other specially developed for the treatment of these liquids, i.e. liquid membranes, adsorption/ion exchange from heterogeneous materials such as biomass, scraps, etc., (de Agreda *et al.*, 2011; Regel-Rosocka and Alguacil, 2013; Díaz-Pavon *et al.*, 2014).

One of the newest developments in this field is the use of carbon nanotubes as adsorbents for these metallic elements; this paper reviewing some of the recent results about the uses of these revolutionary adsorbents in this area of interest.

2. SYNTHESIS AND USES OF CARBON NANOTUBES

Essentially these materials are carbon atoms linked to form macromolecules which formed hollow cylinders with diameters ranging from a few to tens of nanometers and lengths up to various millimeters. Regarding to the nanotubes structure, they are divided into single walled nanotubes or multi-walled materials. Figure 1 shows the SEM images of non-functionalized single-walled (a) and multi-walled carbon nanotubes (b). The nanotubes structure consisting the walls of a flat molecular carbon network (otherwise named graphene) with different and somewhat tailored end caps.

Carbon nanotubes can be synthesized by the use of different technologies including laser ablation and chemical vapour deposition, whereas they are available mainly as powders or thin sheets.

With respect to the current uses of these materials, and due to their remarkable properties: good heat conduction across the tube axis, electrical conduction, large surface area, etc., carbon nanotubes are very useful in fuel cells, enhancement of properties of composite materials, nanoelectronics, etc., by no doubt, their large surface area, with typical BET surface area (after Brunauer-Emmet-Tellet) values of their specific surface in excess of $600 \text{ m}^2 \text{ g}^{-1}$, makes them as excellent candidates to their use as adsorbents for metals and organic compounds. These adsorption properties are usually enhanced by functionalizing, normally oxidative treatment, the nanotubes by various techniques.

3. CARBON NANOTUBES AS ADSORBENTS OF METALS

3.1. Rare earths elements

The removal of Eu(III) using a composite of multi-walled carbon nanotube and iron oxide was investigated under various experimental conditions (Chen *et al.*, 2009a), and under the presence or absence of PAA (Polyacrylic Acid). The removal of this rare earth is enhanced by the increase of the aqueous pH but decreased as the initial metal concentration increased in the solution. On the other hand, the adsorption of PPA on the substrate decreased as the pH of the solution increased and is not greatly affected by the presence of Eu(III) in the solution. The presence of the organic compound enhanced the adsorption of Eu(III) at pH values below 4.5, though the system is not adequate for its practical use at pH values above 5 since the formation of soluble Eu(III)-PAA complexes resulted in a decrease of metal adsorption. The Freundlich model responded well for the Eu(III) adsorption either in presence or absence of PAA.

The Freundlich model is represented in its linearized form as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln [M]_e \quad (1)$$

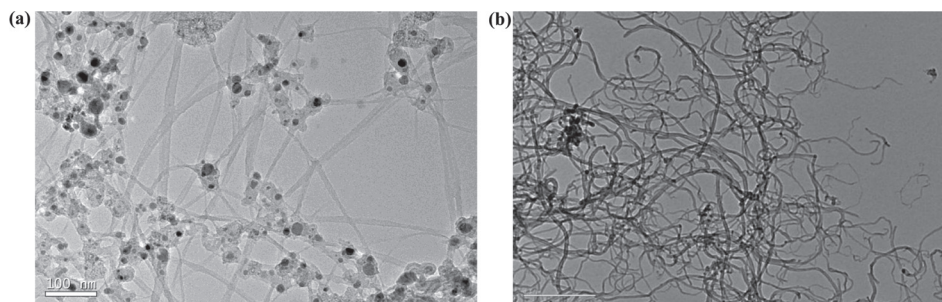


FIGURE 1. SEM images of non-functionalized single-walled (a) and multi-walled carbon nanotubes (b).

where q_e is the equilibrium amount of the metal in the solution per unit weight of the adsorbent (i.e. mg g^{-1}), $[M]_e$ is the equilibrium concentration of the metal in the solution (i.e. mg L^{-1}), K_F is a constant related to the adsorption capacity and n is a constant in relationship with the adsorption intensity.

It was reported the adsorption and desorption of the above element on multi-walled carbon nanotubes (Lu *et al.*, 2011a). In this investigation, several experimental conditions were studied, concluding that the adsorption of europium is strongly dependent on aqueous pH values, dependent on the ionic strength at low pH values but independent of this condition at high pH values. The desorption of Eu(III) from loaded nanotubes can be performed using HCl solutions, and thus, at a low pH values.

A so-called environmental friendly adsorbent was prepared by modifying multi-walled carbon nanotubes with tannic acid (Tong *et al.*, 2011). This material was used in the adsorption of La(III), Tb(III) and Lu(III) under otherwise known experimental conditions. The major adsorption mechanism was attributed to ion exchange and surface complexation, whereas the kinetics of the adsorption follows a pseudo-second order model. The adsorbed elements can be desorbed from the surface with 1 M HCl.

The pseudo-second order model follows the equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_m^2} - \frac{1}{q_m} t \quad (2)$$

where k_2 is the rate constant of adsorption (i.e. g min mol^{-1}), q_t and q_m is the amount of solute adsorbed at time t and the maximum metal load in the adsorbent (i.e. mol g^{-1}) and t is the elapsed time (i.e. min).

It was described (Lu *et al.*, 2011b), that magnetic composites (iron oxide/multi-walled carbon nanotube) might be considered as excellent adsorbents for europium(III), and though the metal adsorption was strongly pH dependent, the large adsorption capacity and the easy magnetic separation method for the composites make these materials excellent candidates for the removal of this element in nuclear waste management.

Nitric acid-oxidized multi-walled carbon nanotubes were used to adsorb cerium(III) and samarium(III) from aqueous solutions (Naderi Behdani *et al.*, 2013). In both cases, the percentage of metal removal increases with the increase of the aqueous pH, being the maximum metal uptake 88.6 and 93.3 mg g^{-1} for Sm(III) and Ce(III), respectively. Thermodynamic parameters indicated that the adsorption process is spontaneous and exothermic at 30–60 °C. As it is expected, the metals desorption

is favoured by the use of acidic solutions, i.e. 70% desorption for each element at pH of 1.55 and 30 °C.

3.2. Transition metals

Functionalized carbon nanotubes were used in the removal of nickel(II), copper(II), zinc(II) and cadmium(II) from single to quaternary solutions (Gao *et al.*, 2009). In all the cases, copper(II) adsorption fitted to Langmuir model, whereas in the case of the other three elements, experimental results reveal the effect of competition for adsorption sites. In single and binary systems, metal uptake is in the Cu(II)>Ni(II)>Cd(II)>Zn(II) order, however in ternary and quaternary systems it changes to Cu(II)>Cd(II)>Zn(II)>Ni(II). This behaviour can be explained in terms of the influence of adsorbent surface features, ion exchange process and electrochemical potential on the metal adsorption mechanism.

The linearized expression of the Langmuir model is represented by:

$$\frac{[M]_e}{q_t} = \frac{1}{q_m K_L} + \frac{[M]_e}{q_m} \quad (3)$$

In the above equation, $[M]_e$ represented the metal equilibrium concentration in the solution (i.e. mg L^{-1}), q_e is the solute equilibrium loading in the adsorbent (i.e. mg g^{-1}), q_m is the maximum metal uptake in the adsorbent (i.e. mg g^{-1}) and K_L is a constant in relation with the energy of adsorption (i.e. L mg^{-1}).

Oxidized multi-walled carbon nanotubes were used in the adsorption of nickel(II) from aqueous medium (Yang *et al.*, 2009). Near quantitative metal removal using these adsorbents can be achieved in 2–9 pH range. The presence of PAA in the aqueous solution on metal removal was also investigated, and in this case, it has also a positive effect at pH values below 8, and negative at higher values.

Copper(II) adsorption onto non-functionalized and oxidised (H_2SO_4 and $\text{H}_2\text{SO}_4/\text{KMnO}_4$) multi-walled carbon nanotubes was investigated under various experimental conditions (Kuo, 2009). As it was somewhat expected, the adsorption of the metal is increased in the functionalized nanotubes with respect to the as-grown materials, and specially at pH values of 6, having the increase of the temperature a positive effect on the metal adsorption for all the materials tested. The results suggested that in the material derived from the $\text{H}_2\text{SO}_4/\text{KMnO}_4$ oxidation, the Cu(II) adsorption proceed simultaneously by physisorption and chemisorption, but in the non-functionalized and materials derived from the sulphuric acid oxidation the metal adsorption responded to a physisorption process.

Multi-walled carbon nanotubes and iron oxide composite was used in the removal of Ni(II) and

Sr(II) from aqueous solutions (Chen *et al.*, 2009b). Results suggested that the metals adsorption depended greatly on the pH of the solution and its ionic strength, being the greater the metal uptake in the composite material if compared with the nanotubes or the iron oxide, separately.

Air-modified carbon nanotubes were used in the removal of phenol and cadmium(II) from synthetic effluent (Díaz-Flores *et al.*, 2009). The individual adsorption capacity for cadmium is 7.9 mg g^{-1} , being the adsorption of the metal favoured when the concentration of phenol increases, though the adsorption uptake of the organic compound was only slightly affected with the metal concentration.

Batch investigation about the adsorption of lead(II) into carbon nanotubes demonstrated that these materials can eliminate this toxic element up to 96% after 80 minutes, at pH of 5 and using an adsorbent dosage of 40 mg L^{-1} . Metal uptake is in the 100 mg g^{-1} order, being the adsorption process well represented by the Langmuir model (Kabbashi *et al.*, 2009).

Microwave/chemical modified carbon nanotubes were used in the separation of cadmium(II) from a given aqueous solution (Kuo, 2009). The microwave treatment process of the nanotubes was supported by the oxidation by sulphuric acid or sulphuric acid/ KMnO_4 of the starting material. Results suggested that the microwave heating reduced the nanotubes oxidation time increasing the area of active adsorption sites of the adsorbent. At a given pH value, the metal uptake of the microwave-sulphuric acid- KMnO_4 carbon nanotube exceeded that of the microwave-sulphuric acid or the non-treated carbon material.

Oxidized multi-walled carbon nanotubes were investigated to remove chromium(VI) from aqueous solutions (Hu *et al.*, 2009). From initial chromium(VI) concentrations of 3 mg L^{-1} , the optimum pH values for metal adsorption were in the < 2 range (more than 80% metal adsorption), having the ionic strength ($I=0.01\text{--}0.1$) no influence in the adsorption yields at a fixed pH value. The results indicated that the pseudo-second-order kinetics model was well suited to model the adsorption of chromium(VI), but this adsorption involves redox reaction of adsorbed Cr(VI) on the surface of the nanotubes to the formation of chromium(III) and further adsorption of this species on the functionalized carbon nanotube seems to lead the mechanism of metal uptake to the adsorbent. The presence of both chromium species, (Cr^{3+} and $\text{Cr}_2\text{O}_7^{2-}$) on the oxidized nanotube was confirmed by X-ray photoelectron spectroscopic analysis.

Three different carbonaceous materials were investigated for the elimination of copper(II) and cobalt(II) from an aqueous solution (Pyrzynska and Bystrzejewski, 2010). The three materials used in the investigation were: activated carbon,

carbon nanotubes and carbon-encapsulated magnetic nanoparticles. As a result of the experiments, it was concluded that activated carbon presented less efficiency than the other two materials with respect to the metals adsorption, being this difference attributed to the surface change density and the overall graphitization degree. However, at aqueous high ionic strength, the metal uptake is primarily governed by the particle size.

Ethylenediamine-functionalized multi-walled carbon nanotubes were used in the adsorption of cadmium from aqueous solutions and in different experimental conditions (Vukovic *et al.*, 2010). The carbon nanotubes were functionalized *via* chemical modification of carboxyl groups using O-(7-azabenzotriazol-1-yl)-N,N,N',N'-tetramethyluronium hexafluorophosphate. Best metal uptake (25.7 mg g^{-1}) was obtained by the use of the above adsorbent if compared with that of the raw material, whereas metal adsorption is pH dependent and it is well fitted to the Langmuir model.

Cadmium(II) adsorption together with that of lead(II), were investigated onto oxidized nitrogen-doped multi-walled carbon nanotubes (Pérez-Aguilar *et al.*, 2010). As experimental results shown, maximum metals uptake is reached at a pH of 5 with values of 8.9 and 29.0 mg g^{-1} for Cd(II) and Pb(II), respectively; having the adsorbent a higher selectivity for lead(II) when both metals were in the aqueous solution.

Mixed composites of carbon nanotubes and calcium alginate were used in the adsorption of copper(II) (Li *et al.*, 2010). This adsorbent, in which the carbon nanotubes were immobilized by calcium alginate, showed a copper(II) removal efficiency of 70% at pH of 2.1 and gradually increases to near 83% at pH 5. The adsorption capacity was of 67.9 mg g^{-1} at a metal equilibrium concentration of 5 mg L^{-1} .

In the comparison of three carbon-based adsorbents for cadmium(II) (Pyrzynska, 2010), it was shown that carbon-encapsulated magnetic nanoparticles has higher affinity for this metallic element that activated carbon or carbon nanotubes (Table 1), despite the fact that in all the three cases, the metal adsorption increased with the increase of the aqueous pH. Metal elution is well performed with 0.5 M nitric acid.

TABLE 1. Metal uptake at pH 8 for three carbon-based materials

Material	Cadmium(II) uptake, (mg g^{-1})
Activated carbon	9.9
Carbon nanotubes	20.4
Carbon-encapsulated magnetic nanoparticles	91.0

Since organic materials appearing in the aqueous solution may affect the adsorption capacity of carbon nanotubes, the influence of humic and fulvic acids in the adsorption of copper(II) onto multi-walled carbon nanotubes was investigated (Sheng *et al.*, 2010). A positive effect of the presence of the above organic acids in the aqueous solution on metal uptake was found at pH lower than 7.5, but this effect is reversed for pH values above 7.5. Metal adsorption in the absence or presence of the acids is well fitted to the Freundlich model.

Oxidized carbon nanotubes sheets were used to adsorb a number of elements presented in the aqueous solution in cationic form: Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} and Co^{2+} (Ahmadzadeh Tofighy and Mohammadi, 2011). The oxidation of the starting material was carried out using concentrated nitric acid at room temperature. A sequential adsorption order was described as: lead>cadmium>cobalt>zinc>copper.

It was described, that the combination of multi-walled carbon nanotubes properties with the magnetic properties of iron oxides results in a material which can be usefully used to remove chromium(III) from aqueous environments (Gupta *et al.*, 2011a). As it is somewhat expected, the adsorption capacities of the as-obtained composites are greater than that of activated carbon (90% adsorption against 10% after 1 hour contact time), being the metal adsorption strongly dependent on contact time, agitation speed and pH (Table 2) in the batch mode, and on the flow rate and the bed thickness in continuous mode.

The effect of surfactants on the adsorption of lead(II) on multi-walled carbon nanotubes was also investigated (Li *et al.*, 2011). The adsorption of the metal is enhanced in the presence of sodium dodecylbenzene sulfonate but slightly inhibited in the presence of benzalkonium chloride, this behaviour being linked to the own adsorption of the surfactants. Several interactions: electrostatic, hydrophobic and π - π are responsible of the metal adsorption in the lead-surfactant-oxidized nanotubes ternary systems.

Alumina-coated carbon nanotubes were also used in the adsorption of lead(II) (Gupta *et al.*, 2011b). Experiments were carried out in batch and continuous operation modes, and whereas in batch operation results indicated that pH of the aqueous solutions plays a key role in the adsorption of the metal since this becomes greater as the pH of the

aqueous solution increases from 3 to 7, in fixed bed columns, increasing the thickness and decreasing the flow rate enhanced the removal of lead. A further conclusion of the work is that the adsorption of the coated material is greater than given by the uncoated nanotubes, however at pH values of 7, the difference in the metal uptake from these two adsorbents becomes negligible.

Various types of carbon nanotubes were evaluated to adsorb cadmium(II) (Pérez-Aguilar *et al.*, 2011). The materials used were oxidized nitrogen-doped multi-wall carbon nanotubes, oxidized multi-wall carbon nanotubes and oxidized single-wall carbon nanotubes. By far, the morphology of the three carbon nanotubes determined metal diffusivity. In the case of the single-walled material, the high amount of sidewall pores limited cadmium diffusion and is the responsible for the slow diffusion rate of 180 minutes; this adsorption time is reduced to a mere 15 minutes in the case of the nitrogen-doped nanotubes, being the short length, small surface area and bamboo-type morphology of the material responsible for such behaviour.

Acidic oxidized multi-walled carbon nanotubes were used to investigate about the adsorption of Mn(VII), Cr(III) and Cr(VI) from aqueous solutions in which the metals were presented separately at concentrations of 1 g L^{-1} , dosage of $0.1 \text{ g } 100 \text{ mL}^{-1}$ of the carbon materials were used in all the experimental series (Bahgat *et al.*, 2011). Manganese was effectively removed by the adsorbent, however the complete adsorption of the element was not fully performed until 4 hours. In the case of chromium(III), it was not after until 8 hours that the element was not totally removed from the aqueous solution; the system did not completely remove chromium(VI) even after these long contact times.

Amino modified multi-walled carbon nanotubes were used as adsorbents against Pb^{2+} and Cd^{2+} from aqueous solutions (Vukovic *et al.*, 2011). In the case of diethylenetriamine modified nanotubes, and whereas the found extraction order was lead>cadmium, maximum metal uptakes were 58.3 and 31.5 mg g^{-1} for lead and cadmium, respectively.

Multi-walled nanotubes impregnated with D2EHPA-TOPO mixtures (D2EHPA: di-2-ethylhexyl phosphoric acid, TOPO: tri-n-octylphosphine oxide) were successfully used to remove copper(II), nickel(II) and zinc(II), being the maximum of adsorption reached at an aqueous pH value of 5.0. Interestingly, metal uptake for the three elements was found to be in the 4.8 mg g^{-1} order for each of the above. Metal desorption was well accomplished by the use of 2 M nitric acid (Vellaichamy and Palanivelu, 2011).

As it is described in the literature (Atieh, 2011), activated carbon coated with carbon nanotubes is an excellent adsorbent for chromium(VI) with an adsorption capacity of 9.0 mg g^{-1} .

TABLE 2. Influence of the aqueous pH on Cr(III) adsorption by iron oxides/multi-walled carbon nanotubes

pH	% adsorption
3	10
4	30
5	90

The above same element was subjected to adsorption investigations using carbon nanotubes chemically functionalized with various oxygen-containing surface groups (Xu *et al.*, 2011). The surface oxygen content in the treated materials was calculated to be 22% against a mere 3% of the non-oxidised carbon nanotubes, and this makes the difference in the adsorption properties of these materials against Cr(VI), i.e. 13.0 mg g⁻¹ for the former against 0.52 mg g⁻¹ for the un-treated material, in both cases with a Cr(VI) equilibrium concentration of 130 mg L⁻¹ in the aqueous solution. The adsorption of Cr(VI) is related to the adsorption of CrO₄²⁻ species, however and very strange, these authors justified in the Introduction Section of their work the existence of Cr⁶⁺ species in aqueous solution, when this cationic form of chromium(VI) is literally non-existent.

Multi-walled carbon nanotubes-polyacrylamide composites were used to investigate its behaviour on the lead(II) and humic acid adsorption from aqueous solutions (Yang *et al.*, 2011). Though both the adsorption of the metal and the organic acid were strongly dependent on the pH and the ionic strength, the presence of humic acid led to an important increase of the metal adsorption for experiments carried out at low pH values, however, this decreases at high pH values of the aqueous solutions. The presence of lead(II) led to an increase in humic acid adsorption. More interestingly, the adsorption capacity for the organic acid is enhanced after metal adsorption on the carbon nanotube, whereas the adsorption capacity for Pb(II) at pH 5 was also enhanced after adsorption of humic acid on the nanotube.

Mercury(II) is another targeted and toxic element which removal using carbon nanotubes technology was investigated (Jamshidi Shadbad *et al.*, 2011). As it is very common in these systems, the adsorption of the metals is pH-dependent, increasing in the present case continuously, 0 to near 70% adsorption from pH 1 to 7, and decreasing at alkaline pH values, until reaching a 40% adsorption at pH 13. This behaviour can be explained in terms of the formation of non-adsorbable Hg(OH)₃⁻ and Hg(OH)₄²⁻ complexes in the aqueous solutions. In comparison with other mercury(II) adsorbents, the

present carbon nanotubes needed a lesser dosage to remove the same amount (90%) of the metal as results in Table 3 summarize.

Ethylenediamine-grafted multi-walled carbon nanotubes were used for lead(II) removal from various aqueous media (Hu *et al.*, 2012). The adsorption is quantitative in the aqueous pH range of 4–7, having the functionalized material a greater adsorption capacity than the as-received carbon nanotube, 157 mg g⁻¹ versus 89.2 mg g⁻¹. Metal desorption is achieved using 1 M nitric acid.

It was described, the adsorption of cobalt(II) onto multi-walled carbon nanotubes in batch conditions and various experimental conditions (Chen *et al.*, 2012). The results obtained shown that the metal uptake is pH-dependent, i.e. 5.9 mg g⁻¹ at pH 5, 13.6 mg g⁻¹ at pH 7 and 19.4 mg g⁻¹ at pH 8, this behaviour being attributable to the deprotonation of the carboxylic groups as the pH is increased, being the surface charge more negative, and thus Co²⁺ becomes complexed by the adsorbent. Nanotubes size influenced the metal uptake but this influence is really significant at aqueous pH values in the 3–7.5 range (Table 4), being less important or non-significant at pH values above 7.5.

Multi-walled carbon nanotubes were used for the simultaneous removal of copper(II), lead (II), zinc(II) and cadmium(II) from aqueous solutions of different pH values (Salam *et al.*, 2012). As it was expected, the adsorption of these metals is pH dependent, in all the cases the adsorption increased in the aqueous pH range of 3–6, however, an adsorption sequence independent of the aqueous pH (3–9 range) can be established in the form: copper>zinc>lead>cadmium. The maximum in the adsorption is given by the metal into consideration, i.e. copper at pH 6, zinc at pH 7, lead and cadmium at pH above 9.

These same heavy metals were suggested to be adsorbed by multi-walled carbon nanotubes modified with 8-hydroxyquinoline (Kosa *et al.*, 2012). This organic compound, which structure is shown in Figure 2, is a strong complexant, especially for copper(II).

Thus, the extraction order found for these series is Cu(II)>Pb(II)=Zn(II)>Cd(II), being copper quantitatively adsorbed at the whole investigated pH range of 3–9, since this element forms the more stable and strongest complex with the organic ligand. The ability of this quinoline derivative to complex with

TABLE 3. Adsorbent dosage to remove 90% mercury(II)

Adsorbent	Dosage (g)
Multi-walled carbon nanotubes	0.09
Activated carbon	0.40
Keratin powder	1.90
Fuller's earth	9.50

Aqueous solution: 50 mg l⁻¹ mercury(II). Contact time: 1 hour.

TABLE 4. Cobalt(II) uptake at pH 4 by various sized carbon nanotubes

Nanotube size (nm)	Metal uptake (mg g ⁻¹)
10–30	8.8–10.0
30–50	5.9–7.7
60–100	<5.9

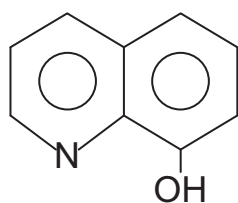


FIGURE 2. 8-hydroxyquinoline.

copper(II) is due to the formation of a five-ring chelate between the metal and the organic ligand, resulting in a complex with a high structural stability, together to this chelation, copper(II) is cationic exchangeable with the proton atom of the hydroxyl group of the organic compound:



The adsorption results are corroborated by desorption studies onto metal-loaded modified carbon nanotubes and using aqueous solutions of pH 2, in which copper(II) is not desorbed, against the behaviour of cadmium and lead (100% desorption) and zinc (69%).

The polymerization of aniline molecules formed polyaniline which was used to modify multi-walled carbon nanotubes, this modified material was used in the removal of lead(II) from aqueous solutions (Shao *et al.*, 2012). The modified adsorbent enhanced its adsorption capabilities in comparison with the starting carbon nanotube, because of the presence of amine and imine functional groups in the polyaniline which have a strong affinity for lead(II) ions. These composites are also magnetic, thus, they can be separated and recovered from aqueous solution by a magnetic separation.

Thiol-functionalized multi-walled carbon nanotubes-magnetite oxycomposites were used to study their performance on the removal of lead(II) and mercury(II) (Zhang *et al.*, 2012). In both cases, the adsorption of the metal is pH dependent, increasing from pH 1 (5% for Hg^{2+} and 12% for Pb^{2+}) to pH 6.5 (near 60% for Hg^{2+} and near 45% for Pb^{2+}). Maximum metal capacities are estimated as 65.5 and 42.1 mg g^{-1} for mercury and lead, respectively, values which are greater than these estimated for the non-functionalized carbon nanotubes 37.6 and 31.9 mg g^{-1} . The adsorption kinetics of both metals was described by the pseudo-first-order kinetic equation.

The pseudo-first order equation is:

$$q_t = q_m (1 - e^{-k_1 t}) \quad (5)$$

In which k_1 is the rate constant (i.e. min^{-1}), q_t is the amount of metal adsorbed at time t (i.e. mg g^{-1}), and q_m is the maximum metal uptake (i.e. mg g^{-1}).

TABLE 5. Adsorption uptakes for cationic nickel

Adsorbent	Ni ²⁺ uptake (mg g^{-1})
Oxidized multi-walled carbon nanotubes	17.9
Calcium alginate	10.5
Chabazite	4.5
Clinoptilolite	0.9
Fly ash	0.03
Bagasse	0.001

There is a real possibility of finding organic compounds together with metals in liquid effluents, thus their influence on the adsorption of these metals and the performance of the adsorbents may have a paramount importance, this is because it was described the effect of humic acid on the properties and Cd(II) adsorption of multi-walled carbon nanotubes (Tian *et al.*, 2012). The as-received carbon nanotubes had a low adsorption capacity for cadmium, 0.93–1.5 mg g^{-1} , but the bound of the humic acid to the carbon nanotubes introduced oxygen-containing functional groups and negative charges to the resulting adsorbent, increasing its adsorptive capacities to the 5.4 to 18.4 mg g^{-1} range. This increasing in cadmium uptake is attributable to chemical complexation and electrostatic attraction processes.

Nickel(II) ions were adsorbed by nitric acid-treated multi-walled carbon nanotubes (Mobasherpour *et al.*, 2012). In this system, the increase of the reaction temperature from 25 to 65 °C increased the metal uptake from 8.1 to 11.8 mg g^{-1} , respectively, being the adsorption equilibrium well fitted by the Langmuir isotherm model (maximum uptake 17.9 mg g^{-1}). Though direct comparison between different systems is not always easy, since the experimental conditions would not be the same, these adsorbents compare well against other potential nickel(II) adsorbents, as results summarized in Table 5 show.

Two forms of oxidation of carbon nanotubes were experimented and the resulting materials were tested to adsorb lead(II) (Bayazit and Inci, 2013). The oxidation techniques were ultrasonication and UV-light. For the two obtained materials the adsorption of lead(II) increased from pH 4 to 7 and then levels off; however, the metal uptake varies with the technique used to oxidize the single-walled carbon nanotube, in the case of UV-light, the loading in the resulting material is near 512 mg g^{-1} , whereas in the nanotubes obtained from ultrasonication, the resultant adsorbent presented a loading capacity of 342 mg g^{-1} .

This metal was also subjected to adsorption studies using functionalized multi-walled carbon nanotubes with tris(2-aminoethyl)amine (Saber Tehrani *et al.*, 2013). The adsorption is pH-dependent, increasing from pH 1 to 3, with a further little

variation in the adsorption until the limited pH value investigated of 9. In relation with the above, lead desorption can be accomplished with acidic aqueous solutions (pH<2). With respect to the selectivity of this functionalized adsorbent, results show that neither Co(II) nor Zn(II) were adsorbed, with adsorption percentages of 6, 20 and 47 for nickel(II), manganese(II) and copper(II), respectively. Furthermore, the performance of these nanotubes in the removal of lead was investigated under various cycles of adsorption-desorption, the efficiency of lead adsorption was near 96% but decreased after the fourth cycle.

Different outer diameters and oxygen content multi-walled carbon nanotubes were used to adsorb lead(II) (Yu *et al.*, 2013). In these materials, the adsorption properties with respect to lead remarkably increased with decreasing the outer diameter and this is attributable to the larger specific area in these nanotubes. Also this adsorption increases with the increase of the oxygen content in the adsorbent, being the adsorption of lead endothermic and spontaneous.

In a laboratory-based investigation, electrodes of stainless steel net coated with single wall carbon nanotubes were used as both the anode and cathode in an electrochemical procedure to remove lead(II) from aqueous solution (Liu *et al.*, 2013). Metal removal depends of the aqueous pH, being near quantitative in the pH range of 2–6.5 for an initial lead concentration of 20 mg L⁻¹ in the solution, though this removal depends on the contact time, 100 minutes at pH 2 versus 50 minutes at pH 6.5. Being an electrochemical process, it is expected that the cell voltage also affected the process, and it is found that the percentage of lead removal increased from 36% to 96% after 30 minutes, as the voltage shifted from -0.5 to -2.5V (vs. SCE). The performance of the system was investigated on a factory lead wastewater, after 17 hours of continuous operation, the removal for aluminium, iron and lead averaging 87.6%, though at longer times a thick layer of flocs from the wastewater were formed in the electrode, and the process lost efficiency. The problem was over after rinsing the electrode with water, demonstrating that the loss of efficiency was due to the presence of the flocculants in the wastewater and not to an overloading of the electrode.

Sugarcane bagasse is the fibrous waste left after the extraction of sugar juice from crushed cane, being this a waste that is inexpensive and widely available. This bagasse forms a composite with multi-walled carbon nanotubes, and these were used to adsorb Pb²⁺ from aqueous media (Hamza *et al.*, 2013). The adsorption process is almost independent of the temperature in the 22–45 °C range, being the adsorption capacity of the composite 56.6 mg g⁻¹, which compares well with 23.8 mg g⁻¹ of bagasse alone. Optimum pH for lead removal is in the 4.5

range, thus desorption is fairly efficient with acidic solutions, i.e. 0.1 M HCl.

A novel solid-phase adsorbent based on functionalized multi-walled carbon nanotubes with 5-aminosalicylic acid was used to remove metals from aqueous solutions (Soliman *et al.*, 2013). Of the metals investigated Cr(III), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II), the latter exhibits the highest percentage of adsorption with maximum lead uptake of near 32.8 mg g⁻¹.

The material resulting from the nitric acid oxidation of multi-walled carbon nanotubes was subjected to investigations in order to know its performance in the removal of zirconium(IV) from aqueous phases (Yavari and Davarkhah, 2013). It is obvious that with the oxidation process, the adsorption properties of the resulting material are enhanced with respect to these of the raw material, and this is demonstrated from results shown in Table 6 in which the Zr(IV) uptake for both materials is compared.

The adsorption of mercury ions is enhanced by the use of thiol derivatized single wall carbon nanotubes (Murthy Bandaru *et al.*, 2013). These thiol derivatives were obtained by reaction of the acid-cut carbon nanotubes with cysteamine hydrochloride using carbodiimide coupling. The as-synthesized thiol (-SH) derivatives presented a threefold higher capacity with respect to Hg(II) ions if compared with that of un-treated carbon nanotubes, and a fourfold higher capacity if compared with that presented by activated carbon. Besides this awesome numbers, the adsorption capacity of these thiol-derivatives depends upon the pH of the aqueous solution, thus the percentage of mercury removal of adsorption increased continuously from pH 1 to 9 (solutions with 30 mg L⁻¹ mercury and 0.25 mg mL⁻¹ thiol-derivative dosage), reaching a 98% metal removal at the highest aqueous pH value, though it is not clear that all this removal is due to metal adsorption onto the nanotubes or there is any contribution attributable to mercury hydroxide precipitation; a more realistic pH value for mercury only carbon nanotube adsorption is around 5 with a percentage of metal removal of near 80%. The maximum metal uptake of these thiol-derivative powders is in the 130 mg g⁻¹ order, and the adsorption efficiency of these materials was maintained up to near 90% after five adsorption-desorption cycles.

Diamine modified mesoporous silica on multi-walled carbon nanotubes were prepared and used for the adsorption of heavy metals in aqueous solutions (Yang *et al.*, 2013). The adsorption studies were carried out at a pH value of 6.2, being the extraction order and the percentage of metal removal found from these series of experiments Pb(II) (70%)>Cu(II) (45%)>Zn(II) (27%)>Ni(II) (22%).

It was reported, the influence of the presence of hydroxylated and carboxylated fullerenes in copper(II) adsorption onto oxidized multi-walled

TABLE 6. Zr(IV) uptake of un-oxidized and oxidized nanotubes^a

Material	[Zr(IV)] at equilibrium, (mg L ⁻¹)	Metal uptake, (mg g ⁻¹)
un-treated	10	<5
	40	5<metal uptake<10
	60	5<metal uptake<10
oxidized	10	30<metal uptake<35
	40	35<metal uptake<40
	60	40

^a Aqueous solution of pH 1. Time: 24 hours. Temperature: 25 °C.

carbon nanotubes (Wang *et al.*, 2013). The adsorption of the metal was increased with increasing the pH value up to pH 5, and decreased at higher values, moreover, the increasing presence of hydroxylated fullerene in the aqueous solution decreased the adsorption of copper. In the case of carboxylated fullerene, its presence inhibited the adsorption of the metal at pH 4-6.

The adsorption of copper(II) from solutions were investigated studying the influence of functionalized groups (alcohol or acid) present in multi-walled carbon nanotubes on copper removal (Rosenzweig *et al.*, 2013), results demonstrated that the highest copper adsorption was obtained when OH-nanotubes were used to remove copper from near neutral aqueous solutions.

Single wall carbon nanotubes were used for copper(II) removal from aqueous solutions (Geykci *et al.*, 2013). As it is expected for this type of adsorbents, the metals adsorption is strongly dependent upon the pH of the aqueous solution, increasing in this case slowly at pHs values below 7 and increasing rapidly at pHs values above 7. The performance of the present system for the removal of copper(II) has been compared with that of other adsorbents (Table 7). As can be seen, this single walled carbon nanotube has a good adsorption capacity when compared with others adsorbents.

The above element together with cadmium(II) was also subjected to adsorption studies on silver nanoparticles deposited in multi-walled carbon nanotubes composites (Venkata Ramana *et al.*, 2013). The adsorption properties of such materials

were investigated using established parameters such as temperature, pH, metals concentrations, etc. In the case of the influence of pH on metals adsorption it was found that the behaviour of the adsorbent is the same for the two metals, i.e. increasing with the increasing of the aqueous pH, but reaching a maximum in adsorption (near 99%) at low pH value for copper than for cadmium, 6 against 7, respectively. In the case of temperature, both adsorptions are favoured with increasing the solution temperature in the 20–40 °C range. For both metals, the adsorption data fitted to the pseudo-second-order kinetic model and Langmuir model. Metal desorption and regeneration of the silver- functionalized carbon nanotubes were investigated using HCl (0.05–0.25 M) and four consecutive cycles of adsorption-desorption. It was found that desorption efficiencies vary between 86–95% using 0.25 M HCl, and the percentage of Cu(II) and Cd(II) removal was decreased after each cycle. In the work this is attributed to the inevitable weight loss of adsorbent, though it is more probable that this will be due to the use of HCl as desorbent for the metals, which also attacked the silver present in the nanotubes and thus losing them their adsorptive properties.

The adsorption of Zn²⁺ was compared using functionalized carbon nanotubes and magnetic biochar (Mubarak *et al.*, 2013a). In the case of the nanotubes, maximum removal is achieved at pH of 10, with an efficiency of 99% for an initial metal concentration of 1.1 mg L⁻¹, being that of the biochar of 75%.

Multi-wall carbon nanotubes functionalized with 6-arm aminopolyethylene glycol were used to adsorb cadmium(II) and lead(II) (Velickovic *et al.*, 2013). Cadmium(II) and lead(II) uptake depend of the pH of the aqueous solutions, increasing the adsorption capacity as the pH of the aqueous solution is increased. Maximum metal uptake is near 40.2 mg g⁻¹ for Cd²⁺ at pH 8, whereas for lead(II) is near 32.5 mg g⁻¹ at a pH of 6, being the adsorption of both metals an endothermic character.

A supramolecular carbon nanotube-based magnetic adsorbent was formed by coating magnetic multi-walled carbon nanotubes with poly(vinylpyridine) and its adsorbents properties

TABLE 7. Adsorption capacity of Cu²⁺

Adsorbent	pH	mg g ⁻¹
Single walled carbon nanotubes	5	120
Granular biomass	4–5.5	55.4
Crab shell	5	62.3
Carbon nanotubes sheets	5	9.8
Fly ash	5	8.1

were investigated against the presence of divalent cationic copper, zinc and lead in aqueous solutions (Maggini *et al.*, 2013). In the metals adsorption process, the adsorbent forms insoluble bundles in which the cations are trapped through pyridyl- M^{2+} -pyridyl interactions. Magnetic filtration allowed the separation of the lean solution from the metals-bearing solid material. The adsorbent can be recycled after acidic treatment of the supramolecular threads. The system performs well in the case of copper(II) and lead(II), with removals of 91 and 99% for the metals, respectively, and initial concentration of 60 mg L^{-1} each with 0.5 mg adsorbent dosage. The adsorption of zinc(II) from the same initial concentration and adsorbent dosage does not perform as well, since the percentage of metal removal is around 57%. The above results being in accordance with the higher affinity of the π -acceptor pyridil ligand for larger and polarisable cations.

3.3. Uranium and nuclear elements

The adsorption of uranium(VI) on carbon nanotubes has been investigated when these materials are oxidised (Schiers and Zänker, 2009). This oxidation or increase of the amount of acidic surface groups on the nanotubes, leads to an increase of the colloidal stability of these carbonaceous materials and on the adsorption capacity for uranium(VI).

Taunit carbon nanotubes were investigated for the adsorption of radionuclides from aqueous solutions of different compositions (Mokhdoeva *et al.*, 2011). These materials came from Russia, and they are formed by unidimensional whisker-like formations of polycrystalline graphite, some of their properties are as follows: external diameter 15–40 nm, internal diameter 3–6 nm, fiber length greater than $2 \mu\text{m}$, BET surface area greater than $120 \text{ m}^2 \text{ g}^{-1}$ and total pore surface area of $69.7 \text{ m}^2 \text{ g}^{-1}$. In the case of uranium(VI) it is demonstrated that at an equilibrium pH of 8, the metal uptake is about 27 mg g^{-1} , whereas these materials adsorbed the various forms

(Pu(III), polymeric Pu(IV), Pu(V) and Pu(VI)) of a very hazardous element such plutonium is. The adsorption is performed either in weakly acidic or basic solutions. Impregnation of Taunit carbon nanotubes with various organophosphorous derivatives enhanced their adsorptive properties (Table 8).

It is shown (Fasfous and Dawoud, 2012), that in the adsorption of uranium(VI) by multi-walled carbon nanotubes, the optimum pH for the removal of this element is around 5, whereas the metal uptake increased from 24.9 mg g^{-1} to 39.1 mg g^{-1} as the temperature increased from $25 \text{ }^\circ\text{C}$ to $45 \text{ }^\circ\text{C}$.

The stable isotope ^{56}Fe was used to simulate the radioactive ^{55}Fe , ^{59}Fe , and ^{52}Fe ions existing in wastewaters generated by nuclear medicine, and then the removal efficiency of $^{56}\text{Fe}^{2+}$ in these wastes was investigated using chitosan functionalized multi-walled carbon nanotubes as adsorbent (Ren *et al.*, 2013). The adsorption capacity of chitosan-functionalized nanotubes is significantly better when compared to the non-functionalized multi-walled carbon nanotubes. Both adsorbents exhibit a better adsorption efficiency of Fe^{2+} in neutral solutions than in acidic solutions. The adsorption equilibrium is reached in near 3 hours, being the metal adsorption of an endothermic character. At $25 \text{ }^\circ\text{C}$ and pH of 5, the maximum adsorption capacity of functionalized nanotubes is 51.0 mg g^{-1} , and that of the untreated materials is 27.0 mg g^{-1} .

3.4. Miscellaneous metals

The adsorption of cesium(I) by functionalized multi-walled carbon nanotubes was investigated in order to explore the possibilities of this technology for the removal of this element from nuclear waste solutions (Yavari *et al.*, 2011). Equilibrium data for the non-functionalized and the functionalized materials were well described by the known Freundlich and Langmuir isotherms. Though the system performed well, adsorption equilibrium was not achieved until 80 minutes, with percentages of adsorption dependent on the initial metal concentration, i.e. 30% with 0.005 g L^{-1} against 20% with 0.02 g L^{-1} Cs(I). As it is seen in Table 9, the pH solution influenced the percentage of metal removal

TABLE 8. Percentage of radionuclides adsorption with impregnated Taunit nanotubes^a

Impregnation	Pu(IV)	U(VI)	Np(V)	Am(III)
without	25	0	0	0
$\text{Ph}_2\text{Bu}_2\text{CMPO}^\dagger$	99	99	95	100
TOPO ^{††}	93	96	–	100
Cyphos IL101 ^{†††}	95	–	–	0

^a Aqueous phase: element and 3M nitric acid. Reagent concentration in the nanotube: $0.6\text{--}1 \text{ mmol g}^{-1}$.

[†] $\text{Ph}_2\text{Bu}_2\text{CMPO}$: diphenyl [dibutylcarbamoylmethyl]phosphine oxide.

^{††} TOPO: tri-n-octylphosphine oxide.

^{†††} Cyphos IL101: phosphonium ionic liquid.

TABLE 9. Influence of the pH on the percentage of Cs(I) removal

pH	0.005 g L^{-1}	0.02 g L^{-1}
3	3	3
5	20	15
7	30	22
9	38	30
10	45	37

from the aqueous solution. It is described, that the adsorption mechanism is attributable to an ion exchange process. As it is described above, as the pH is increased, the acidic functional groups of the oxidized nanotubes are more deprotonated and the surface of the adsorbent become more negatively charged which causes an increasingly electrostatic attraction for Cs⁺.

It was investigated the adsorption of arsenic from water using a multi-walled carbon nanotube-zirconia nanohybrid. The adsorption capacity of the material is dependent on the oxidation state of arsenic in the solution, i.e. 2.0 mg g⁻¹ for As(III) and 5.0 mg g⁻¹ for arsenic(V), but in both cases is not-pH dependent. The material with 4.85% zirconia is effective to reach the drinking standard levels of 0.01 mg L⁻¹ arsenic (AddoNtim and Mitra, 2012).

2,2'-diaminodiethylamine covalently modified multi-walled carbon nanotubes were used for the adsorption of Au(III) and Pd(II) (Li *et al.*, 2012). Under the optimal experimental conditions, the maximum adsorption uptakes for Au(III) and Pd(II) were 50.5 and 25.7 mg g⁻¹, respectively. Langmuir isotherm model agreed well with the equilibrium experimental data of Au(III) while Freundlich isotherm model agreed with those of Pd(II). Adsorption kinetics of Au(III) and Pd(II) could be well described by the pseudo-second-order model. The highest elution ratios were determined as 95% for Au(III) and 89% for Pd(II) using 1.0 M thiourea-hydrochloric acid solution as the eluent.

The adsorption of alkali-earth metals (Mg(II), Ca(II) and Sr(II)) on capped single-walled carbon nanotubes was used to investigate their influence on the nanotubes properties (Liu *et al.*, 2012). The metals are adsorbed on two polygons of the nanotube structure, and results concluded that the adsorption energy and work function reduction of the alkali-earth metals adsorbed on the hexagon are slightly larger than that on pentagon.

Multi-walled carbon nanotubes were used to remove antimony(III) from aqueous solutions (Abdel Salam and Mohamed, 2013). As it is often found in these systems, the metal adsorption is pH dependent, reaching in the present case a maximum in metal removal (near 80%) at an aqueous pH value in the 5–6 range, a further decrease in metal removal with the increasing pH value is attributable to the presence of non-adsorbable SbO₂⁻ in the aqueous phase. In this system, the adsorption of the metal is increased as the reaction temperature is decreased.

Mixed Ce-Fe oxide decorated multi-walled carbon nanotubes materials were investigated to adsorb As(III) and As(V) from solutions (Chen *et al.*, 2013). Whereas the Ce-Fe oxide was uniformly dispersed on the surface of the nanotubes with a mean size of 7 nm, the adsorption experimental results showed that this type of adsorbents presented and excellent performance for the adsorption of both arsenic

oxidation states. Arsenic(V) is loaded at lower pH values (in the 4 range) than As(III) (pH of 7.5), being the metal uptake for a 10 mg L⁻¹ arsenic(III) or (V) equilibrium concentration of near 28.7 and 30.0 mg g⁻¹, respectively.

Functionalized 6-arm aminopolyethylene glycol multi-walled carbon nanotubes were used as solid-extractants for arsenic(V) (Velickovic *et al.*, 2013). Metal removal from aqueous solutions strongly depends on the pH, being maximum at pH 4 with a metal uptake of 7.5 mg g⁻¹ and progressively decreasing as the pH increases to 8. The removal process is endothermic.

Three-dimensional graphene-carbon nanotube-iron oxide nanostructures were used for the efficient removal of arsenic from contaminated water (Vadahanambi *et al.*, 2013). The unique three-dimensional nanostructure shows that carbon nanotubes are vertically standing on graphene sheets and iron oxide nanoparticles are decorated on both the graphene and the carbon nanotubes. Maximum arsenic uptake is near 6 mg g⁻¹ for a metal equilibrium concentration of 6–10 mg L⁻¹, showing the material with iron oxide nanoparticles good performance for its application in the adsorption of arsenic from contaminated water. This performance is due to the high surface-to-volume ratio and open pore network of the graphene-carbon nanotube-iron oxide three-dimensional nanostructures.

The effectiveness of Sn²⁺ removal from aqueous solution by using magnetic biochar and functionalized multi-walled carbon nanotube was investigated under various experimental conditions, namely: solution pH, adsorbent dosage, agitation speed and contact time (Mubarak *et al.*, 2013b). Statistical analysis revealed that the optimum conditions for the highest adsorption of Sn²⁺ are at pH 5, dosage 0.1 g with agitation speed and time of 100 rpm and 90 minutes, respectively. At the initial metal concentration of 0.1 mg L⁻¹, the removal efficiency of Sn²⁺ using the functionalized carbon nanotube was 93% and 85% with magnetic biochar. Hence, results prove that these nanotubes are adsorbents with a higher adsorption capacity compared to that of magnetic biochar.

4. CONCLUSIONS

The various forms of carbon nanotubes seem promising as adsorbents for the metals presented in aqueous solutions, though in most of the cases, if not all, this technology stands today in a “what if” solution for its use in the above role. Very much investigations must be done using multi-elemental solutions and using real aqueous wastes, besides continuous operations studies, where other problems such as nanotubes attritions, etc., may arise, being these the real challenges for these carbon materials.

By no doubt, the future of carbon nanotubes in the environmental field related to the removal of metals from aqueous solutions, of different nature, is fascinating.

ACKNOWLEDGEMENTS

To the Agencia CSIC (Spain) for support.

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