



Removal of Cr(VI) and Au(III) from aqueous streams by the use of carbon nanoadsorption technology

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ABSTRACT

The potential of adsorptive removal of Cr(VI) (hazardous element) and Au(III) (valuable element), from aqueous solutions, with carbon nanotubes was investigated. Kinetic experiments were performed in order to investigate the influence of different variables on the adsorption kinetics, that is, the stirring speed (250–2,000 min⁻¹) and adsorbent dosage (0.25–1.5 g L⁻¹) in the case of chromium(VI) as well as temperature (20°C–60°C) and HCl (0.1–10 M) concentration in the case of gold(III).

Keywords: Chromium(VI); Gold(III); Carbon nanotubes; Adsorption; Kinetics

1. Introduction

The presence of pollutant and even valuable anions in industrial effluents and ground water is both an environmental and profitable issue that it is necessary to be solved due to the toxicity of most of these compounds and the value of others. In either case the resolution of these problems is also of interest in order to minimize the impact of the generation of these residues and somewhat to compensate the costs associated with their treatment. Thus, the development of some kind of smart technology to resolve these affairs is of growing interest to the industry, the academia and the scientific community.

The main tasks in the development of a given recovery process, (from here onwards liquid effluents will be the focus of research) are associated with (i) low concentration of the solutes and (ii) the complexity, in terms of composition, normally encountered in these liquid effluents where the target is present in a heterogeneous mixture with different concentrations of accompanying cations and anions. Among the different processes developed or into development for the treatment of such liquids, besides the most conventional (i.e., precipitation), the followings: liquid-liquid extraction,

membrane based technologies, ion exchange and adsorption using different substrates, are considered [1–5].

Included in these most recent developments, adsorption of metals using nanomaterials is the utmost novelty. The nanomaterials most commonly used are functionalized or non-functionalized carbon nanotubes, carbon nanofibers, Ti-based nanomaterials, oxidized graphene, etc [6–11].

In the present work, two different uses for functionalized carbon nanotubes have been considered: (i) separation and solidification of hexavalent chromium anions contained in acidic solutions at low concentration and (ii) separation and recovery of gold(III) contained in acidic solutions as those obtained in the treatment of printed circuit boards (PCBs).

The wide use of chromium in the industry enables the potential of chromium contamination of surface and groundwater. Due to the high toxicity of this element in this oxidation state, clean and efficient technologies are needed for the treatment of the polluted effluents, also allowing the recovery and stabilization of the metal species.

Furthermore, the treatment of discarded PCBs produces acidic chloride solutions with a high concentration of accompanying metals, that is, copper(II), nickel(II), and also gold(III). Thus, these solution contain low concentrations of a very valuable metal in an environment of less valuable

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metals and high acidity; the development of a process, which in short time allows to the recovery of gold(III) under conditions of high purity, would increase the overall output of the treatment of PCBs.

2. Experimental

The carbon nanotubes used in the investigation are of the functionalized multi-walled type, where the functional groups are carboxylic ones (–COOH) (Fluka, Switzerland). Their main characteristics are: average diameter 9.5 nm, length 1.5 μm , purity 97.44%, grade of functionalization > 8%, BET 307 $\text{m}^2 \text{g}^{-1}$, and they were used without further manipulation.

Stock metal solutions were prepared from $\text{K}_2\text{Cr}_2\text{O}_7$ (Merck) or HAuCl_4 (Fluka, Switzerland). All other chemicals used in the work were of AR given in full grade.

Adsorption experiments were performed in a glass reactor provided of mechanical shaking and reflux. 100 mL of the solution and the proper nanomaterial dosage were placed into the reactor and then aliquots were subsequently taken at elapsed times in order to analyse metals via AAS. The metal content in the carbon nanotubes was then calculated by mass balance.

3. Results and discussion

The rate law governing the adsorption of chromium(VI) and gold(III) onto the nanotubes had been determined considering three possible adsorption mechanisms which evaluated if the adsorption of these metals onto the nanotubes must be considered as a liquid-solid phase reaction which includes (i) the diffusion of metal species from the aqueous solution to the nanotubes surface, or (ii) the diffusion of ions within the nanotube or (iii) the moving boundary process. The rate equations for these cases are [12]:

(i) film –diffusion controlled process:

$$\ln(1 - F) = -Kt \quad (1)$$

(ii) particle-diffusion controlled process:

$$\ln(1 - F^2) = -Kt \quad (2)$$

(iii) moving boundary process:

$$3 - 3(1 - F)^{2/3} - 2F = Kt \quad (3)$$

In all the above equations, k is the corresponding rate constant and F is the factorial approach to equilibrium, defined as:

$$F = \frac{[M]_t}{[M]_e} \quad (4)$$

where $[M]_t$ and $[M]_e$ were the metal concentrations in the carbon nanotubes at an elapsed time and at equilibrium, respectively.

3.1. Chromium(VI)

For the adsorption of chromium(VI), different kinetic experiments were performed in order to analyze the influence of the stirring speed on the rate of chromium loading onto the carbon nanotubes. The aqueous solution was of 0.19 mmol L^{-1} Cr(VI) and 0.1 M HCl, whereas the carbon dosage was of 1 g L^{-1} . Starting with an initial speed of 250 min^{-1} , several stirring speeds up to 2,000 min^{-1} were investigated and the results obtained are shown in Fig. 1. This figure shows the comparison of the kinetic removal and metal uptake at these various stirring speeds. It can be observed that there is an influence of the stirring speed on the metal loading kinetics of chromium(VI) in the adsorption step.

The best removal rate is obtained when a stirring speed of 500 min^{-1} were used, decreasing the rate of separation and the metal uptake as the stirring speed is increased up to 2,000 min^{-1} . This is probably due to an excess of agitation which results in the formation of local equilibria between the aqueous solution surrounded the nanomaterial particles and thus decreasing the adsorption or the removal of the metal from the aqueous solution. After 2 h of reaction, the percentages of metal removed from the aqueous solution are 64, 82, 78, 68 and 61 for stirring speeds in the 250–2,000 min^{-1} range (see Fig. 1 for stirring speeds details).

On the other hand, maximum adsorption and removal rate are obtained for a speed of 500 min^{-1} , this means that at this stirring speed a minimum in the thickness of the aqueous diffusion layer is obtained and adsorption (82%) is a maximum.

The results on the rate law using 500 min^{-1} (Table 1), allows us to determine that the particle-diffusion controlled mechanism governed the adsorption of chromium(VI) onto the nanotubes.

A further set of experiments using the same aqueous solution as above and various carbon nanotubes dosages were developed for 4 h of experimental running, in order to investigate the influence of this variable on chromium(VI)

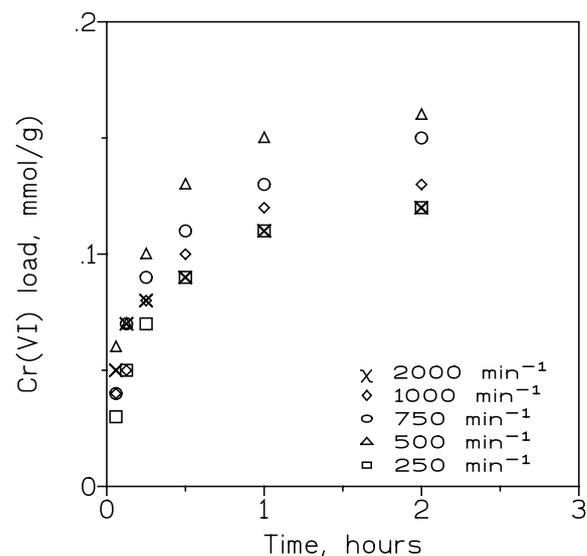


Fig. 1. Influence of stirring speed in chromium(VI) uptake onto the nanotubes. Temperature 20°C.

loading onto the nanotubes. Fig. 2 shows the results obtained from this set of experiments using the same aqueous solution as above and a stirring speed of 500 min⁻¹. By the use of the correct carbon nanotubes dosage (1.5 g L⁻¹), the concentration of chromium in the aqueous solution decreased from the initial 0.19 mmol L⁻¹ to 1.9 × 10⁻³ mmol L⁻¹, resulting in an adsorption percentage of 99%. However, the metal uptake decreases as the carbon nanotubes dosage increases. In all the cases, near an 85% of the maximum adsorption percentage was achieved within the first hour of reaction.

Table 2 shows the results concerning the investigation on the rate law governing the adsorption of chromium(VI) onto the various carbon nanotubes doses. It can be seen, that the particle-diffusion controlled process best explained the metal adsorption for all the different carbon nanotubes doses investigated in this work.

Once the metal is adsorbed onto the nanotubes as HCrO₄⁻ since this species is the predominant at the initial chromium(VI) concentrations used in this work, the elution or desorption of the loaded metal can be accomplished using that is, a solution of hydrazine sulphate, which reduces chromium(VI) to the less harmful chromium(III) [13]. Through this way, the pollutant is successfully concentrated and when considering the chromium-loaded carbon nanomaterial as a solid product, this can be dumped in safe deposits.

3.2. Gold(III)

Previous experiments had shown that in this case, the minimum in the thick of the aqueous layer, and thus,

Table 1
Results on the rate law governing the adsorption of Cr(VI) onto the nanotubes

Equation	<i>k</i> , min ⁻¹	<i>r</i> ²
1	0.023	0.8674
2	0.018	0.9746
3	0.005	0.8847

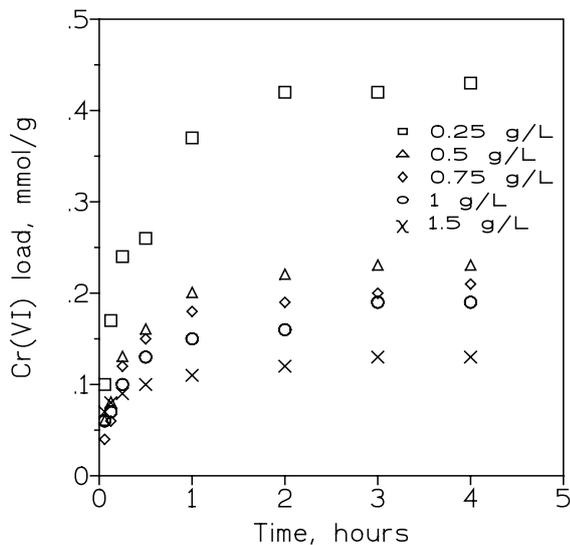


Fig. 2. Influence of carbon nanotubes dosage in chromium(VI) uptake onto the nanotubes. Temperature 20°C.

maximum adsorption, was obtained at 1,500 min⁻¹, being this stirring speed kept constant for the subsequent experiments.

For the recovery of gold(III) from acidic aqueous solutions, a group of experiments were performed with aqueous solutions of 2.5 × 10⁻² mmol L⁻¹ Au(III) and varying HCl concentrations. Fig. 3 shows a comparison of the kinetic results in the removal of gold(III) at these various hydrochloric acid concentrations. In relation with this influence, it can be observed that the decrease in the acid concentration results in an increase in the amount of gold uptake from the solution at a given time, whereas a near complete gold removal (near 99.5% and maximum metal loading within the present experimental conditions) from the solution is achieved after 1 h of reaction in the 0.1–2.5 M HCl concentrations range.

Table 2
Results on the rate law governing the metal adsorption at various nanotubes dosages

Nanotube dosage, g L ⁻¹	Equation	<i>k</i> , min ⁻¹	<i>r</i> ²
0.25	1	0.024	0.9117
	2	0.019	0.9853
	3	0.005	0.9160
0.50	1	0.024	0.9162
	2	0.019	0.9926
	3	0.005	0.9191
0.75	1	0.023	0.8990
	2	0.018	0.9841
	3	0.005	0.8462
1.0	1	0.023	0.8674
	2	0.018	0.9746
	3	0.005	0.8847
1.5	1	0.024	0.6056
	2	0.019	0.9042
	3	0.005	0.6426

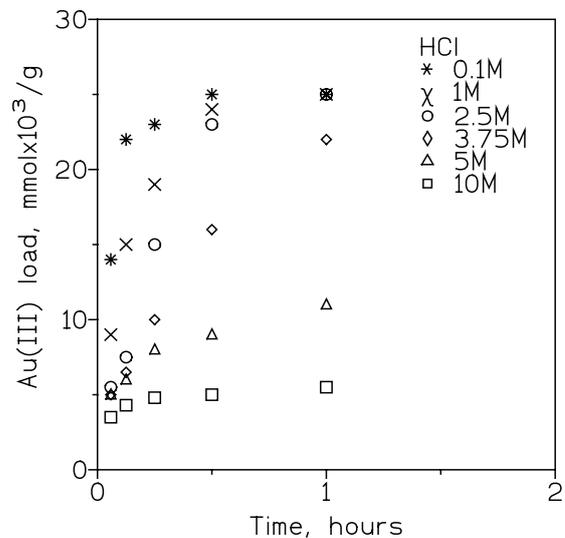


Fig. 3. Influence of the hydrochloric acid concentration in gold(III) uptake onto the carbon nanotubes. Temperature 20°C.

At 0.1 M HCl, the rate law governing the gold adsorption is the particle-diffusion controlled process, as results presented in Table 3 shown.

The influence of temperature on gold removal from the solution containing 2.5×10^{-2} mmol L⁻¹ gold in 0.1 M HCl was investigated in the 20°C–60°C range. From results shown in Fig. 4 it can be observed that the increase of temperature tends to decrease the rate of gold(III) loading onto the nanotubes from the acidic solution, however it increases the metal uptake, resulting in 0.14 mmol g⁻¹ at 20°C and 0.19 mmol g⁻¹ at 60°C, though the adsorption process is controlled by particle-diffusion at all the temperatures (Table 4).

If the gold distribution coefficient between the carbon nanotubes and the aqueous solution is defined as:

$$D_{\text{Au}} = \frac{[\text{Au}]_{c,e}}{[\text{Au}]_{s,e}} \quad (5)$$

where $[\text{Au}]_{c,e}$ and $[\text{Au}]_{s,e}$ are the gold concentrations in the nanomaterial and in the solution at equilibrium, respectively, a plot of $\log D_{\text{Au}}$ vs. $1/T$ allowed to estimate the nature of the adsorption process [14]. In the present system, such a plot resulted in a ΔH° estimated as 12 kJ mol⁻¹, thus the adsorption is endothermic.

At a first instance, gold(III) may be adsorbed onto the nanotubes as AuCl_4^- , or as the ion pair $\text{H}^+\text{AuCl}_4^-$, because

Table 3
Results on the rate law governing the adsorption of gold(III) onto the nanotubes

Equation	k , min ⁻¹	r^2
1	0.165	0.9118
2	0.134	0.9836
3	0.034	0.6906

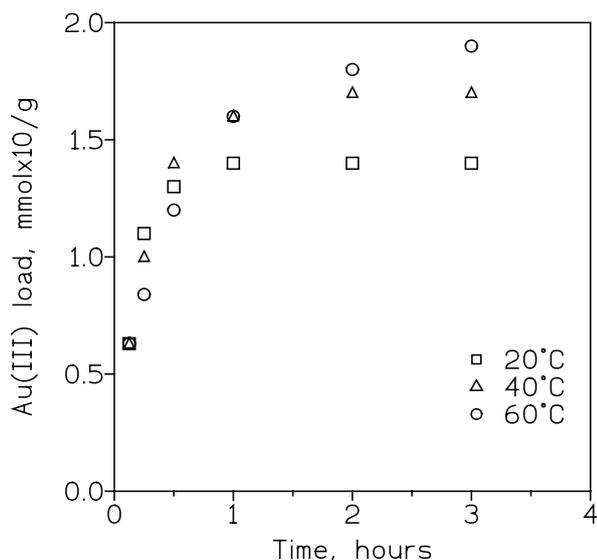


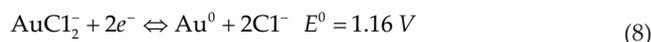
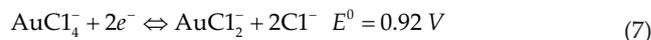
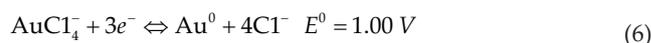
Fig. 4. Influence of temperature in gold(III) loading onto the nanotubes.

Table 4
Dependence of the rate law of gold adsorption with the temperature

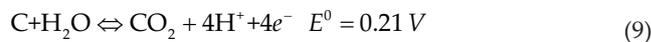
Temperature, °C	Equation	k , min ⁻¹	r^2
20	1	0.165	0.9118
	2	0.134	0.9836
	3	0.034	0.6906
60	1	0.0292	0.9856
	2	0.0228	0.9902
	3	0.0066	0.9828

this species is the predominant in the solution within the gold(III) concentration used in this work, however, a detailed study of the gold-loaded carbon nanotubes by electron microscopy showed the presence of metallic gold particles deposited in the nanomaterial, thus and, at least partially, the gold(III)-tetrachloride complex will be reduced and deposited in the functionalized carbon nanotubes as Au⁰. Fig. 5(a) shows two dark particles on the Au-loaded multi-walled carbon nanotubes, whereas the TEM-EDS spectra for the dark particles is showed in Fig. 5(b), and shows the significant peaks ($M\alpha$ 2.1 keV and $L\alpha$ 9.7 keV) corresponding to Au⁰ [15].

The reactions involved in gold reduction are:



with direct gold reduction from the AuCl_4^- complex (Eq. 6), or *via* the intermediate AuCl_2^- (Eqs. (7) and (8)) or Eqs. (6)–(8) altogether, whereas the electrons are provided by the carbon nanomaterial [16]:



A further set of experiments was performed in order to investigate the influence of gold-accompanying metals which can be presented after leaching the PCBs, the most common of them being copper(II), iron(III) and nickel(II). Using aqueous solutions containing 2.5×10^{-2} mmol L⁻¹ Au(III), or 1.6 mmol L⁻¹ Cu(II), or 1.8 mmol L⁻¹ Fe(III) or 1.7 mmol L⁻¹ Ni(II) in 2.5 M HCl and 1 g L⁻¹ carbon nanotubes dosage, it was observed that in these binary solutions the presence of these base metals did not affect either the percentage of gold(III) adsorbed onto the nanotubes or the rate of gold adsorption (see results in Fig. 3). This is not the case of experiments carried out with solutions containing the four elements simultaneously, in which the rate of gold(III) adsorption is not affected by the presence of the metals in the solution at the initial stages of the adsorption process (i.e., up to 15 min) but then the rate of gold adsorption begins to decrease if compared with

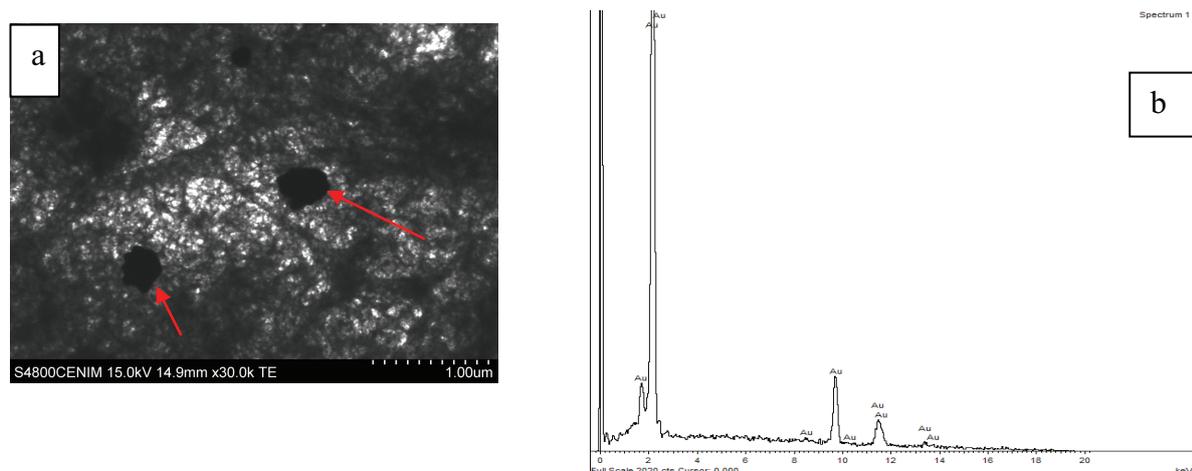


Fig. 5. (a) TEM image of Au-loaded multi-walled carbon nanotubes. Red arrows indicated zero valent gold particles. (b) X-ray dispersive energy spectrum of the gold particles.

that of the obtaining using single or binary solutions. This negative influence, attributable to the so-called “population” or “crowding” effect, commonly found in metal-liquid membrane systems [17], results in a slow down of the overall adsorption kinetics of the targeted metal despite the fact that the accompanying metals are poorly or not adsorbed at all by the carbon nanotubes. In the present system, with the exception of the latter, very good gold(III)-metals separations ($\beta_{\text{Au/Metal}} > 1$) can be achieved in this 2.5 M HCl medium, as results in Table 5 show.

Since apparently gold(III) is loaded onto the nanotubes as native gold, the recovery of this metal may be considered more as a dissolution problem than a desorption process, thus, the normal approach to recover this native gold from the loaded nanotubes is by dissolution with *aqua regia*, which dissolves gold again and yields a concentrated (in the order of g L^{-1} gold(III)) and pure, and thus highly valuable, metal solution from which gold can be precipitated that is, as gold nanoparticles [18]. Figs. 6 and 7 show images of the zero valent gold nanoparticles obtained from a gold(III) solution of 0.5 mmol L^{-1} , and resulting from the sequence adsorption-desorption (leaching)-precipitation described above. It can be seen how gold nanoparticles agglomerate in coarse fractions due to the stir of the aqueous solutions contained them.

Table 5
Experimental separation factors (β) obtained from quaternary metal solutions

Metal	$D, \text{ L g}^{-1}$	$\beta_{\text{Au/Metal}}$
Au(III)	2.5	
Fe(III)	0.043	58
Cu(II)	0.025	100
Ni(II)	0.075	33

Aqueous solution: $2.5 \times 10^{-2} \text{ mmol L}^{-1}$ Au(III) and 1.8 mmol L^{-1} Fe(III) and 1.6 mmol L^{-1} Cu(II) and 1.7 mmol L^{-1} Ni(II) in 2.5 M HCl. Carbon dosage: 1 g L^{-1} . Temperature: 20°C . Time: 1 h. D defined as in Eq. (5). β defined as the ratio $D_{\text{Au}}/D_{\text{Metal}}$

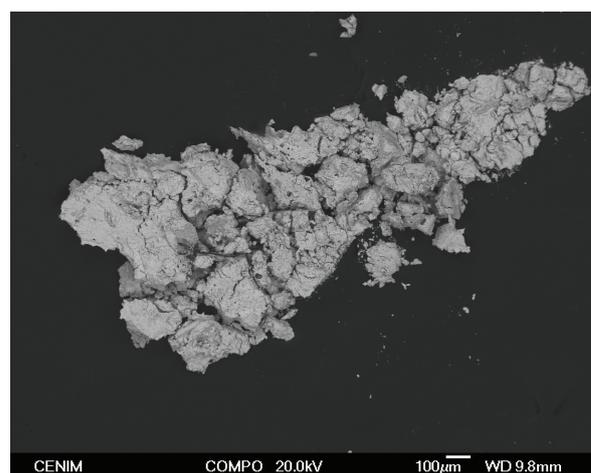


Fig. 6. Agglomeration of zero valent gold nanoparticles.

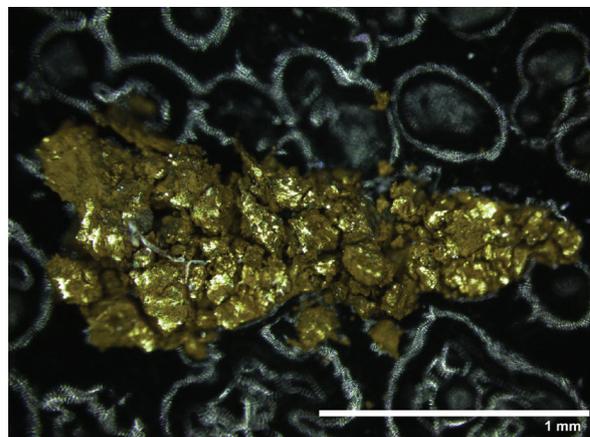


Fig. 7. Optical image of the agglomerated nanogold particles showed in Fig. 6.

4. Conclusions

The use of carbon nanomaterials as potential adsorbents of metals from aqueous solutions is investigated. Two cases are considered, chromium(VI) and gold(III), and the main variables affecting in their removal from the aqueous solutions are given.

In the case of chromium(VI), best adsorption rate and maximum in metal uptake are achieved using 500 min^{-1} as stirring speed in the reaction tank, whereas a maximum in the percentage of metal adsorption is reached as the dosage of the nanomaterial is increased from 0.25 to 1.5 g L^{-1} . The particle-diffusion controlled process seemed to describe the adsorption of Cr(VI) onto the functionalized carbon nanotubes.

In the case of gold(III), the HCl concentration in the solution influences the metal adsorption, resulting in an increase of the amount of metal removed from the solution as the initial HCl concentration is decreased, however near complete metal recovery (in the 99.5% range) from the solution containing 0.1–2.5 M HCl is achieved. The increase of the temperature increased the adsorption rate and the gold uptake, resulting in an endothermic process. Again, the T^{M} -diffusion controlled process governed the adsorption of gold(III) in the 20°C – 60°C range, with gold being adsorbed onto the carbon nanotubes, at least partially, as zero valent gold. In the case of multielemental solutions, gold is conveniently separated from accompanying metals such as copper, iron and nickel.

Acknowledgments

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