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Recovery of Nd(III) in coexistence with Fe(III) ions from aqueous phase using functionalized multiwalled carbon nanotubes: An environmental benign approach

Kinshuk Dasgupta*, R. Vijayalakshmi, M. Anitha

Rare Earths Development Section, Materials Group, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

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ABSTRACT

The present paper reports an environmental benign process for the selective adsorption of Nd(III) in presence of Fe(III) on functionalized multiwalled carbon nanotubes (MWCNT) from a synthetic aqueous solution, which can be utilized for the rare earth recovery from scraps or end of life products. Effects of metal ion concentration, aqueous phase acidity (pH), weight of MWCNT, temperature, complexing agents and contact time on the adsorption of Nd(III) and Fe(III) over MWCNT have been studied in detail. The Nd (III) adsorption followed Langmuir isotherm in presence of Fe(III)and showed favourable adsorption at pH 3. The maximum adsorption capacities for Nd(III) and Fe(III) were found to be 44 mg/g and 30.8 mg/g respectively. Pseudo second order kinetics was followed by both Nd(III) and Fe(III) adsorption on MWCNT. For selective adsorption, ascorbic acid was found to be the best among different complexing with a selectivity coefficient of 120 for Nd(III) with respect to Fe(III). The adsorbed ions could be fully desorbed with 0.2 M HCl, indicating the process feasibility in terms of ease of recovery of loaded metal ions as well as regeneration of functionalized MWCNT. This process eliminates the use of hazardous organic solvents for the recovery of rare earths.

1. Introduction

Rare earth elements (REEs) have become increasingly important, because of their essential role in permanent magnets, lamp phosphors, catalysts, rechargeable batteries and other applications [1–3]. The increasing popularity of hybrid and electric cars, wind turbines and compact fluorescent lamps is causing an unprecedented increase in the demand and price of rare earths (for example the price of neodymium (Nd) has increased from \$16 per kg in 2001 to \$94 per kg in 2014). In fact, the green economy cannot further develop without rare earths. Given this global demand for green and sustainable products in energy, military, and manufacturing industries, REE demand throughout the world is projected to increase [4]. Kingsnorth's supply demand statistics [5] indicate that at least until 2020 there will be shortages for Nd (25%), Dy (23%), Tb (29%) and Er (39%). China is presently producing more than 97% of the global production of the rare earths [6]. For the past few years, China is strictly regulating the export of rare earths [3]. Therefore, attempts are being made worldwide to develop technologies for the recovery of rare earths from existing scraps.

Neodymium (Nd) in combination with iron (Fe) and boron (B) is used in the preparation of Nd-Fe-B permanent magnets, which have very high energy products compared to other magnets. During the fabrication of magnets for a variety of applications and from the end of life products, significant quantities of scrap materials are generated. It is essential to separate valuable rare earths from them. No standard commercial recycling exists for rare earths derived from end of life Nd-Fe-B magnets [7]. In reality less than 1% of REEs were recycled in 2013. Several years ago, Japanese company Dowa began harvesting circuit board, hard drives, computer chips and other components for rare earth metals. They smelt the component to 1400 °C, where 300 tons e-waste results in 150 g of REE [8]. Ames laboratory is developing a method of isolating REEs from magnets using molten magnesium. The process is not actually new-it was developed by Iowa State University in1990 to create a Nd-Mg alloy. Ames process breaks the magnets into 2–4 mm pieces which are added to a crucible with solid Mg. A radio frequency furnace heats the Mg until it liquefies at which point the REEs diffuse into the molten metal leaving behind the Fe and B. The molten mixture is cooled and cast, only to have Mg vaporized off again so that only REEs remain [9].

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* Corresponding author.
E-mail address: kdg@barc.gov.in (K. Dasgupta).

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Researchers from KU Leuven, Belgium are using ionic liquids to separate REEs from transition metals in magnets. The process uses trihexyl(tetradecyl)phosphonium chloride to remove transition metals like Fe, Co, Mg and Cu into a liquid phase, leaving the rare earths behind in aqueous phase [10]. Conventional methods for the separation of rare earth metal ions include techniques such as ion-exchange, solvent extraction and membrane based separation [11–13]. Several researchers have used organo phosphorous extactant like di-2-ethylhexyl phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA), etc or ammonium salt based extractant like Aliquat 336 [14–16]. The TRUEX liquid–liquid has been applied for recovery of lanthanides from nuclear waste by utilizing the organophosphorous ligand octyl-phenyl-*N*,*N*-diisobutyl-carbamolymethyl-phosphine oxide [17]. US patent application number 2001/6312653 [18] discloses a functionalized calixarenes with carbamoylmethylphosphine oxide (CMPO) for using in extraction of rare earths from radioactive solutions. However, these methods have some disadvantages such as high consumption of reagent and energy, low selectivity and generation of secondary waste solutions [19].

One potential method, which so far has not been tried in a significant way for the recovery of rare earths, is the use of functionalized carbon nanotubes (CNTs). CNTs have high surface area, excellent chemical and thermal stability. Carbon nanotubes (CNTs) act as potentially efficient adsorbents for metal ions removal from different kinds of environments, and have attracted great interest in metal ion adsorption from aqueous solutions [20–25]. The presence of active sites on the surface, inner cavities and inter-space contribute to high metal removal capabilities. There is an excellent review by Rao et al. [26] on the sorption of divalent metal ions from aqueous solution by carbon nanotubes. They discussed about the sorption mechanism and the effect of process parameters on the sorption capacity of CNTs. Removal of toxic heavy metals from contaminated water and recovery of noble metals from waste water by pristine as well as functionalized CNT have been tried by several researchers [27–30]. Table 1 summarizes findings by different researchers on metal removal using CNTs [27–53]. It can be observed although the adsorption of metal ions on different kinds of CNTs has been studied; the literature on the adsorption of rare earths is scanty [only Ref. [53]]. One anticipated drawback of using CNT is its high cost. However, we have been successful in preparing this exotic material in an economic way by using cheap raw materials and by reducing number of processing steps [54].

The present work aims at understanding the adsorption of Nd (III) in presence of Fe(III) from aqueous chloride solution by functionalized multiwalled carbon nanotubes (MWCNT). The findings will help in designing a scheme by which Nd can be preferentially adsorbed on MWCNT in presence of other metal ions (Fe). This is important for recycling or recovery of Nd from end of life magnets. This process eliminates the use of hazardous organic solvents and thus environmental benign. To the best of our

Table 1
Published data on metal ion adsorption by CNT.

Metal ions	Kind of CNTs	Observations/Adsorption capacity	References
Hg(II):	Oxidized CNTs	3.83 $mg\,g^{-1}$	[31]
Hg(II)	Oxidized CNTs impregnated Chitosan beads	183.2 $mg\,g^{-1}$	[20]
Pb(II)	CNTs and TiO_2/CNT composites	CNTs: 33.0 $mg\,g^{-1}$; TiO_2/CNTs: 137.0 $mg\,g^{-1}$	[32]
Pb(II)	CNTs grafted with 2-vinylpyridine (VP)	37.0 $mg\,g^{-1}$	[33]
Pb(II)	Oxygen-plasma-oxidized CNTs	The adsorption is strongly dependent upon the pH values	[21]
Pb(II)	CNTs/MnO_2 nanocomposite	98.9% removal	[34]
Pb(II)	CNTs/Fe_3O_4 modified with 3-aminopropyltriethoxysilane	75.02 $mg\,g^{-1}$	[35]
Mn(II)	Oxidized CNTs	96.82% removal	[36]
Cd(II)	Discharged CNTs	55% removal	[37]
Cd(II)	Ethylenediamine functionalized CNTs	25.7 $mg\,g^{-1}$	[23]
Cd(III)	Humic acid modified CNTs	18.4 $mg\,g^{-1}$	[38]
Cu (II)	CNTs/calcium alginate composites	69.9% of Cu(II) removal even at a lower pH of 2.1	[24]
Cu(II)	Sodium p-aminobenzene- sulfonate grafted CNTs	An improved adsorptive performance for the removal of low concentrations of Cu(II)	[25]
Cu (II)	CNTs/Fe_3O_4	88% removal	[39]
Cu (II)	Magnetic functionalized CNTs	97% removal	[40]
Sr (II)	CNTs and oxidized CNTs	CNTs: 1.62 $mg\,g^{-1}$; oxidized CNTs: 6.62 $mg\,g^{-1}$	[41]
Cr(VI)	Nano zero-valent iron (nZVI)-CNT composites	Around 36% higher efficiency on Cr(VI) removal	[42]
Cr(VI)	Magnetite nano particles supported on CNTs	Enhanced adsorption compared to oxidized CNT	[43]
Na(I)	Oxidized CNT film	About 60%	[44]
As(V), As(III)	Magnetic iron oxide/CNT composites	As(V): 9.74 mg g–1, As(III): 8.13 mg g–1	[45]
Zn (II), Cd (II)	Oxidized CNTs	Surface oxygen enhances the sorption of both ions	[46]
Cu(II), Zn(II), Pb (II), Cd(II), Co(II)	Oxidized CNTs	With the adsorption capacity of Pb(II) > Cd(II) > Co(II) > Zn(II) > Cu(II)	[30]
Cr(III), Pb(II)	Oxidized nitrogen doped CNTs	The adsorption capacity for Cr(III), Pb(II) is 0.083 and 0.139 $mmol\,g^{-1}$	[47]
Hg(II), Pb(II)	3-mercaptopropyltriethoxysilane grafted CNTs/Fe_3O_4	Hg(II): 65.52 $mg\,g^{-1}$ Pb(II): 65.40 $mg\,g^{-1}$	[48]
Cr(III), Zn(II), Ni (II), Pb(II), Ag(I), Hg(II)	Nitrogen-doped magnetic CNTs	The amount of heavy metal ions uptake were ca. 12.28 [Cr(III)], 9.31 [Zn (II)], 8.06 [Ni(II)], 6.74 [Pb(II)], 3.73 [Ag(I)], 2.59 [Hg(II)] $mmol\,g^{-1}$, respectively	[49]
Pb(II), Cd(II)	CNTs, oxidized CNTs, ethylenediamine, diethylenetriamine and triethylenetetramine modified CNTs (e-CNTs, d-CNTs and t-CNTs)	The maximum adsorption capacities of Pb(II) and Cd(II) on d-CNTs were 58.26 and 31.45 $mg\,g^{-1}$	[50]
Cu(II), Pb(II), Cd (II) and Zn(II)	8-hydroxyquinoline grafted CNTs	99.2%, 51.4%, 5.77%, and 83.2% removal of Cu(II), Pb(II), Cd(II) and Zn(II), respectively	[51]
Cu(II), Ni(II), Zn (II)	CNTs impregnated with di-(2-ethyl hexyl phosphoric acid) (D2EHPA) and tri-*n*-octyl phosphine oxide (TOPO)	The adsorption capacity of CNTs-D2EHPA-TOPO was found to be 4.90, 4.78 and 4.82 $mg\,g^{-1}$ for Cu(II), Ni(II), Zn(II), respectively	[52]
Ce(III), Sm(III)	Oxidized CNT	Ce-92.59; Sm-89.28 $mg\,g^{-1}$	[53]