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Sorption of indium (III) onto carbon nanotubes

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ABSTRACT

Indium has numerous applications in different industrial sectors and is not an abundant element. Therefore appropriate technology to recover this element from various process wastes is needed. This research reports high adsorption capacity of multiwalled carbon nanotubes (MWCNT) for In(III). The effects of pH, kinetics, isotherms and adsorption mechanism of MWCNT on In(III) adsorption were investigated and discussed in detail. The pH increases improves the adsorption capacity for In(III). The Langmuir adsorption model is the best fit with the experimental data. For the kinetic study, the adsorption onto MWCNT could be fitted to pseudo second-order. The adsorption of indium(III) can be described to a mechanism which consists of a film diffusion controlled process. Metal desorption can be achieved with acidic solutions.

1. Introduction

In recent years, the modernization and the technological development have generated a fast growing of different industrial sector, increasing by one way the raw materials needed to produce it and in the other way generating a large amount of pollutant (Sheng et al., 2012; Liu et al., 2008).

The presence of heavy metal in the industrial effluent is a crucial preoccupation nowadays due to the adverse environmental effect. These are no biodegradable and can be related with a serious environment problem due to their toxicity, bioaccumulation tendency and persistency in nature (Jaishankar et al., 2014). On the other hand, some of these metals are considered such as valuable or strategic one. In either case the elimination or recover of these from effluents is an important social challenge.

One strategic metal with wide applications range in advanced technological areas is indium (European commission, 2014). It is extensively used in the LCDs (Liquid Crystal Displays) manufacture and other industries (alloys, electrical components, etc.), rising its price to near USD700 per kg as January 2015. In addition, indium could have negative effect on the health, can be damage heart, kidney, and liver of humans (Nishihama et al., 1999; Carolyn et al.,2002; Tsai et al., 2012).

Due to high indium(III) demand and his toxicity (Kuo-Hsin et al., 2015; Jeong et al. 2015) new recovery routes from waste and liquid effluents have been investigated (Inoue and Alam, 2015; Dang et al., 2014; Wang S. and Wang Y.L. et al., 2013). Different articles in relation to the separation and enrichment of indium from solution waste with different methods such as solvent extraction (Tsai H.-S. and Tsai T.-H, 2012; Hoogerstraete et al., 2013; Kato et al., 2013; Yang et al., 2014), adsorption (Yuan et al., 2010; Li et al.,2012; Katsutoshi and Safig, 2015; Xiong et al., 2010) have been studied. However, the search of new technologies to recover or eliminate heavy metals and/or improvement the existing knowledge is continuous.

Solid phase extraction is an important methodology to separation and enrichment of valuables (strategies) or toxic metals, Au, In, Cr, Cd etc. (Kanemaru et al., 2012) due to is easy adaptation, automatization and the simplicity of this. Different adsorbent can be use, such as, starch (Ma et al., 2015, Soylak and Akkaya, 2002), activated carbon, activated carbon clothes, fly ash, chitin, prawn shell, peanut hull pellets, clay minerals, zeolites and resins etc. (Sheng et al., 2013, 2014a, 2014b; Wang et al. 2013a; Ozkantar et al., 2015; Memon et al., 2015; Ma et al., 2015). The advance of this technology is associates with the search of new adsorbent and in the improvement of existing.

Nanotechnology is a new area which is in continues development. Over the last two decades, CNTs, either single walled carbon nanotubes (SWCNTs) or multi walled carbon nanotubes (MWCNTs) present a wide range of applications over other materials due to their excellent properties (Bu and Hu, 2016; Wang and Qui, 2016; Kin et al., 2016; Ravi and Vadukumpully, 2016; Sheng et al., 2016).

Among carbon nanomaterial carbon nanotubes, CNT, have been

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used as adsorbent of different inorganic and organic molecules due to their high surface area, hydrophobicity and adsorption capacities (Alguacil et al., 2014; Sahmetlioglu et al., 2014; Wang et al., 2015; Mohammadi et al., 2015; Arvind et al., 2015; Wang et al., 2013b).

A deep bibliography study showed different research about toxic and strategy metal (Au, Cu, Cr, Pb, Ni, Cd, Zn) adsorption onto the CNT materials (Soylark and Emre 2011; Mubarak et al., 2013; Sharma et al., 2009; Yab-Hui et al., 2003; Chungsying and Huantsun, 2006; Qu et al., 2013; Gadupudi et al., 2007; Pyrzynska, 2010; Tuzen et al., 2008; Yubing et al., 2013; Wang et al., 2015). However, no data can be found in the literature about the use of carbon nanotubes in indium-bearing solutions processing. Thus, no systematic study has been conducted to evaluate the effectiveness of such nanomaterials for adsorption of indium(III) onto them.

The aim of the present investigation is describe the use of multi-walled carbon nanotubes as adsorbents of indium from aqueous solutions optimizing several parameters such as pH, stirring velocity, temperature, etc. to obtain an efficient adsorbent system. This research also study desorption process because it is important in the process. The adsorption isotherm model of Langmuir and Freundlich were used to fit the adsorption data. The kinetics of indium adsorption onto the multiwalled was investigated by fitting the adsorption data to a pseudo first- and second order reaction. And finally the rate law that govern the adsorption of In(III) onto the nanomaterial was also studied.

2. Experimental

2.1. Materials

Multi-walled carbon nanotubes were obtained from Fluka. They were used without any further manipulation. All chemical, $In_2(SO_4)_3$ and different salt to study the effect of the ionic strength (LiCl, Li_2SO_4, $LiNO_3$), used in the present work were of AR grade obtained from Merck.

2.2. MWCNT characterization

Zeta potentials of the MWCNT were measured across the pH range 1–12. Suspension in water at different pH was prepared by sonication during 5 min. The measurement was done just after finish the sonication due to the low stability of the suspension. Measurements were made on a Malvern Zetasizer, five measurements were made for each value of pH and the average value was taken as the zeta potential of the MWCNT under the pH conditions.

Micro-Raman spectroscopy of the virgin MWCNT was done in a confocal Raman microscope Renishaw Invia equipped with a Leica microscope and an electrically refrigerated CCD camera. Laser excitation lines were provided by a Renishaw Nd; YAG laser (532 nm). The laser output was 25 mW. The frequencies were calibrated with silicon.

2.3. Batch adsorption experiments

A stock solution of In(III) was prepared to adsorption experiments dissolving $In_2(SO_4)_3$ in a aqueous solution, which a final In (III) concentration of 1000 mg/L. Adsorption studies were performed using a glass reactor, in which 100 mL of solution containing the desired indium concentration prepared by the dilution of the In(III) stock solution and the convenient nanotubes dosages were put into contact by means of mechanical shaking using a four blades impeller. At elapsed times (30, 60, 120 and 180 min), convenient samples were retired from the mixture to check the metal concentration in the solution by AAS in a Perkin Elmer 1100B spectrophotometer.

The percentage of In(III) adsorbent on the MWCNT were obtained by the following equation:

$$\%_{ad} = [In]_0 - [In]_e x100 \tag{1}$$

The adsorption capacity of the adsorbents for In(III) at equilibrium (qe mg/g) was calculated according to the following equation:

$$q_t = \frac{[In]_t - [In]_e xV}{W} \tag{2}$$

Where $[In]_0$, $[In]_t$ and $[In]_e$ are the initial, at time t and equilibrium metal concentration (mg/L). V is the volume of solution (L) and W is the amount of adsorbent (mg).

2.4. Batch desorption experiments

The solution was filtered and then in the indium loaded MWCNT were carried out desorption studies. The convenient desorption solution and indium-loaded carbon nanotubes were put in contact using a four blandes impeller.

3. Results and discussions

3.1. Materials characterization

The superficial charge of the adsorbent could affect in the adsorption process. The isoelectric point (IEP) is obtained at pH around 3.6. This value is similar to obtain by other authors in this kind of materials (Vatanpour et al., 2014).

The Micro-Raman spectra show different characteristic signal of MWCNT. The spectra was deconvoluted by origin, after the baseline correction and normalization, the different quantitative parameters were obtained. Table 1 shows the peak positions and the relative intensity. The ratio I_D/I_G was also studied.

Two narrow bands are observed in the Raman spectrum, the G band located at 1573 cm^{-1}, it is feature of all Sp^2 bonded carbon, and the D band around 1339 cm^{-1}, this become active in presence of disorder (Soin et al., 2010). The D band is attributed to Sp^3 bonding defects in the nanotubes (Liu et al., 2014). Apart from these first–order bands the MWCNT Raman spectra shows also a weaker band around 1607 cm^{-1}, D', it is defect dependent and a stronger one located 2675 cm^{-1}, 2D or G′ band, it is associated with a overtone of D band (Dersselhaus et al., 2002).

The I_D:I_G relation can provide information about the defect in the MWCNT. Smaller ratio indicate carbon atoms bonded with few defects, in contrast larger quantities of defects in the nanotubes were indicated by a high ratio (Wepasnick et al., 2010). The I_D:I_G low value obtained in the MWCNT indicate a few defects in the structure of this material.

3.2. Adsorption experiments

Using batch conditions, at a first instance the adsorption of

Table 1
Raman peak position, area signal and I_D/I_G ratio.

	D	G	D′	2D	G+D
Raman shift (cm^{-1})	1339	1573	1607	2675	2913
Area signal	102.4	76.2	6.8	90.1	106.8
I_D/I_G	1.34				