Kinetics of scandium ion sorption onto oxidized carbon nanotubes

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Abstract

The present study investigates the sorption behavior of oxidized multiwalled carbon nanotubes (CNTs–COOH) for the separation and removal of scandium ions from aqueous solutions. The results indicated that CNTs–COOH showed an excellent scandium adsorption capacity of 40.1 mg g^{−1} (at pH 3) with an uptake time less than 2 min. The pseudo-second-order kinetic model and the film diffusion are the main controlling factors.

Graphic abstract

Keywords Extraction · Nanostructures · Scandium · Surface

Introduction

Carbon nanotubes (CNTs) have been proven to be effective sorbents for the removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media as it was presented in the recent reviews [1–3]. Their surface could act as a Lewis base toward polar solutes and is also involved in π – π interactions as well as dispersive interactions with aromatic analytes. Oxidized CNTs, obtained after the introduction of oxygen-containing functional groups (such as –OH, –C=O, and –COOH) on their surface, show high sorption capacity and efficiency for the removal of heavy metal ions [1, 4]. CNTs are also employed in combination with other nanoparticles with the aim to improve the removal efficiency [5].

Scandium, together with lanthanides and yttrium, belongs to rare earth elements. It is widely dispersed in the lithosphere, but there are only a few minerals that have a reasonable concentration of scandium. Since the application of scandium is growing in new technologies due to its unique magnetic, electric and optical properties, there is a warning about its accumulation in the environment following the anthropogenic inputs [6]. The content of Sc in different kind of natural samples is very often lower than the limit of detection of the most usually applied detection techniques such as inductively coupled plasma optical emission or mass spectrometry; thus, a preliminary preconcentration step is often required. Solid-phase extraction has been widely used for this purpose [7, 8].

The broad range of sorbent materials along with the various chelating reagents make solid-phase extraction technique very attractive for sample pretreatment. Various chelating reagents immobilized on silica or polymeric supports, such as 1-(2-pyridylazo)-2-naphtol and acetylacetone [9, 10], glycol amic acid [11], lysine [12], and bifunctional ionic liquid trioctylmethylammonium

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1-phenyl-3-methyl-4-benzoyl-5-onate [13], have been recently reported for the enrichment of scandium. However, some silica materials are not stable and they lose the efficiency towards Sc(III) after the desorption step, so the additional regeneration step is needed for their reusability [13, 14]. The chelating resins containing iminodiacetate functional groups exhibit also affinity for alkali and alkaline earth elements, thus the additional washing step with the excess of buffer is required to remove the matrix components [15]. Carbon-based sorbents [16–18] have also been proposed for the enrichment of scandium.

The comparative study of Sc(III) sorption showed that its affinity under acidic conditions was increasing in the order: oxidized activated carbon < Chelex 100 < graphene oxide < CNTs–COOH [17]. Both applied nanosized carbon materials showed superiority over the routinely used chelating resin Chelex-100. In the present paper, we investigate in more detail the important parameters of the sorbent characteristics such as sorption capacity and kinetics. Particularly, sorption kinetics may strongly constrain the applicability of the sorbent. The low sorption kinetics significantly enlarges the operation time, which makes the removal processes unfavorable.

Results and discussion

Sorption behavior of Sc(III) onto oxidized carbon nanotubes was investigated at pH 3 as at pH > 4 its removal could be mostly by precipitation [9, 17]. It is the advantage in the view of application of CNTs–COOH for the separation of Sc(III) from heavy metal ions as they exhibit very low affinity for carbon nanotubes under these conditions [1–3].

The adsorption isotherm of Sc(III) on CNTs–COOH, studied in metal concentration range from 1

to 300 mg dm^{−3}, showed that the maximum value of sorption capacity equals to 40.1 mg g^{−1}. Table 1 compares the sorption behavior of Sc(III) on different sorbent materials reported recently. The obtained high adsorption capacity value of CNTs–COOH under acidic conditions suggested that these carbon-based nanostructures are efficient adsorbents for the removal and/or enrichment of Sc(III) from aqueous solutions.

Reusability is an important factor for an effective adsorbent, particularly to be employed in the practical application. 50 mg of CNTs–COOH was used to study the recovery of Sc(III) from its solution at concentration of 2 mg dm^{−3}. Scandium was eluted using 5 cm³ of 2 mol dm^{−3} HNO₃ solution. After each adsorption–desorption cycle, the sorbent was washed only with water. The recovery was in the range of 97–105% for ten subsequent sorption/elution cycles (Table 2).

Table 2 Effect of number of reused cycles on the recovery of Sc(III)

Number of cycles	Percent of recovery of Sc(III) ± SD/%
1	105.9 ± 5.3
2	101.3 ± 5.1
3	99.8 ± 5.0
4	97.6 ± 4.9
5	100.9 ± 5.0
6	102.3 ± 5.1
7	101.4 ± 5.1
8	98.1 ± 4.9
9	101.3 ± 5.1
10	102.4 ± 5.1

Table 1 Comparison of different adsorbents for preconcentration of Sc(III)

Adsorbent	pH	Adsorption capacity/ mg g ^{−1}	References
Silica gel modified with PAN and acetylacetone	4–6	24.1	[10]
Resin with glycol amic acid groups	1	2.8	[11]
Cellulose–silica nanocomposite	6	23.8	[14]
CNTs modified with AC	2	5.8	[18]
Silica gel modified with AEP	4	32.5	[20]
TRPO/SiO ₂ –P	2	13.3	[21]
CNTs–COOH	3	40.1	This work

PAN 1-(2-pyridylazo)naphthol, AC activated carbon, 8-HQ 8-hydroxyquinoline, AEP 1-(2-amino ethyl)-3-phenylurea, TRPO/SiO₂–P trialkyl phosphine oxide immobilized on a silica–polymer support

Fig. 1 Adsorption kinetic curve of Sc(III) onto carbon nanotubes. Metal concentration 2 mg dm^{−3}, pH 3, solution volume 10 cm³, adsorbent dose 50 mg

The sorption kinetics experiments were carried out for an initial Sc(III) concentration of 2 mg dm^{-3} and pH 3 as a function of contact time in the range of 1–50 min. Figure 1 shows that the adsorption rate rapidly increased during the first 10 min and then, as the number of surface sites for sorption comes down, gradually tended to equilibrium. The results showed that the adsorption of Sc(III) was over 95% during the first 2 min, which indicated that kinetics adsorption equilibrium was very fast.

To investigate the mechanism of Sc(III) adsorption and the potential rate-controlling steps, kinetic models were used to test experimental data. A number of reaction-based and diffusion-based models with various degrees of complexity have been developed to describe the kinetics of metal sorption in batch systems [19]. The finally selected kinetic models will be those, which not only fit closely the data, but also represent reasonable sorption mechanism. In this study, four different kinetic models were used to adjust the experimental data of scandium sorption on CNTs–COOH. These kinetic models

included pseudo-first-order Lagergren model, pseudo-second-order kinetics, simple Elovich model, and intra-particle diffusion equation given by Weber and Morris. The estimated models and related kinetic parameters are listed in Table 3 and the linear regression of these plots are presented in Fig. 2.

The absence of the linear dependence of $\ln(q_e - q_t)$ vs. t indicates that the mechanism of Sc(III) adsorption on CNTs–COOH does not follow the pseudo-first-order kinetic model ($R^2 = 0.8488$). In contrast, very good linear dependence of t/q_t vs. t was obtained and the value of $k_2 = 0.032 \text{ g mg}^{-1} \text{ min}^{-1}$ was calculated. The plot for Elovich equation, which is useful in describing sorption on highly heterogeneous solid surface, did not give a good account of adsorption of Sc(III) as a lower R^2 value for the plot of q_t vs. $\ln t$ was obtained. Therefore, it can be concluded that the sorption of Sc(III) is consistent with the pseudo-second-order kinetic model and the mechanism of that process might be chemisorption [19]. The available literature data regarding the kinetic

Table 3 Parameters of various kinetic models fitted to experimental data

Kinetic model	Equation	Parameters
Pseudo-first-order kinetics	$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t$	$k_1: 0.0643 \text{ min}^{-1}$ $R^2: 0.8488$
Pseudo-second-order kinetics	$t/q_t = 1/k_2 q_e^2 + (1/q_e) \cdot t$	$k_2: 0.032 \text{ g mg}^{-1} \text{ min}$ $R^2: 1.000$
Elovich equation	$q_t = \beta \ln(\alpha \beta) + \beta \ln t$	$\alpha: 4.4 \times 10^{-2} \text{ mg g}^{-1} \text{ min}^{-1}$ $\beta: 0.0019 \text{ g mg}^{-1}$ $R^2: 0.9785$
Intra-particle diffusion	$q_t = \theta + k_i t^{0.5}$	$k_i: 0.393 \text{ min}^{-1}$ $\theta: 0.3930$ $R^2: 0.8845$

Fig. 2 Modeling of Sc sorption kinetics on CNTs–COOH (models: **a** pseudo-first order, **b** pseudo-second order, **c** Elovich, **d** Weber–Morris)

sorption rate of Sc(III) on different solid sorbents were obtained for a broad range of its initial concentration; thus, the direct comparison is difficult. For example, Ma et al. [12] evaluated the sorption rate of $0.0528 \text{ g mg}^{-1} \text{ min}^{-1}$ for Sc(III) on lysine-functionalized mesoporous material (initial metal concentration 20 mg dm^{-3} , adsorbent dose $= 0.25 \text{ g dm}^{-3}$) and the value of $0.00101 \text{ g mg}^{-1} \text{ min}^{-1}$ was reported for CNTs modified with activated carbon [18]. On the other hand, Turanov et al. [13] reported the kinetic sorption rate for Sc(III) on silica doped with trioctylmethylammonium 1-phenyl-3-methyl-4-benzoyl-5-onate ionic liquid equals to $8.64 \text{ g mg}^{-1} \text{ min}^{-1}$ (initial concentration of 1.35 mg dm^{-3} , $V/m = 5 \text{ g dm}^{-3}$). However, for that sorbent, very low (0.27 mg g^{-1}) sorption capacity was obtained [13].

Furthermore, intra-particle diffusion model was used to investigate the contribution of various steps involved in the adsorption process such as intraparticle and film diffusions. The linear plot of experimental data to Weber–Morris equation shows that both of these processes occur. However, none of them is the only rate controlling step as the obtained plot did not pass through the origin. The q_t vs. $t^{0.5}$ trend can be divided into two parts. In the early adsorption step up to 10 min, the process is generally controlled by both the limiting factors. The subsequent adsorption step, characterized by lower slope, is mainly controlled by the film diffusion.

Conclusion

CNTs–COOH has a high adsorption ability towards scandium ions for their preconcentration and removal from aqueous solutions. The multilayer adsorption of Sc(III) was observed at pH 3. The adsorption kinetics onto carbon nanotubes was fast and the removal of Sc(III) was over 95% during the first 2 min. The obtained data were fitted using the pseudo-second-order kinetic model and the film diffusion is the main controlling factor.

As compared with recently reported methods regarding the sorption of Sc(III) on different solid materials, carbon nanotubes offer high adsorption capacity and fast sorption kinetics.

Experimental

Stock solution of scandium solutions were prepared from 1000 mg dm^{-3} stock solution from Merck by stepwise dilution. Multiwalled carboxylic acid-functionalized carbon nanotubes (purity > 95%, length 1–5 μm , and average diameter of 9.5 nm) were purchased from Sigma-Aldrich and were used without further purification. Based on the information provided by the manufacturer, CNTs have a hollow structure and were produced by a conventional chemical vapor deposition. The content of surface carboxylic functional groups evaluated by the classical Boehm titration method was 2.40 mmol g^{-1} using a Metrohm Titrando automatic titrator.

Sorption studies

To estimate the sorption capacity, 50 mg of CNTs was mixed with 10 cm^3 of Sc(III) solution at pH 3 and concentration range of $1\text{--}300 \text{ mg dm}^{-3}$. After shaking the solution for 4 h at room temperature, the metal concentration was determined by ICP OES method (Thermo Scientific iCAP 6000 series). The amount of retained metal ions was calculated as the difference between the initial and final concentrations at equilibrium. The sorption capacity q_e (mg g^{-1}) was calculated using the following equation: $q_e = [(c_o - c_e)V] m^{-1}$, where c_o and c_e are the initial and equilibrium concentrations (mg dm^{-3}), respectively, V is the volume of solution and m is the weight of a sorbent.

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