

Scandium Adsorption from Sulfuric-Chloride Solutions by PANI/CNTs Nanocomposite

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Abstract

The article studies the adsorption of the rare-earth element of scandium on a nanocomposite synthesized by carbon nanotubes modified with polyaniline. Using the methods of scanning electron microscopy, Raman spectroscopy and thermogravimetry, the physicochemical properties of the sorbent were determined. Equilibrium and kinetic experimental studies of the adsorption of scandium ions from sulfuric acid-chloride solutions were carried out. Kinetic results were processed using pseudo-first and pseudo-second order models, internal diffusion, and also the Elovich model. The equilibrium sorption data were described by the models of Langmuir, Freundlich, Henry and Dubinin–Radushkevich. The kinetic studies showed that the time to reach sorption equilibrium for the material under study was 10 minutes. The maximum adsorption capacity of the nanocomposite according to the Langmuir model reached 2.23 mg/g. A study of the kinetics of adsorption showed that the extraction of scandium ions proceeds in a mixed diffusion mode along with the sorbate-sorbate interaction. The equilibrium adsorption data correlate well in the coordinates of the Henry, Langmuir and Dubinin–Radushkevich models, which indicated monolayer absorption. The calculated value of the free energy of adsorption indicated the physical nature of the extraction of scandium ions on a nanocomposite.

Keywords

Scandium; nanocomposite; polyaniline; carbon nanotubes; isotherm and kinetic models.

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1. Introduction

One of the most dispersed and lightweight rare-earth elements, scandium, is used for the manufacture of parts in aircraft construction and the production of sports equipment in aluminum alloys; solid oxide fuel cells and metal halide lamps, in laser technology, special ceramics [1, 2]. Its use is limited by the high price and sophisticated technology of passing in the complex processing of bauxite, uranium ores, ilmenites, wolframites, cassiterites, zircon.

Extraction of scandium from solutions is carried out using sorption and extraction methods [2, 3]. When using extractants and materials containing them – impregnates or TWEX [4–10] – there is a transition of extractants and solvents into solution due to solubility, which increases the cost of scandium extraction.

The extraction of scandium present in solutions both in the form of a cation and in the composition of anionic complexes [2, 3] using both known resins [3] and special selective complexing expensive amino-phosphorus-containing ion exchangers [11, 12] distinguishes long time to establish equilibrium (6 hours or more). The rate of metal extraction on fibrous materials increases [13], but their volumetric capacity is much lower, which leads to a significant increase in the volume of apparatuses. Nanocomposites based on carbon nanotubes can be alternative sorption materials, which often have better kinetic characteristics than granular synthetic organic resins [14].

To prepare effective adsorbents with high absorption capacity, porous carriers are treated mechanically, physically, or chemically. The most effective is a chemical method based on modifying the surface of the sorbent.

The choice of polyaniline as a modifier of modern absorbing materials is due to the fact that this polymer, due to the presence of a system of conjugated bonds and chemical composition features, exhibits good adsorption properties with respect to various cations and anions. It is also characterized by non-toxicity, practically insoluble in water, has a low cost. Polyaniline (PANI) is a polymer containing phenylenediamine and iminoquinoid groups.

The PANI amino- and imino-groups can probably interact with some metal cations by the donor – acceptor mechanism; therefore, PANI can be expected to adsorb metal cations from solutions. In the literature, information on the adsorption properties of PANI is insufficient [15, 16].

However, there are a number of works describing the use of absorbers modified with polyaniline in the processes of liquid-phase sorption of pollutants of different chemical nature. The authors of [17] prepared adsorbents by modifying rice husks with polyaniline under different conditions of polymer synthesis. It was found that the adsorbents obtained are characterized by a high adsorption capacity with respect to zinc and chromium cations. Spruce sawdust modified with polyaniline [18, 19] exhibited high adsorption ability with respect to anionic and cationic dyes.

The authors of the study [20] synthesized PANI directly on the surface of sawdust chemically at room temperature ($(22 \pm 2)^\circ\text{C}$). Sawdust coated with polyaniline (PANI/SD) was then used as an adsorbent to remove Green 25 (AG 25) acid dye from aqueous solutions. In [21], the absorption properties of polyaniline immobilized on glass plates (PANI/glass) were studied for the adsorption of methyl orange (MO) dye from aqueous solutions. In the study [22], sawdust was coated with polyaniline using direct chemical polymerization and used as an adsorbent to remove acid dye (Acid Violet 49) from aqueous solutions.

Thus, the use of polyaniline-modified carrier materials as effective adsorbents for organic and inorganic pollutants seems to be very promising, although not sufficiently studied, in the field of science and technology.

The purpose of the work is to study the sorption characteristics of a composite material based on carbon nanotubes and polyaniline (PANI / CNT) during the extraction of scandium from sulfuric acid-chloride solutions.

2. Materials and Experimental methods

2.1. Preparing PANI / CNT nanocomposite

The “polyaniline (60 wt.%) / CNT” nanocomposite used in the study was prepared at the Tambov State Technical University (RF, Tambov). It was obtained by

oxidative polymerization of aniline on the surface of CNTs. The CNTs were modified with polyaniline (outer diameter 8–15 nm; inner diameter 4–8 nm; specific surface area $\geq 300 \text{ m}^2/\text{g}$) produced by the CVD method (RF, Tambov, NanoTechCenter LLC). The content of PANI in these nanocomposites varied within wide limits, from 10 to 90 % of the mass. It was determined by the choice of the number of starting reagents in the synthesis. Carbon nanoparticles acted as texture-forming components, giving the material porosity and a developed surface.

The synthesis of composites was carried out according to the following procedure. A portion of CNTs was ultrasonically dispersed in distilled water. Then, concentrated hydrochloric acid was added to the resulting suspension in an amount necessary for a given initial pH level = 1. After that, aniline hydrochloride (0.05 M) was slowly introduced with stirring, ammonium persulfate (0.06 M) was added. The resulting suspension was placed in a container with a stirrer and stirred for 2 hours. The resulting material was successively washed on the filter with distilled water until the color of the filtrate disappeared, and then with isopropyl alcohol to remove oligomeric products from the reaction mass. The resulting material was dried at a temperature of 80°C to constant weight.

PANI in these nanocomposites were in protonated form (if the synthesis is carried out in an acidic environment), or in the form of a PANI base (if the synthesis product is treated with an ammonia solution). In an acidic and slightly acidic medium it was in protonated form, in a neutral mixture it was a mixture of forms, and in an alkaline medium there was no protonated form.

2.2. Sorption studies

Experiments on the sorption of scandium by the PANI / CNT nanocomposite were carried out under static conditions from sulfuric chloride solutions ($[\text{SO}_4^{2-}]$, $10 \text{ g}/\text{dm}^3$; $[\text{Cl}^-]$, $1 \text{ g}/\text{dm}^3$) with a scandium concentration of $0.44 \text{ mmol}/\text{dm}^3$ ($20 \text{ mg}/\text{dm}^3$) and the chosen acidity corresponding to $\text{pH} = 3$. The ratio of the phases “nanocomposite: solution” upon adsorption was 1 : 200 (g : ml). After the phases contacted, they were separated and the aqueous phase was analyzed for scandium content using the photometric method. The adsorption (A , mg/g) of scandium in the nanocomposite was calculated from the difference in the concentrations of scandium in the initial and final solutions, taking into account the phase ratio. The distribution coefficient of scandium K_d , ml/g , in the nanocomposite was calculated as the ratio of the equilibrium adsorption value of the composite on scandium (mmol/g or mmol/ml) to its equilibrium concentration in the solution (mmol/dm^3).

The kinetics of adsorption of scandium by a nanocomposite was studied by the method of limited volume of a solution in a setup with thermostatically controlled cells at room temperature (temperature measurement error is $\pm 0.1^\circ$). The ratio of the weight of the composite (g) to the volume of the solution (ml) was 1 : 200.

2.3. Material characterization

The morphological and structure characteristics of the materials were examined by scanning electron microscopy (SEM) under a Neon 40 microscope (Carl Zeiss, Jena, Germany). Raman spectra were recorded on a DXR™ Raman microscope (Thermo Scientific Instruments Group, Waltham, MA, USA). To determine mass losses and thermal effects, a STA 449 F3 Jupiter instrument (NETZSCH-Feinmahltechnik GmbH, Selb, Germany), which allows for simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC) measurements, was employed.

3. Results and discussion

3.1. Properties of the PANI / CNT nanocomposite

The authors studied the morphology of the obtained nanocomposite material. In Fig. 1 shows SEM images of CNT “Taunit-M” and PANI / CNT.

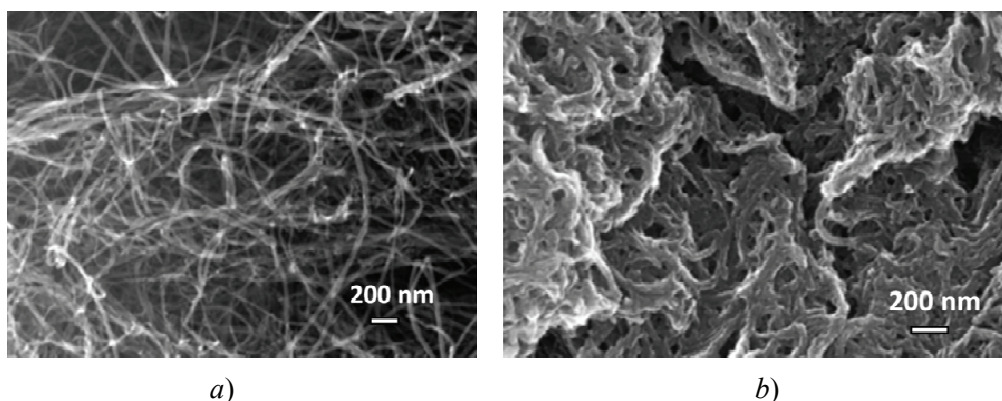


Fig. 1. SEM images of initial Taunit-M nanotubes (a) and PANI / CNT nanocomposite (b)

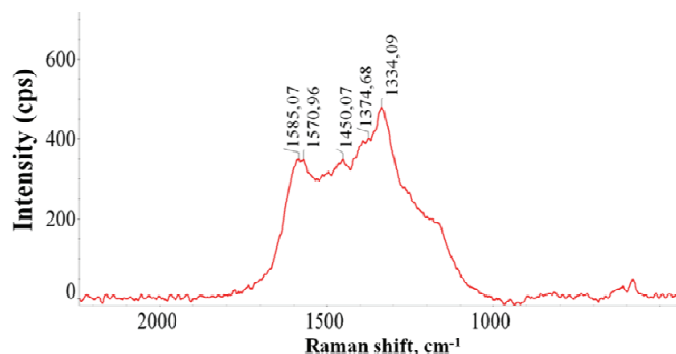


Fig. 2. Raman spectrum of the PANI / CNT composite

A significant change in the structure of CNTs after modification with polyaniline should be noted – the material acquired a denser structure due to the polymer coating the surface of CNTs.

The results of Raman spectroscopy (Raman scattering) are presented in Fig. 2. Peaks characteristic of the protonated form of the polyaniline emeraldine salt are present on the spectra: 1585 cm^{-1} – peak G corresponds to stretching vibrations of C—C bonds in graphene sheets [23], 1570 cm^{-1} – stretching vibrations of C=C bonds in quinondiimine fragments [24], 1450 cm^{-1} – deformation vibrations of C=N bonds in quinondiimine fragments (bipolarons) [25], 1374 cm^{-1} – stretching vibrations of C—N⁺* bonds in delocalized polaron structures [26, 27], 1334 cm^{-1} – peak D indicates the formation of diamond-like sp^3 bonds with the occurrence of topological defects in graphene layers and the presence of amorphous carbon particles [23].

Figure 3 shows the TG and DSC curves taken for the PANI (60 wt.%) / CNT composites. At a temperature of about 350°C , irreversible thermal and thermo-oxidative degradation of the material begins, which ends at 640°C .

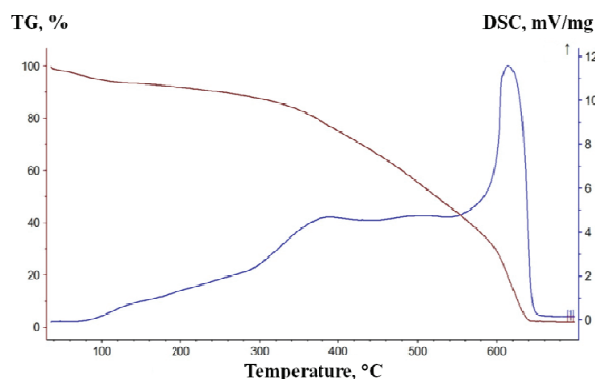


Fig. 3. Thermograms (TG) and differential scanning calorimetry (DSC) curves of PANI / CNT composite

3.2. The findings of adsorption studies

Using the PANI / CNT nanocomposite, we obtained the isotherm of sorption of scandium from sulfuric chloride solutions of the above composition, which has a linear character (Fig. 4) and can be described by the Henry equation.

During adsorption from low-concentration solutions, the amount of adsorbed substance is directly proportional to the content of the adsorbent in the solution. Therefore, the experimental isotherm is a straight line extending from the origin. These initial regions are well described by the Henry isotherm equation [28]:

$$Q_e = K_H C, \quad (1)$$

where Q_e is adsorption capacity, $\text{mg}\cdot\text{g}^{-1}$; C is equilibrium concentration, $\text{mg}\cdot\text{L}^{-1}$; K_H is Henry constant, which characterizes the distribution of the substance between the adsorbent and the solution, $\text{l}\cdot\text{g}^{-1}$.

According to the calculation results, Henry constant $K_H = (0.555 \pm 0.027) \text{ l}\cdot\text{g}^{-1}$.

The experimental data were also processed in the coordinates of the Langmuir equation (2) and Freundlich equation (3)

$$\frac{1}{Q_e} = \frac{1}{Q_{\max}} \frac{1}{b C}, \quad (2)$$

$$\ln Q_e = -\frac{1}{n} \lg C + \lg k, \quad (3)$$

where Q_{\max} is maximum adsorption capacity, $\text{mg}\cdot\text{g}^{-1}$; b is adsorbent-adsorbate affinity distribution (adsorption energy), $\text{L}\cdot\text{mg}^{-1}$; n is adsorption favorability indicator; k is adsorption capacity of the adsorbent, $\text{mg}\cdot\text{g}^{-1}\cdot\text{L}\cdot\text{mg}^{-1}$ [29].

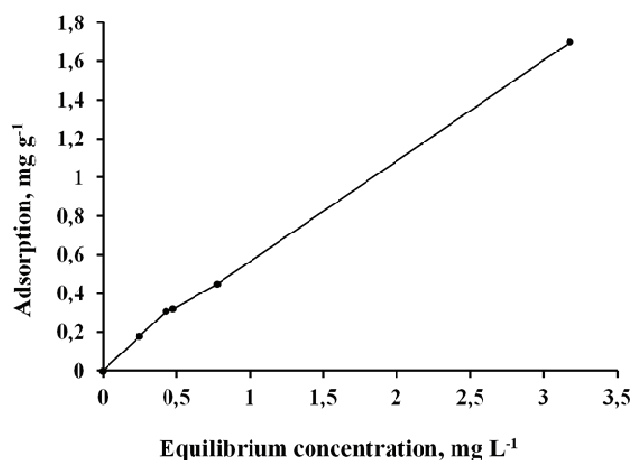


Fig. 4. Scandium sorption isotherm by PANI / CNT nanocomposite

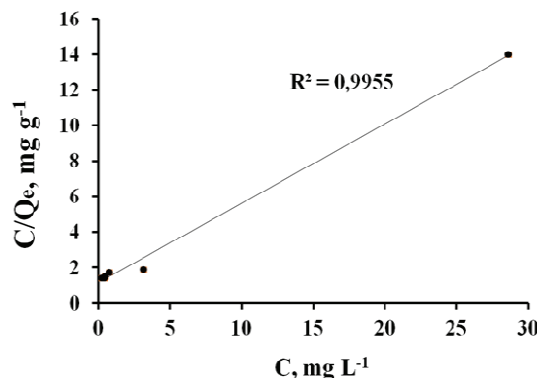


Fig. 5. The isotherm of scandium adsorption on PANI / CNT in Langmuir coordinates

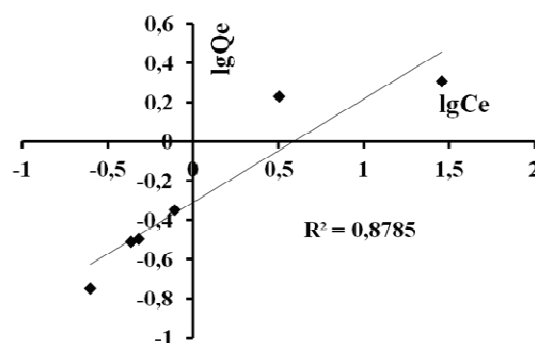


Fig. 6. The isotherm of scandium adsorption on PANI / CNT in Freundlich coordinates

Based on the obtained dependences (Figs. 5, 6), the Langmuir monomolecular sorption with the maximum adsorption capacity of the PANI / CNT nanocomposite for scandium ions $Q_{\max} = 2.23 \text{ mg/g}$ predominates during scandium ion absorption.

These isotherms were processed using the Dubinin–Radushkevich equation, taking into account the porous structure of the adsorbent [29].

In linear form, this equation has the form:

$$\ln Q_e = -K_{\text{DR}} \varepsilon^2 + \ln Q_{\max}, \quad (4)$$

where K_{DR} is Dubinin–Radushkevich constant, associated with sorption energy, mol^2/kJ^2 ; ε is Polanyi potential, $\text{kJ}\cdot\text{mol}^{-1}$.

The linearized dependence is presented in Fig. 7.

The value of the Dubinin–Radushkevich constant was $1.68 \cdot 10^{-2} \text{ mol}^2/\text{kJ}^2$. According to the linearized dependence, the adsorption energy was calculated by the following formula:

$$E = \left(\sqrt{2K_{\text{DR}}} \right)^{-1}, \quad (5)$$

where E is free energy of adsorption, $\text{kJ}\cdot\text{mol}^{-1}$.

The sorption energy was 5.46 kJ/mol , which indicated the predominance of physical adsorption during the absorption of scandium ions from sulfuric chloride solutions [29].

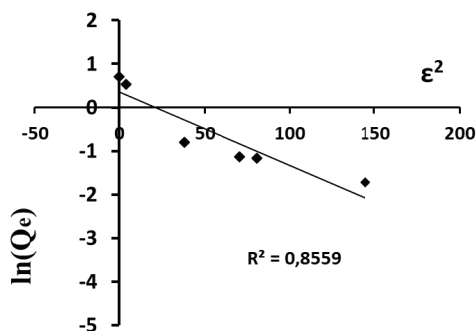


Fig. 7. Scandium sorption isotherm in linearized coordinates (Dubinin–Radushkevich equation)

The findings of kinetic studies of the scandium sorption from model sulfur-chloride solutions with a nanocomposite at room temperature and at 40 °C showed that the integral kinetic curves of scandium adsorption had a characteristic convex shape (Fig. 8).

According to experimental studies, the adsorption capacity of the PANI / CNT nanocomposite upon absorption of scandium ions was 0.3 mg/g at room

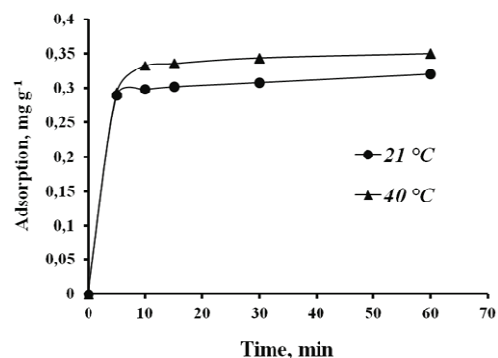


Fig. 8. Integrated kinetic curves of scandium adsorption on the PANI / CNT nanocomposite

temperature and 0.34 mg/g at 40 °C. The equilibrium time was 10 min at the studied temperatures.

The data of these curves were processed in accordance with the kinetic equations of the pseudo-first and pseudo-second-order models (Table 1, Figs. 9, 10), as well as the Elovich model (Fig. 11) and the intra-diffusion Weber–Morris model (Fig. 12).

Table 1

Models implemented to describe the adsorption kinetics* [30, 31]

Model	Equation
Pseudo-first-order	$\lg(Q_e - Q_t) = \lg(Q_e) - \frac{k_1 t}{2.303}$ (6)
Pseudo-second-order	$\frac{t}{Q_e} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t$ (7)
Elovich	$Q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln(t)$ (8)
Intraparticle diffusion	$Q_t = k_{i,d} t^{0.5} + c$ (9)

* t – adsorption time, min; Q_e – adsorption at equilibrium, mg g^{-1} ; Q_t – adsorption at time t , mg g^{-1} ; k_1 – pseudo-first-order adsorption rate constant (min^{-1}); k_2 – pseudo-second-order adsorption rate constant, $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$; $k_{i,d}$ – intraparticle diffusion coefficient, $\text{min}^{-1/2}$; c – boundary layer thickness constant, $\text{mg} \cdot \text{g}^{-1}$; α – initial flow rate, $\text{min}^{-1} \cdot \text{mg} \cdot \text{g}^{-1}$; β – desorption constant (degree of surface coverage and activation energy of chemisorptions), $\text{g} \cdot \text{mg}^{-1}$.

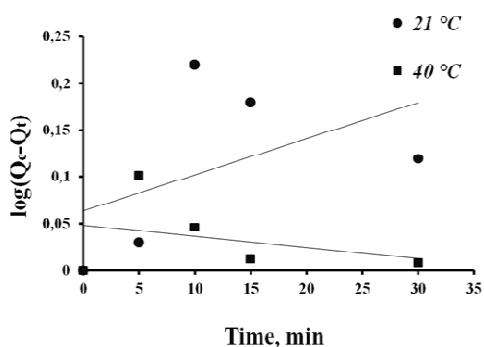


Fig. 9. Linearization of kinetic data on scandium adsorption on a PANI / CNT nanocomposite using a pseudo-first order model

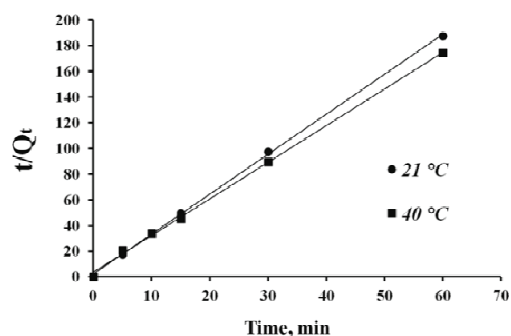


Fig. 10. Linearization of kinetic data on scandium adsorption on a PANI / CNT nanocomposite using a pseudo-second order model

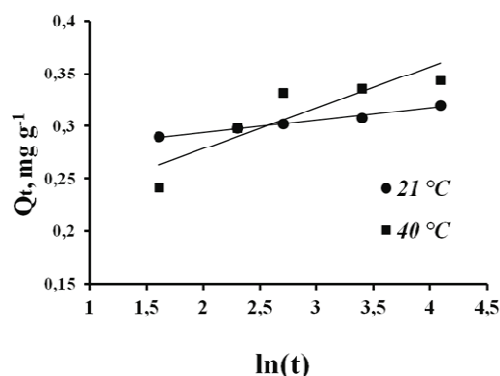


Fig. 11. Linearization of kinetic data on scandium adsorption on the PANI / CNT nanocomposite according to the Elovich model

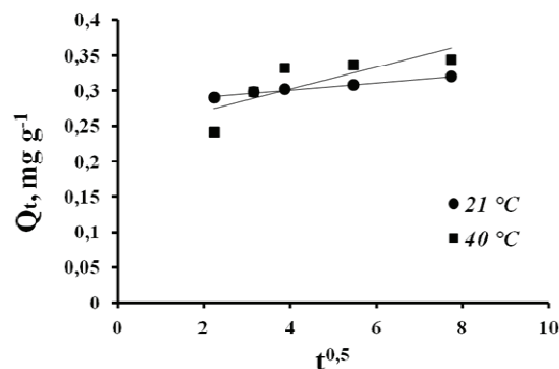


Fig. 12. Linearization of kinetic data on scandium adsorption on the PANI / CNT nanocomposite according to the internal diffusion model Weber–Morris

Table 2

Scandium sorption constants on the PANI / CNT nanocomposite at various temperatures

Pseudo-first-order model		Pseudo-second-order model		Elovich model		Weber–Morris internal diffusion model	
k_1	R^2	k_2	R^2	β	R^2	K_p	R^2
<i>Room temperature</i>							
0.0089	0.223	5.03	0.999	86.21	0.9832	0.005	0.98
<i>Temperature 40 °C</i>							
0.027	0.104	2.41	0.998	25.64	0.7951	0.016	0.64

The kinetic constants and determination coefficients obtained by processing the data for the considered models (Table 2) indicated that the kinetics of scandium sorption by the nanocomposite was satisfactorily described using the pseudo-second order model, the Elovich equation, and the model of intraparticle diffusion.

Thus, we can assume that the mechanism of sorption of scandium by the PANI / CNT nanocomposite has a diffusion character with the contribution of chemical interaction by the second-order reaction between scandium ions. The intradiffusion model allowed for identification of sorption mechanisms. The constant C in the equation was proportional to the thickness of the boundary layer (film). If it is zero, that is, the line passes through the origin, and then the sorption process limits the internal diffusion. In the opposite case, which was observed when studying the kinetics of scandium sorption by a nanocomposite, the process proceeded in the external diffusion region, or in the mixed-diffusion region. The correlation according to the Elovich model indicates the energy heterogeneity of the active centers of the PANI / CNT nanocomposite.

4. Conclusion

In the present study, the adsorption capacity of the developed CNT-based nanocomposite modified with polyaniline was determined. The physicochemical characteristics of the sorbent were studied by scanning electron microscopy, Raman spectroscopy, and thermogravimetry. Adsorption studies were carried out at various temperatures, namely, isotherms and kinetic absorption curves of scandium ions from sulfuric acid-chloride solutions were constructed. It was found that the sorption time was 10 min at the maximum adsorption capacity according to the Langmuir model equal to 2.23 mg/g, and an increase in temperature does not significantly affect the size of the adsorption capacity. To determine the sorption mechanism, the equilibrium experimental data were processed in the coordinates of the equations of Henry, Langmuir, Freundlich, Dubinin–Radushkevich. And kinetic data – models of pseudo-first and pseudo-second order, Elovich and internal diffusion. The rate-limiting stage of the scandium sorption process on the PANI / CNT nanocomposite is apparently diffusion rather than the cation exchange of protons for Sc^{+3} cations, which is confirmed by the value of the adsorption free energy $E = 5.46$ kJ/mol and correlation according to the internal diffusion model.

Acknowledgements

The research was funded by the Ministry of Education and Science of the Russian Federation (Project No.16.1384.2017/PCh).

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