

Pb Removal on Carbon Nanotubes Membrane Decorated by ZnO Nanoparticles

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Metal pollution is one of the major environmental concerns. Many natural waters are polluted by metal ions as a result of their release by industrial plants or mining activities. Two different nanocomposites based on carbon nanotubes, obtained by catalytic chemical vapour deposition (CVD) and template CVD, supporting ZnO nanoparticles, were used for the removal of lead. The results (Pb removal up to 99,7%) indicate that the self-standing and handling membrane has an excellent metal retention capacity towards lead, due to the combination of the high adsorption selectivity of ZnO well dispersed on the adsorbent and the accessible surface area (CNTs diameter size larger than mesopores) of the carbon nanotubes inner walls.

1. Introduction

Since the industrial revolution, rapid developments in industrialization, population expansion, and urbanization have largely contributed to the severe air, water and soil pollution. A high number of pollutants discharged from industrial processes and households annually have caused significant effects on the eco-environment and human life. A number of physical, chemical and biological technologies have been developed to control the pollution successfully (El-Geundi, 1997; Biswas et al., 1998; Gadd, 2009).

Elements, such as Cr, Cd, Hg, As and Pb are the most common toxic heavy metals in water system. The improvement of water quality has provided incentives to develop new technologies and/or increase the performance of existing technologies. Various methods exist for the removal of metal ions from aqueous solutions, but adsorption is the most versatile and widely used process because of its extremely high removal efficiency and economic consideration. Additionally adsorption does not result in any secondary pollution by producing harmful substances during the process. These make it a better option than the common methods and create a research interest in developing low-cost adsorbents. Several inorganic and organic adsorbents have been proposed for use in adsorption methods, including zeolites, biosorbents, and activated carbon (Savage and Diallo, 2005). There is also a large amount of interest in the use of nanoparticles for the removal of heavy metals (Afkhami et al., 2010) thanks to their numerous special properties, such as high surface area and adsorption capacity, and simple production (Afkhami et al., 2010).

A great deal of attentions has been focused onto the application of nanostructured materials as adsorbents or catalysts to remove toxic substances from wastewater and natural waters too. Carbon nanotubes (CNTs) have been applied as one of the most potential adsorbents for removal of environmental pollutants thanks to their high adsorption capacity and good regeneration capability (Del Canto et al., 2012; Fang et al., 2012). Due to their large specific surface area, acid alkaline and thermal stability, CNTs have been chosen as an efficient adsorbing material for removing and recycling metals from aqueous solutions. Therefore, membranes based on carbon nanotubes with a number of interesting structures have been produced in recent years (Hinds et al., 2004; Srivastava et al., 2004; Kim et al., 2007).

In addition, the adsorption capacity of CNTs can be improved by surface modifications, such as oxidation and chemical or physical modifications, impregnation or coating. Due to their high surface area, high mechanical properties and good resistivity to thermal degradation, some adsorbents such as alumina, silica and zirconia are widely used in metal adsorption; the uses of CNTs as supports for these adsorbents could enhance their orientation degree, sorption capacity and surface area. Aluminium oxide supported on CNTs

(CNTs/Al₂O₃ composites) were reported for treating Pb (II) solutions, and the composites exhibited better removal ability over uncoated CNTs (Gupta et al., 2011); nanosized metal oxides were taken very seriously into consideration for adsorption of heavy metals from aqueous systems. This is partly because, of their large surface areas and high activities caused by the size-quantization effect (Mostafa 2001).

With the idea to explore the ZnO surface, for the first time, and to exploit the high surface area and the adsorbent capacity of carbon and the activity of the high surface area of the metallic oxides stabilized on the carbon surface, we focus our attention on CNTs as ZnO nanoparticles support for Pb removal.

CNTs were grown by a template chemical vapour deposition (CVD) in the channels of alumina membranes (Whatmann anopore membrane) (Sarno et al., 2012; Sarno et al., 2014a) and by catalytic CVD over Co/Fe supported catalyst (Di Bartolomeo et al., 2009). They were decorated by ZnO nanoparticles (NPs) by in-situ reduction of a suitable precursors and through a very promising bottom-up chemical strategy. Zinc oxide was chosen thanks to its unique physical and chemical properties such as high chemical stability and adsorption ability (Hua et al., 2012). A comprehensive characterization of the obtained nanocomposites was performed. The results indicate that the self-standing and handling membrane, made of carbon nanotubes inside alumina membrane channels, has an excellent metal retention capacity, due to the combination of the high adsorption selectivity of ZnO dispersed on the CNTs inner walls and the accessible mesopores surface area of the carbon nanotubes.

2. Experimental Section

2.1 Preparation of CNTs and CNTs/Al₂O₃ membrane

CNTs have been prepared by catalytic ethylene chemical vapour deposition (CCVD) on Co/Fe supported Al₂O₃ powder, as reported elsewhere (Di Bartolomeo et al., 2009, Sarno et al. 2012, Sarno et al., 2014a).

Carbon nanotubes were synthesized by chemical vapour deposition of ethylene within the channels of alumina membranes (Whatmann anopore commercial membranes), as described elsewhere (Ciambelli et al., 2011; Sarno et al., 2013).

2.2 Preparation of CNTs/ZnO nanocomposite

The CNTs/ZnO nanocomposite was produced using a wet chemistry approach, in a laboratory plant under a nitrogen flow, by zinc acetate dihydrate decomposition in organic solvent in the presence of surfactants (Altavilla et al., 2011; Sarno et al., 2015a; Sarno et al., 2015b) and a certain amount of CNTs. In particular, 0.443g of zinc acetate dihydrate (C₄H₆O₄Zn • 2 H₂O), 0.5 g of CNTs, 10 mmol of 1,2-hexadecanediol, 6 mmol of oleic acid, 6 mmol of oleylamine and 20 mL of benzylether were mixed and then sonicated for 5 minutes before the synthesis. The black coloured mixture was put in a three necked flask, heated to 200°C for 2 h and, then, heated to reflux (~ 285°C) for 10 minutes. After cooling, the obtained product was washed using ethanol and hexane in equal volumes and, successively, precipitated, separated via centrifugation and filtered to obtain a ZnO NPs enriched bucky-paper.

2.3 Preparation of CNTs/Al₂O₃ membrane decorated by ZnO nanoparticles

For the preparation of CNTs/Al₂O₃ membrane decorated by ZnO nanoparticles, in the following named CNTs/Al₂O₃_ZnO, a wet chemistry approach was used, too. The decorated membrane was prepared starting from the ZnO precursor using the same procedure described above in presence of a CNTs/Al₂O₃ membrane 2 mg in weight.

In particular, the nanoparticles, synthesized by thermal decomposition of a precursor in organic solvent in the presence of surfactants, were capped by an oleylamine/oleic acid organic coating that favours the dispersion on the CNTs hydrophobic surface.

The decorated membrane in solution was cooled to room temperature by removing the heat source and, then, under ambient conditions, the membrane was easily separated from the rest of the solution.

2.4 Characterization

All the obtained samples were characterised by numerous techniques. Simultaneous analysis (TG–DTG) in air and nitrogen flow were performed with a Thermogravimetric Analyser SDTQ 600 TA Instruments, at 10 K/min heating rate, coupled with a mass spectrometer. XRD measurements were performed with a Bruker D8 X-ray diffractometer using CuK_α radiation. Raman spectra were obtained at room temperature with a micro-Raman spectrometer Renishaw inVia with a 514 nm excitation wavelength (laser power 30 mW) in the range 100–3000 cm⁻¹.

2.5 Adsorption tests

For the adsorption tests, stock solutions at a concentration of lead (II) acetate trihydrate 0.13 g/l were used. In particular, the stock solutions were prepared at room temperature dissolving 0.13 g of lead (II) acetate trihydrate in 1 L of bidistilled water. They were pre-equilibrated for three days. The adsorption capacity experiments were conducted in vials containing 0.1 g of the carbon in 1 L of solution at their native pH. The two prepared samples were left for two hours in the solution, at room temperature, and successively tested with TG-DTG and inductively coupled plasma mass spectrometry (ICP-MS). The ICP-MS analysis was performed using an Agilent 7500ce ICP-MS instrument.

All the adsorption tests were performed in triplicate and the mean of three values was expressed in the results.

3. Results and discussion

3.1 Materials characterization

The XRD patterns of the two prepared samples, CNTs/ZnO and CNTs/Al₂O₃_ZnO, are shown in Figure 1a. The XRD pattern of CNTs/ZnO shows a broad peak at around 2θ value 26.0° due to CNTs. The diffraction peaks located at 2θ values 31.8°, 34.70°, 36.50°, 47.70°, 56.76°, 62.30° and 68.13° have been indexed as hexagonal wurtzite phase of ZnO (Zhou et al., 2007; Casa et al., 2016) with lattice constants $a=b=0.324$ nm and $c=0.521$ nm (JPCDS card number: 36-1451) (JCPDS, 1977). The XRD pattern of CNTs/Al₂O₃_ZnO shows the most intense carbon materials peaks at about 25° and 43° on the halo of the Al₂O₃ membrane spectrum. It is evident the low level of crystallinity of the CNTs after the synthesis. In the spectrum, peaks from hexagonal wurtzite phase of ZnO are also visible. The ZnO particles size has been evaluated by the Scherrer formula. For our evaluation we used the (001) signal and the diameter was found to be equal to 16 nm for CNTs/ZnO and 12 nm for CNTs/Al₂O₃_ZnO.

Figure 1b shows a comparison of the Raman spectra of CNTs/ZnO and CNTs/Al₂O₃_ZnO. Raman spectra of CNTs/ZnO shows the most prominent features of the sp² carbon materials, which are known as the G band and the 2D (or G') band, were observed at 1570 cm⁻¹ and 2660 cm⁻¹, respectively, using 514 nm excitation wavelength. A very small D-band due to disorder or edge of a graphite sample can be also seen at about half of the frequency of the G' band at the 1334 cm⁻¹. The Raman spectrum of CNTs/Al₂O₃_ZnO, with CNTs obtained in the channels of the alumina membranes, without catalyst, shown in the same figure (black line), exhibits the typical Raman profile of CNTs as produced (D and G bands are not separated and partially overlapped). The D band is indicative of defect in the nanotube walls (Di Bartolomeo et al, 2009). The fact that the two peaks have nearly identical magnitude indicates the presence of nanocrystalline graphite with domain size less than 10 nm (Ciambelli et al., 2011).

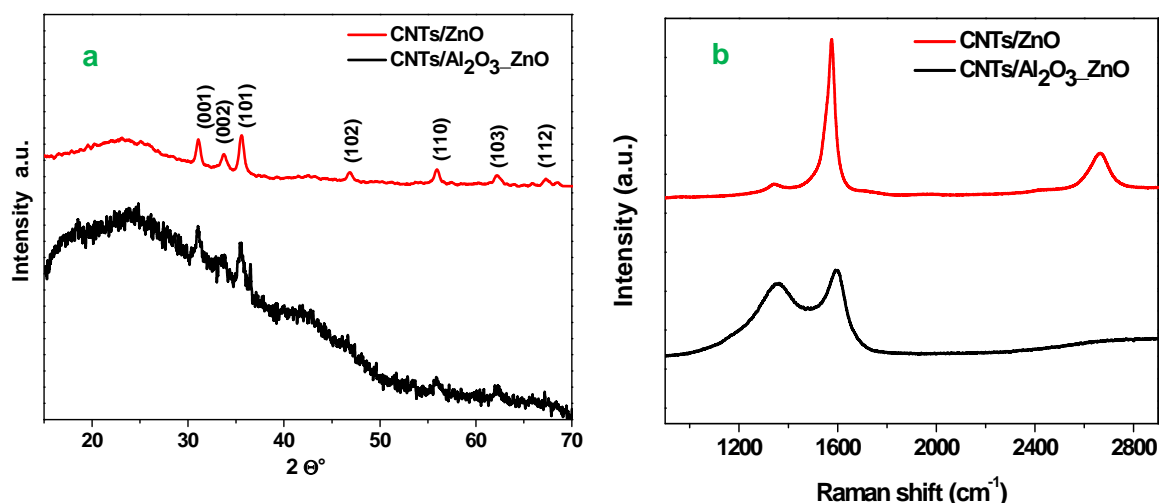
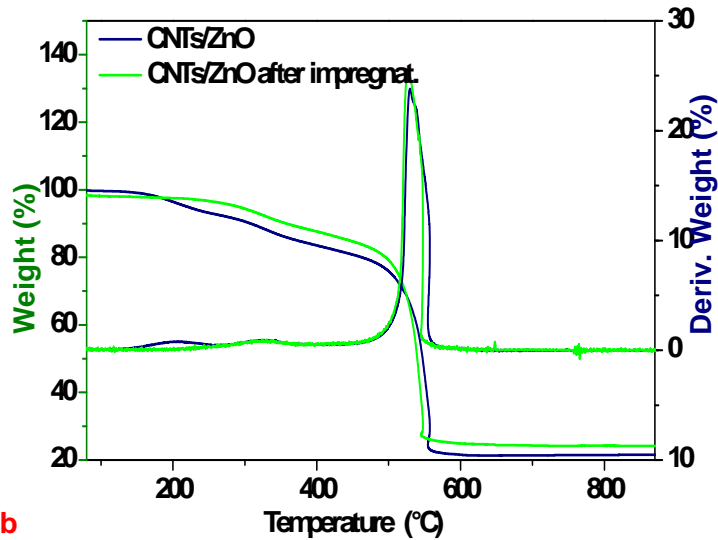


Figure 1: Comparison of XRD patterns (a) and Raman Spectra (b) of CNTs/ZnO and CNTs/Al₂O₃_ZnO

The thermal conversion, in air flow, in a temperature range 25 - 900°C of the samples before and after impregnation in the solutions of lead (II) acetate trihydrate are shown in Figure 2. TG-DTG results, from the higher residual weight after impregnation, show that the two samples are capable of removing and retaining

lead from the solution of lead (II) acetate trihydrate. It is evident that the CNTs/Al₂O₃_ZnO is capable of containing a higher percentage of lead (TG-DTG thermograms evaluation and confirmed by ICP-MS analyses).

a



b

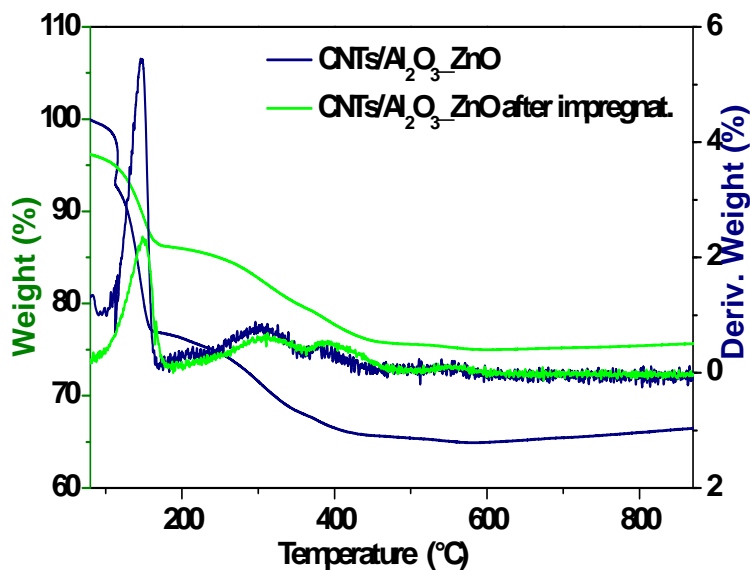


Figure 2: TG-DTG profiles of CNTs/ZnO (a) and CNTs/Al₂O₃_ZnO(b)

In particular, in Table 1 the key parameters used to evaluate the process efficiency were reported for the two adsorbents.

The results reported in the Table 1, obtained starting from known value of ZnO NPs size and density, evidence that a higher NPs loading of smaller nanoparticles was obtained after ZnO synthesis in the channel of the carbon nanotubes inside alumina membrane, probably due to the simplest wetting during ZnO formation (CNTs diameter size larger than mesopores). On the other hand, the specific lead retention capacity is very high (Kikuchi et al. 2006; Mahdavi et al., 2012) and similar in the two cases (see the adsorbent capacity of a single nanoparticle).

The results indicate that the self-standing and handling membrane of CNTs in the channel of alumina has the best and an excellent metal retention capacity, due to the the high adsorption selectivity of ZnO dispersed on the accessible CNTs/Al₂O₃ pores.

Table 1: Key parameters of the efficiency of the process TG/DTG evaluation.

	CNTs/ZnO	CNTs/Al ₂ O ₃ _ZnO
Carbon (g)	0.1	0.1
ZnO NPs (g)	3.23E-02	1.42E-01
Pb adsorbed (g)	9.68E-03	7.08E-02
Mass Pb/ZnO (mg/g)	3.00E+02	5.00E+02
Mass Pb/mass ZnO+CNTs (mg/g)	7.32E+01	2.93E+02
Mass Pb/mass ZnO+CNTs+Al₂O₃ (mg/g)	/	1.10E+02
Pb removal percentage (%)	13.7	99.7
Total NPs volume (cm ³)	5.75E-03	2.14E-02
Number of NPs	3.35E+14	2.96E+15
Pb adsorbed for ZnO NP (g)	2.89-17	2.39E-17
NPs diameter d (nm)	1.6E+01	1.2E+01
A (m ²)	2.01E-16	1.13E-16
Density of NPs (g/cm ³)	5.61	6.61
Volume of single NPs (cm ³)	1.71E-23	7.23E-24

4. Conclusion

In this work, two different nanocomposites based on carbon nanotubes/ZnO nanoparticles were used for the removal of lead.

The simplicity and reliability of the technique used for the preparation of nanomaterials combined with the high removal capacity towards lead makes our approach very attractive and economical.

The results shown that the self-standing and handling membrane of CNTs in the alumina channels has an excellent lead retention capacity, due to the high ZnO NPs loading and accessible surface area of the adsorbent.

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