

Sorption of Cs(I), Sr(II) and Eu(III) on Modified Nickel Oxide

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Abstract

⁹⁰Sr and ¹³⁷Cs belong to the main fission products existing in the radioactive wastes produced in nuclear power plant. Additionally, europium is a typical member of the lanthanide series and can be utilized as a homologue for the prediction of other lanthanides behavior. In this paper, a novel composite sorbent based on nickel oxide and titanium dioxide was synthesized, characterized and applied for removal of ⁹⁰Sr, ¹³⁷Cs and ¹⁵²⁻¹⁵⁴Eu from aqueous solution. The prepared nanomaterials were characterized by methods of X-ray diffraction (XRD), scanning electron microscopy (SEM) and specific surface area measurements. The main method used for evaluation of nanomaterials retention properties was batch sorption experiment, based on contact of solid material with tracer solution under defined boundary conditions (solid/solution ratio, time, solution composition as pH and ionic strength). The nanomaterials were tested as prospective adsorbents for efficient removal of cesium, strontium or europium from aqueous solution.

Key words: radionuclides, sorption, titanium dioxide, nickel oxide

1. INTRODUCTION

Any activity that produces or uses radioactive materials generates radioactive waste. Disposal of radioactive waste is a complex issue, not only because of the nature of the waste, but also because of the need not to burden future generations. The cesium and strontium are key nuclides in nuclear waste. The reasons for this are following: long half-life of their isotopes (from ~ 30 years for ¹³⁷Cs and ⁹⁰Sr to 2.3 million years for ¹³⁵Cs) and they both can penetrate into the living organism and get it exposed to internal irradiation. Europium is a typical member of the lanthanide series and can be utilized as a homologue for the prediction of other lanthanide behavior. Therefore it is necessary to prevent migration leaking of these radionuclides to the biosphere and develop progressive retention techniques.

Nickel oxide (NiO) is transition metal oxide which has broad applications as catalyst [1], magnetic material [2] or in batteries [3], [4], gas sensors [5] and in solar cells [6]. In recent years there were studies about utilizing of NiO as sorbent for several contaminants. Mahmood [7]–[9] described sorption properties of NiO for Cd(II), Zn(II) and Co(II). Behnajady and Bimehgdar [10] synthesized mesoporous NiO nanoparticles for sorption of Cr(IV). There were several studies about sorption of Pb(II) on NiO or modified NiO [11]–[13]. Another authors synthesized nanosorbents based on NiO for sorption of Congo red [14]–[16]. Noor et al. [17] and Franco et al. [18] synthesized composites based on NiO for sorption of Pb(II) and asphaltenes respectively.

TiO₂ is commercially cheap photocatalyst material, but the interest in TiO₂ is not concentrated only in its photocatalytic properties. Several authors studied sorption of Eu(III) on TiO₂ in different conditions [19]–[21]. Sharygin studied sorption of gaseous iodine and methyl iodide on TiO₂ [22], [23]. Another authors studied sorption of different contaminants on nanosized TiO₂ [24] and on composites based on TiO₂ [25], [26].

In presented work, nanomaterials based on pure nickel oxide (NiO) and composite of nickel oxide and titanium dioxide (NiO-TiO₂) were synthesized by the photo-induced method [27]. These nanomaterials could be effective and cheap adsorbents for remediation of waters contaminated by radionuclides or for reprocessing of nuclear waste.

2. MATERIALS AND METHODS

Materials were analyzed via X-ray powder diffraction (XRPD), using vertical θ -2 θ diffractometer Rigaku MiniFlex 600 with Cu-K α 1,2 radiation ($\lambda_{av} = 0.15418$ nm). ICDD PDF-2 database was used for identification of crystalline materials. The specific surface area (SSA) was measured by selective adsorption of nitrogen from the mixture of hydrogen and nitrogen at the temperature of liquid nitrogen. The SEM was measured on FEI NOVA NANOSEM 450.

2.1 Sorption Materials

NiO powder was produced by calcination (250 °C, 2 h) of the solid precursor, which was formed during irradiation of aqueous solutions containing soluble nickel salts by UV light.

Composite NiO-TiO₂ was prepared by hydrolytic decomposition of TBOT (tetrabutyl orthotitanate) in the presence of nano NiO suspension. TBOT was dissolved in propan-2-ol and intensively stirred. The aqueous suspension of NiO was added in the solution of TBOT and product was filtered and dried. NiO used was photochemically prepared and calcined at 250 °C, as described above.

2.2 Sorption experiments

The sorption properties of produced nanomaterials were evaluated by batch sorption experiments, based on contact of solid material with tracer solution. The volume of solution was 3 ml and the mass of sorbent was 0.02 g or 0.1 g. The contact time was 24 hours unless otherwise specified. Sorption experiments were carried out at 25 °C under atmospheric conditions. After the adsorption of radionuclides, the suspension was centrifuged and an aliquot of the supernatant was measured on the gamma spectrometer (EMPOS MC1256) using NaI(Tl) detector. The volume of measured aliquot was 0.5 ml. The pH of solution was modified by adding of HClO₄ or NH₄OH. The ionic strength of solution was modified by NaClO₄.

The sorption experiments were described by the distribution coefficient (K_d) and percentage of sorption. The definition of K_d is following.

$$K_d = \frac{C_{\text{mass}}}{C_{\text{volume}}} \frac{V}{m} \text{ [ml/g]}, \quad (1)$$

where C_{mass} is concentration of solute adsorbed onto the solid phase, C_{volume} is the concentration of the solute in solution, V [ml] is volume of liquid phase and m [g] is the mass of the sorbent. This model is generally utilized for describing of radionuclide sorption [28].

3. RESULTS AND DISCUSSION

As can be seen from the Fig. 1, XRPD patterns confirmed a nanocrystalline cubic structure of nickel oxide (bunsenite) in the samples of NiO. No diffraction lines corresponding to TiO₂ crystalline phases (anatase, rutile or brookite) were observed in NiO-TiO₂ sample. In this case, NiO is probably covered by the amorphous phase of TiO₂.

The morphology of NiO and NiO-TiO₂ samples is very similar. As it can be demonstrated from SEM in Fig. 2 the photo-induced synthesis followed by the calcination at 250 °C leads to the formation of small spherical nanoparticles assembled into rather big agglomerates.

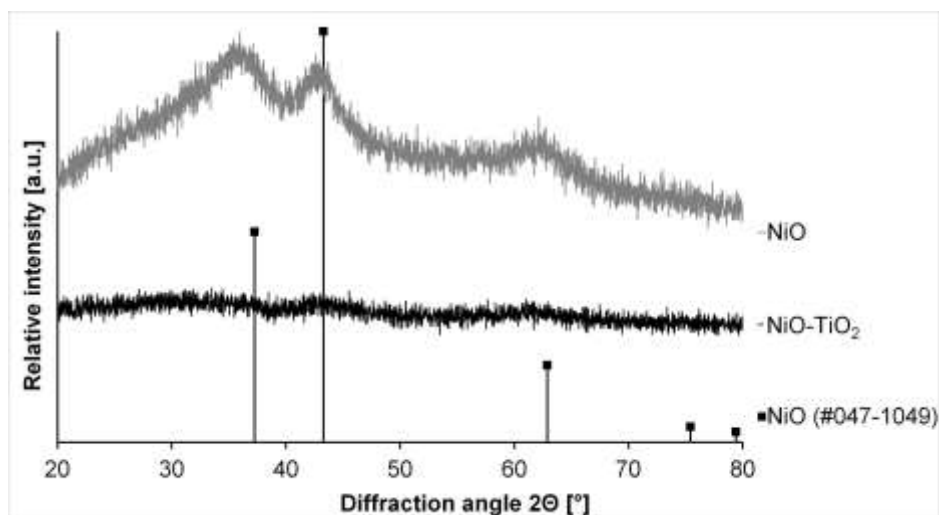


Figure 1: X-ray diffraction patterns of the prepared samples of NiO and NiO-TiO₂.

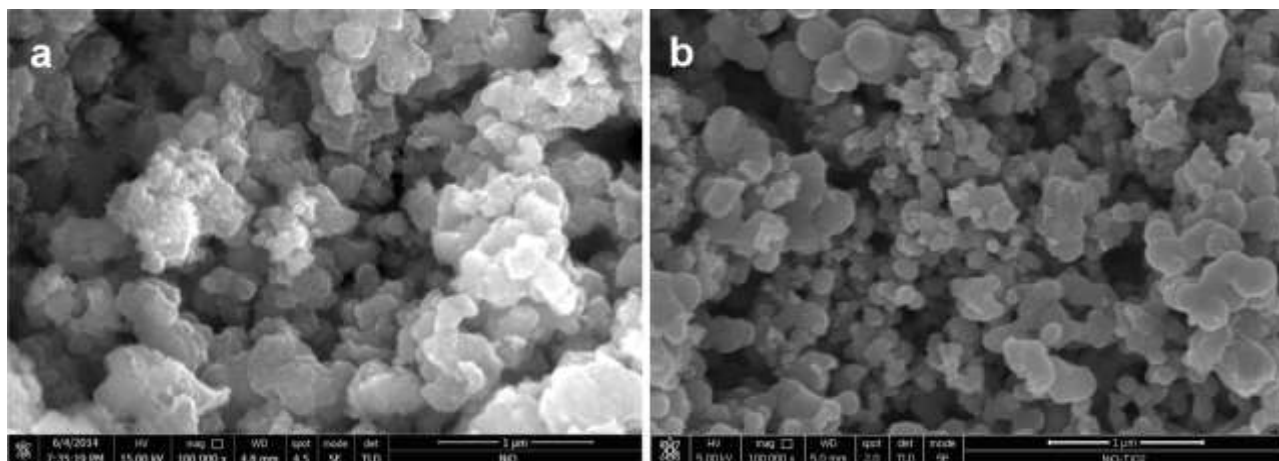


Figure 2: Scanning electron microscopy observations of the prepared nanomaterials: NiO (a) and NiO-TiO₂ (b).

Table 1: The specific surface area (SSA) and sorption on selected materials, $V=3$ ml; $m=0.1$ g; temperature 25 °C; contact time 24 hours

	SSA	Sr	Eu	Cs	Sr	Eu	Cs
	[m ² /g]	Removal %	Removal %	Removal %	K_d [ml/g]	K_d [ml/g]	K_d [ml/g]
NiO	173.9	99.4	99.9	5.8	4896	28983	4
NiO-TiO ₂	84.5	99.6	99.9	95.9	39988	17352	3511
NiO std*	2.2	0.5	99.3	1.4	0	4377	2
TiO ₂	8.5	45.1	99.9	34.9	25	29459	-

* commercially available (Lachema) nickel oxide

The sorption properties are summarized in Table 1. The NiO and NiO-TiO₂ were produced by photo-induced method. The NiO std. and TiO₂ are standard materials. All studied sorbents demonstrate high sorption capabilities for europium, there were not europium left in solution after centrifugation. The NiO and NiO-TiO₂ demonstrate high sorption capability for strontium; the K_d values for NiO and NiO-TiO₂ were in range of thousands and ten thousands ml/g respectively. The K_d value of NiO-TiO₂ for cesium is very high. There is practically no sorption of cesium on NiO. The sorption properties of NiO std. and TiO₂ are very low for

strontium and cesium.

The Figure 3d demonstrates that the sorption kinetics is very fast and the radionuclide uptake does not substantially decrease during interval of 6 days. The kinetics was measured in solution of $4 \cdot 10^{-3}$ M NH_4OH to set ~ 7.5 pH.

The results of sorption dependence on pH and concentration of NaClO_4 for NiO-TiO_2 are summarized in Figure 3a-3c. The pH range was measured from 6.5 to 10 because NiO dissolve in lower pH [7]. There is no dependence of sorption on pH in measured interval. The NaClO_4 was added to solution to modified ionic strength. The sorption of cesium decreases with higher ionic strength - this suggests that sorption mechanism of Cs is ionic exchange. The sorption of strontium and europium is not dependent on ionic strength. This was observed by Bouby et al [29] and Tan et al [30]. This behavior suggests the formation of inner-sphere surface complexes [31] but it is not possible to draw straightforward conclusions on the sorption mechanism from macroscopic data alone, especially if the sorption was measured only in limited interval of pH.

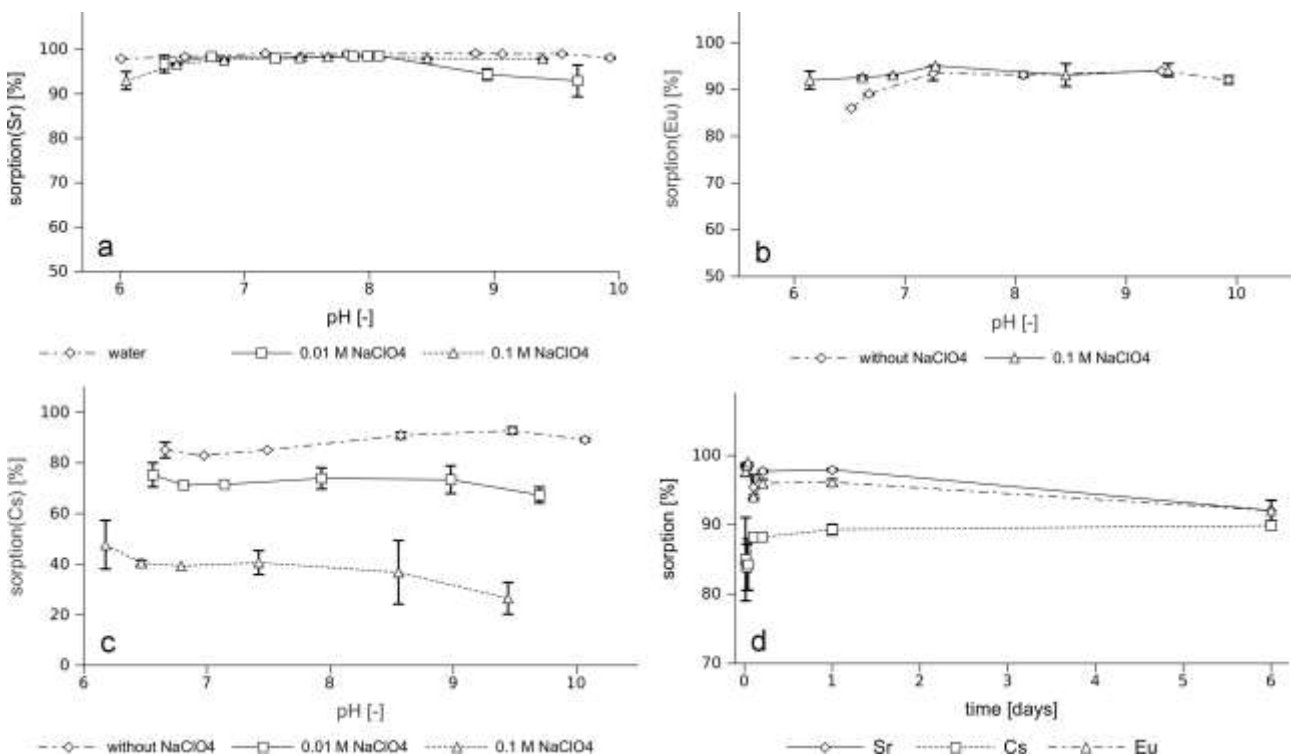


Figure 3: The dependence of sorption on Sr (a), Eu (b) and Cs (c) on pH and concentration of NaClO_4 and kinetics (d) for NiO-TiO_2 , $V=3$ ml; $m=0.02$ g; temperature 25 °C; contact time 24 hours. The error bars represent confidence interval.

4. CONCLUSION

Nanomaterials (NiO and NiO-TiO_2) have been successfully prepared by the photo-induced synthesis. This method leads to the formation of small spherical nanoparticles.

The results demonstrate that NiO produced by photochemical method has enhanced sorption properties, especially for strontium. The composite material based on this NiO and hydrated titanium dioxide has enhanced sorption properties not only for strontium but also for cesium. The results of sorption experiments demonstrate that enhanced sorption properties are not just sum of sorption properties of single components of composite (NiO and TiO_2) but that there is synergic effect. The results from measuring of SES and SEM

suggest that the enhanced sorption properties could be result of greater specific surface area of TiO₂ on the surface of nanosized NiO than TiO₂ has alone.

ACKNOWLEDGEMENTS

Acknowledgements: We thank for the support from Ministry of the Interior of the Czech Republic (Project No. VG20132015132).

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