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ORIGINAL ARTICLE

Sorption Of Cerium By The Pani / Cnt Composition From Sulfuric Chloride Solution

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KEYWORDS

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Isotherm;
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Kinetic models

ABSTRACT: 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 cerium from sulfuric chloride solutions. The sorption characteristics of a composite material based on carbon nanotubes and polyaniline (PANI/CNT) during the extraction of cerium from sulfuric chloride acid solutions are investigated. Nanocomposite polyaniline (60 wt.%)/CNT was prepared by oxidative polymerization of aniline on the CNT surface. Morphological and structural characteristics of the material were obtained using scanning electron microscopy.Using the PANI/CNT nanocomposite, a isotherm of cerium adsorption was obtained from aqueous solutions of the above composition, which has a linear character and can be described by the Henry equation.The kinetic constants obtained by processing the data on pseudo-first and pseudo-second order models and the Elovich model indicate that the kinetics of cerium adsorption on the PANI / CNT nanocomposite with a higher value of the correlation coefficient is described using a pseudo-second order model. Moreover, it was found that the equilibrium sorption time was 30 min, and the adsorption capacity of the sorbent was 15 mg g^{-1}. Data processing using kinetic models showed that absorption occurs due to the chemical interaction of cerium and the functional groups of the nanocomposite. As a consequence, it can be assumed that the chemical interaction with surface functional groups-carboxylic, phenolic, etc. – contributes to the adsorption mechanism of cerium by the PANI-CNT nanocomposite.

INTRODUCTION

Cerium is a widespread rare-earth element used for alloying structural steels, polishing optical and mirror glass, and producing catalysts, special-purpose glasses, refractory materials, light sources, pyrophoric alloys, fuel cells, and chemical current sources [1]. It is obtained by isolation of rare earth elements, mainly from carbonatites and alluvial deposits [2,3]. In hydrometallurgical processing of raw materials for the extraction of cerium, its concentration and separation from other rare earth elements used, as a rule, sorption and extraction methods [4].

The use of cerium, present in solutions in the form of a cation or in the composition of anionic complexes [5,6], traditional resins in sorption processes, distinguishes a long time of establishing equilibrium - more than 4 hours. When using fibrous materials for the extraction of metals, the process speed can be increased [7], however, their volumetric capacity is much lower, which can lead to a significant increase in the volume of apparatuses.

To improve the kinetic characteristics of sorption with an

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increase in selectivity, materials can be used that combine the properties of sorbents and extractants — impregnates, TVEKSs, microencapsulated extractants [8]. The disadvantages of these materials include the gradual loss of extractant from the carrier, which leads to a decrease in capacitive characteristics.

Alternative sorption materials, which often have better kinetic characteristics than granular synthetic organic resins, can be carbon sorbents — nanotubes and graphenes, as well as composites based on them [9,10].

Mechanical, physical or chemical methods of surface treatment can increase the absorption capacity of porous carbon carriers. A chemical method based on modifying the surface of the sorbent is most effective in this regard.

The choice of polyaniline (PANI) as a modifier containing phenylenediamine and iminoquinoid groups is due to its good adsorption properties with respect to cations and anions, which correlates with the presence of a conjugated bond system in it. Moreover, this polymer, characterized by low cost, is non-toxic, practically insoluble in water.

The amino and imino groups of PANI can probably interact with some metal cations by the donor – acceptor mechanism; therefore, PANI can be expected to adsorb metal cations from solutions. Information on the adsorption properties of PANI is limited [11]. The absorbers modified with polyaniline were used in the processes of liquid-phase sorption of pollutants of various chemical nature. The authors of [12] obtained 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.Polyaniline-modified spruce sawdust [13] exhibit high adsorption ability with respect to anionic and cationic dyes. Modification of eucalyptus sawdust with polyaniline allowed to obtain an effective adsorbent for the isolation of chromium cations.

The authors of the study [14] synthesized PANI directly on the surface of sawdust chemically at room temperature (22 ± 2°C). Sawdust coated with polyaniline (PANI/SD) was then used as an adsorbent to remove Green 25 acid dye (AG 25) from aqueous solutions. In work [15] the absorption properties of polyaniline immobilized on glass plates (PANI/glass) for adsorption of methyl orange (MO) dye from aqueous solutions were studied. In the study [16] polyaniline was coated with sawdust by direct chemical polymerization and used as an adsorbent to remove acid dye (Acid Violet 49) from aqueous solutions.

Thus, the use of carrier materials modified with polyaniline as effective adsorbents for inorganic compounds 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 cerium from sulfuric chloride solutions.

MATERIALS AND METHODS

Obtaining Pani / Cnt nanocomposite

The nanocomposite polyaniline (60 wt.%)/CNT used in the work was made at the Tambov State Technical University (Tambov). It is obtained by oxidative polymerization of aniline on the surface of CNTs. CNTs were modified with polyaniline (outer diameter 8–15 nm; inner diameter 4-8 nm; specific surface area ≥ 300 $m^2 g^{-1}$) produced by the CVD method (Tambov, NanoTechCenter LLC). The content of PANI in these nanocomposites can vary within wide limits, from 10 to 90% of the mass. It is determined by the choice of the number of starting reagents in the synthesis. Carbon nanoparticles act 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. Then, aniline hydrochloride (0.05 M) was slowly added thereto 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 can be 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 is in protonated form, in a neutral mixture of forms is possible, in an alkaline medium there is no protonated form.

Methods for characterizing Pani-Cnt

Morphological and structural characteristics of the material were obtained using scanning electron microscopy using 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 the mass loss and thermal effects, the STA 449 F3 Jupiter instrument (NETZSCH-Feinmahltechnik GmbH, Selb, Germany) was used, which allows continuous thermogravimetry (TG) and differential scanning calorimetry (DSC).

Studies of sorption

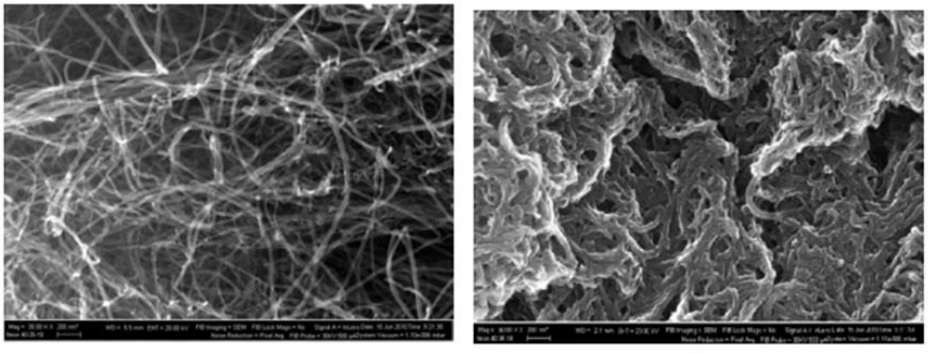
Experiments on the sorption of cerium by the PANI/CNT nanocomposite were carried out under static conditions from sulfuric chloride solutions ((SO_4^{2-}), 10 g dm^3; (Cl^-), 1 g dm^{3-1}) with a cerium concentration of 0.71 mmol dm^{3-1} (100 mg dm^{3-1}) and the selected acidity corresponding to pH 3.4. The phase ratio of the nanocomposite: solution upon adsorption was 1: 500 (g: ml). After the phases contacted, they were separated and the aqueous phase was analyzed for cerium using the photometric method. The adsorption (A, mg g^{-1}) of cerium in the nanocomposite was calculated from the difference in cerium concentrations in the initial and final solutions, taking into account the phase ratio. The distribution coefficient of cerium Kd, ml/g in the nanocomposite was calculated as the ratio of the equilibrium adsorption of the composite by cerium (mmol g^{-1} or mmol ml^{-1}) to its equilibrium concentration in the solution (mmol dm^{3-1}).

The kinetics of cerium adsorption by a nanocomposite was studied by the method of limited solution volume in a setup with thermostatically controlled cells at room temperature (temperature measurement error is ± 0.1°C). The ratio of the weight of the composite (g) to the volume of the solution (ml) was 1: 200.

RESULTS AND DISCUSSION

Properties of the Pani / Cnt nanocomposite

The authors of the work studied the morphology of nanocomposite material. In Figure 1 shows SEM images of CNT “Taunit-M” and PANI / CNT. A significant change in the structure of CNTs (Figure 1a) after modification with polyaniline (Figure 1b) should be noted – the material acquired a denser structure due to the polymer coating the CNT surface.



a b

Figure 1. SEM images of the initial CNT “Taunit-M” (a) and the PANI/CNT (b) nanocomposite.

The results of Raman spectroscopy (Raman scattering) are presented in Figure 2. The spectra contain peaks characteristic of the protonated form of the polyaniline emeraldine salt: 1585 cm^{-1} - peak G corresponds to stretching vibrations of C–C bonds in graphene sheets [17], 1570 cm^{-1}- stretching vibrations of C=C bonds in quinondiimine fragments [18], 1450 cm^{-1} - deformation vibrations of C=N bonds in quinondiimine fragments (bipolarons) [19], 1374 cm^{-1} - stretching vibrations of C-N^{+*} bonds in delocalized polaron structures [19], 1334 cm^{-1} - peak D indicates the formation of diamond-like sp^3-bonds when topological defects occur in graphene

layers and the presence of amorphous carbon particles [20].

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

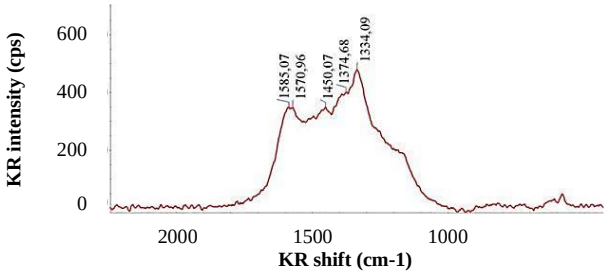


Figure 2. Raman spectrum of the PANI / CNT composite.

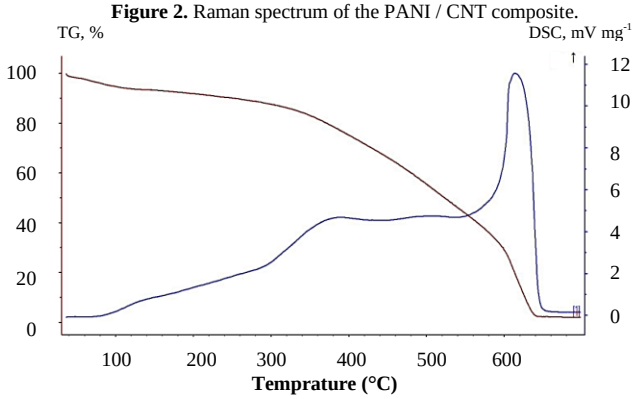


Figure 3. TG and DSC curves of the PANI / CNT composite.

Adsorption of cerium by nanocomposite Pani / Cnt

Using the PANI / CNT nanocomposite, the cerium adsorption isotherm was obtained from aqueous solutions of the above composition, which has a linear character (Figure 4) and can be described by the Henry equation [21].

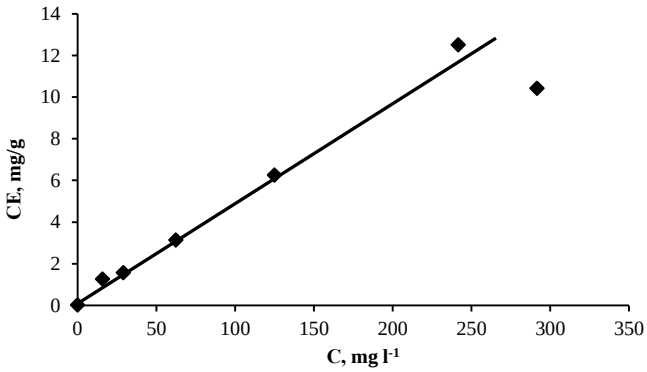


Figure 4. Adsorption isotherm of Cerium with the PANI / CNT nanocomposite.

Henry's constant was calculated according to Henry's equation:

$CE = K_H \cdot C$,

гдеCE – sorption capacity of cerium, mg g^{-1}

K_H – Henry constant, l g^{-1}

C – equilibrium concentration of cerium, mg l^{-1}

Henry's constant was (40 ± 5) ml g^{-1}.

As shown by the results of kinetic studies of the adsorption of cerium from model sulfur-chloride solutions with the PANI-CNT nanocomposite (Figure 5), the integral kinetic curves of cerium adsorption have a characteristic convex shape.

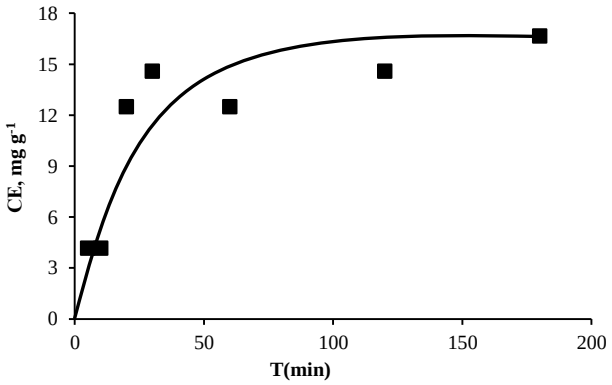


Figure 5. Integral kinetic curve of sorption of cerium on a nanocomposite - PANI / CNT

From Figure 5 it follows that about 80 % of cerium ions are absorbed in the first 30 minutes of the sorption process. The adsorption capacity of the PANI/CNT nanocomposite is 15 mg g^{-1}.

The data of these curves were processed in accordance with the kinetic equations of the pseudo-first and pseudo-second order models, as well as the Elovich model (Eq. 1), which in linear form have the form [22].

$$\log(Qe - Qt) = \log Q_e - \frac{k_1}{2.303}\tau, \qquad (1)$$

$$\frac{\tau}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e}\tau,$$

$$Q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\tau,$$

where, Qe, Qτ–sorption capacity in equilibrium and at time τ, mmol g^{-1}; k_1, k_2 Rate constants of pseudo-first and pseudo-second order, min^{-1}, $g\cdot(mmol\cdot min)^{-1}$, respectively; α– initial rate of the adsorption process, g/(mmol · min); β– Elovich constant, g · $mmol^{-1}$.

Linearization of kinetic data on cerium adsorption on a PANI / CNT nanocomposite using a pseudo first-order model, pseudo-second order model and the Elovich model were shown in Figures 6 - 8.

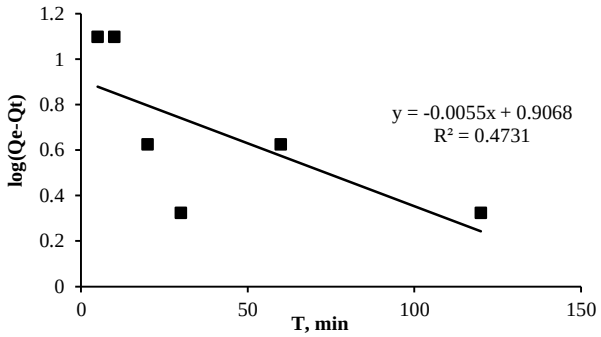


Figure 6. Linearization of kinetic data on cerium adsorption on a PANI / CNT nanocomposite using a pseudo first-order model.

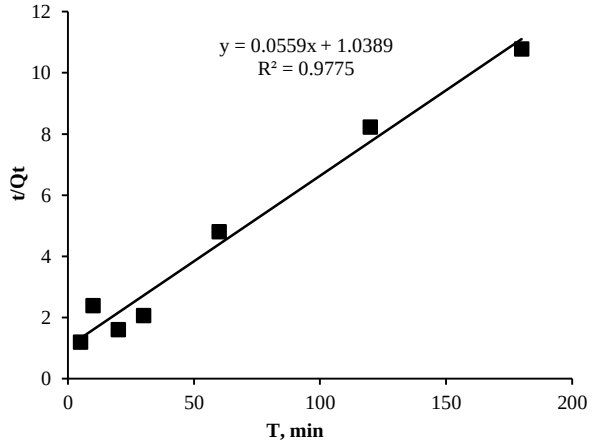


Figure 7. Linearization of kinetic data on cerium adsorption on a PANI / CNT nanocomposite using a pseudo-second order model.

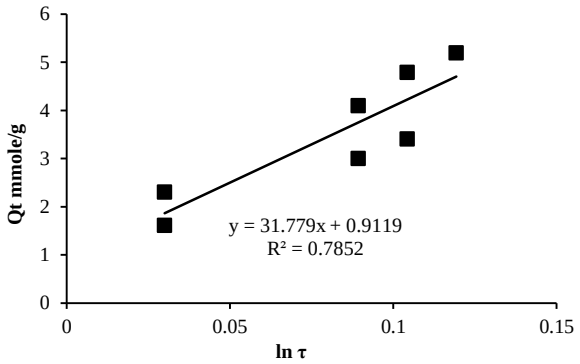


Figure 8. Linearization of kinetic data on the adsorption of cerium on the PANI / CNT nanocomposite according to the Elovich model.

Kinetic constants obtained by processing data on pseudo first and pseudo second order models and the Elovich model [23] (Table 1) indicate that the kinetics of cerium adsorption on the PANI/CNT nanocomposite with a higher correlation coefficient is described using a pseudo second order model.

Table 1. Cerium sorption constants on the Pani / CNT nanocomposite.

Pseudo-first-order		Pseudo-second-order		Elovich	
k_1, 1 min^{-1}	R^2	k_2, $g\cdot(mmol\cdot min)^{-1}$	R^2	β, $g\cdot mmol^{-1}$	R^2
0.01267	0.4731	0.0645	0.9775	0.0314	0.7852

This fact suggests that the mechanism of cerium adsorption by the PANI-CNT nanocomposite contributes to the chemical interaction with the surface functional groups of CNTs - carboxyl, phenolic, as well as donor-acceptor interaction with the phenylenediamine and iminoquinoid groups of PANI.

CONCLUSIONS

Thus, the experimental studies carried out in the work made it possible to establish that the developed PANI / CNT nanocomposite is an effective sorbent for the absorption of Ce^{3+} cations from sulfuric chloride solutions. It was found that the equilibrium sorption time was 30 min, and the adsorption capacity of the sorbent was 15 mg g^{-1}. Data processing using kinetic models showed that absorption occurs due to the chemical interaction of cerium and the functional groups of the nanocomposite.

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Not applicable.

Conflict of interest

The authors declare no conflicts of interest.

REFERENCES

1. Lucas J., Lucas P., Le Mercier T., Rollat A., Davenport W.G., 2018. Rare earths: science, technology, production and use. Elsevier; 2014 Sep 9.

2. Dezhi Q.I., 2018. Hydrometallurgy of rare earths. Extraction and Separation. Elsevier. pp. 804.

3. Fujinaga K., Yoshimori M., Nakajima Y., Oshima S., Watanabe Y., Stevens G.W., Komatsu Y., 2013. Separation of Sc (III) from ZrO (II) by solvent extraction using oxidized Phoslex DT-8. Hydrometallurgy. 133, 33-36.

4. Gupta C.K., Krishnamurthy N., 2016. Extractive metallurgy of rare earths. Taylor & Francis Group, LLC CRC. pp. 869.

5. Kuang S.T., Liao W.P., 2018. Progress in the extraction and separation of rare earths and related metals with novel extractants: A review Sci China Tech Sci. 61, 1319–1328.

6. Korovin V., Pogorelov Y.U., 2011. Comparison of Scandium Recovery Mechanisms by Phosphorus-Containing Sorbents, Solvent Extractants and Extractants Supported on Porous Carrier. Scandium: Compounds, Productions and Applications. Nova Science Publishers Inc., New-York. pp. 77-100.

7. Youcai L.U, Zhang Z., Yanling L.I, Wuping L.I.,

2017. Extraction and recovery of cerium(IV) and thorium(IV) from sulphate medium by an α-aminophosphonate extractant. J Rare Earth. 35(1), 34–40.

8. WU D., Xiong Y., Li D., 2006. Studies on the roles of different components in Cyanex 302 for rare earth ions extraction and separation. Sep. Sci. Technol. 41(8), 1725–1739.

9. Wei H., Li Y., Zhang Z., Xue T., Kuang S., Liao W., 2017. Selective extraction and separation of Ce(IV) and Th(IV) from RE(III) in sulphate medium using Di(2-ethyl-hexyl)-N-heptylaminomethylphosphonate extractant. Solvent Extraction and Ion Exchange. 35(2), 117–129.

10. Komissarova L.N., 2001. Neorganicheskaja i analiticheskaja himija skandija [Inorganic and analytical chemistry of scandium], Moscow: Jeditorial URSS. pp.512.

11. Hérès X., Blet V., Di Natale P., Ouaattou A., Mazouz H., Dhiba D., Cuer F., 2018. Selective extraction of rare earth elements from phosphoric acid by ion exchange resins. Metals. 8(9), 682.

12. Kolodynska D., Hubicki Z., 2012. Investigation of sorption and separation of lanthanides on the ion exchangers of various types. Ion exchange technology. Chapter 6. : IntechOpen. pp. 101–154.

13. Turanov A.N., Karandashev V.K., Sukhinina N.S., Masalov V.M., Emelchenko G.A., 2016. Adsorption of lanthanides and scandium ions by silica sol-gel material doped with novel bifunctional ionic liquid, trioctylmethylammonium 1-phenyl-3-methyl-4-benzoyl-5-onate. Journal of Environmental Chemical Engineering. 4(4), 3788–3796.

14. Oo N.S., Troshkina I.D., Min A., Shilyaev A.V., 2014. Sorption of Rhenium and Vanadium from Mineralized Solutions by Fibrous Ionites. Russ J of Non-Ferrous Metals. 55(3), 242-246.

15. Lee G.S., Uchikoshi M., Mimura K., Isshiki M., 2010. Separation of major impurities Ce, Pr, Nd, Sm, Al, Ca, Fe, and Zn from La using bis (2-ethylhexyl)phosphoric acid (D2EHPA)-impregnated resin in a hydrochloric acid medium. Separ. and Purificat. Technol. 71(2), 186–191.

16. Matsunaga H., Ismail A.A., Wakui Y., Yokoyama T. Extraction of rare earth elements with 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate impregnated resins having different morphology and reagent content. Reactive and Functional Polymers. 49(3), 2001, 189-195.

17. Matsunaga H., Ismail A.A., Wakui Y., Yokoyama T., 2008. Investigation on extraction rate of lanthanides with extractant-impregnated microcapsule. Chem Eng J. 139(1), 93–105.

18. Nishihama S., Kohata K., Yoshizuka K., 2013. Separation of lanthanum and cerium using a coated solvent-impregnated resin. Separ and Purific Technol. 118, 511–518.

19. Ghorbani M., Eisazadeh H., Ghoreyshi A.A., 2012. Removal of Zinc Ions from Aqueous Solution Using Polyaniline Nanocomposite Coated on Rice Husk. Iranica Journal of Energy & Environment. 3(1), 66-71.

20. Kanwal F., Rehman R., Mahmud T., Anwar J., Ilyas R., 2012. Isothermal and thermodynamical modeling of chromium (III) adsorption by composites of polyaniline with rice husk and saw dust. Journal of the Chilean Chemical Society. 57(1), 1058-1063.

21. Ansari R., Mosayebzadeh Z., Keivani M.B., Khah A.M., 2011. Adsorption of Cationic Dyes from Aqueous Solutions using Polyaniline Conducting Polymer as a Novel Adsorbent. Journal of Advances in Scientific Research. 2(2), 27-34.

22. Salvatierra R.V., Oliveira M.M., Zarbin A.J., 2010. One-pot synthesis and processing of transparent, conducting, and freestanding carbon nanotubes/polyaniline composite films. Chemistry of Materials. 22(18), 5222–5234.

23. Šeděnková I., Trchova M., Stejskal J., 2008. Thermal degradation of polyaniline films prepared in solutions of strong and weak acids and in water – FTIR and Raman spectroscopic studies. Polymer Degradation and Stability. 93(12), 2147–2157.

24. Aung W.M., Marchenko M.V., Troshkina I.D., Burakova I.V., Gutnik I.V., Burakov A.E., Tkachev A.G., 2019. Scandium Adsorption from Sulfuric-Chloride Solutions by PANI/CNTs Nanocomposite. Advanced Materials & Technologies. 4(16), 58-65.