

APPLICATION OF EXAFS (X-RAY EXTENDED ABSORPTION FINE STRUCTURE) SIMULATION TO DEFINE BOTH THE STRUCTURE OF Fe/Ce OXIDE-BASED COMPOSITES AND THEIR (ADSORPTIVE) PROPERTIES

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ЗАСТОСУВАННЯ СИМУЛЮВАННЯ СПЕКТРІВ EXAFS (ПРОТЯЖНА РЕНТГЕНІВСЬКА АБСОРБЦІЙНА ТОНКА СТРУКТУРА) ДЛЯ ВИЗНАЧЕННЯ ЯК БУДОВИ КОМПОЗИТІВ НА ОСНОВІ Fe/Ce ОКСИДІВ, ТАК І ЇХ (СОРБЦІЙНИХ) ВЛАСТИВОСТЕЙ

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ПРИМЕНЕНИЕ СИМУЛИРОВАНИЯ СПЕКТРОВ EXAFS (ПРОТЯЖНАЯ РЕНТГЕНОВСКАЯ АБСОРБЦИОННАЯ ТОНКАЯ СТРУКТУРА) ДЛЯ ОПРЕДЕЛЕНИЯ КАК СТРОЕНИЯ КОМПОЗИТОВ НА ОСНОВЕ Fe/Ce ОКСИДОВ, ТАК И ИХ (СОРБЦИОННЫХ) СВОЙСТВ

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Ten new composites based on Fe/Ce oxides containing both crystalline and amorphous phases have been synthesized with the aim of applying successful samples in the removal of toxic anions from water solutions. Due to simulation of EXAFS spectra, we defined not only the structure of these materials (in the entire volume regardless of their crystallinity) but also proposed a methodological approach which allows anticipating the anion exchange properties of inorganic sorbents based on the local structure around major atoms which formed metal oxides of Fe/Ce in their outer coordination shells.

Keywords: inorganic composites, two metal oxides, atomic scale structure, extended x-ray absorption fine structure (EXAFS), EXAFS simulation, XRD, FTIR spectra, sorption, toxic anions, water purification

Синтезовано десять нових композитів на основі оксидів Fe/Ce, які містять як кристалічні, так і аморфні фази, з метою застосування вдалих зразків у вилученні токсичних аніонів із водних розчинів. Завдяки симулюванню спектрів EXAFS встановлено не лише структуру матеріалів (по всьому об'єму незалежно від їх кристалічності), а й запропоновано методологічний підхід, що дозволяє передбачати аніонообмінні властивості неорганічних сорбентів базуючись на локальній структурі навколо головних атомів, що утворили складні оксиди Fe/Ce у їхніх зовнішніх координаційних сферах.

Ключові слова: неорганічні композити, оксиди двох металів, структура на атомному рівні, протяжна рентгенівська абсорбційна тонка структура (EXAFS), симулювання спектрів EXAFS, дифрактограми, ГЧ-спектри, сорбція, токсичні аніони, водоочищення

Синтезировано десять новых композитов на основе оксидов Fe/Ce, содержащих как кристаллические, так и аморфные фазы, с целью применения удачных образцов для извлечения токсичных анионов из водных растворов. Благодаря симулированию спектров EXAFS определена не только структура материалов (по всему объему независимо от их кристалличности), но и предложен методологический подход, позволяющий предвидеть их анионообменные свойства базируясь на локальной структуре вокруг главных атомов, образовавших сложные оксиды Fe/Ce в их внешних координационных сферах.

Ключевые слова: неорганические композиты, оксиды двух металлов, структура на атомном уровне, протяжная рентгеновская абсорбционная тонкая структура (EXAFS), симулирование спектров EXAFS, дифрактограммы, ИЧ-спектры, сорбция, токсичные анионы, водоочистка

INTRODUCTION AND RESEARCH TASKS

Knowledge of a material structure is a principal precondition of its successful application. Over last decades, multiphase composites have gained great popularity in various fields of science and technology due to their advantageous properties compared with individual compounds which is briefly explained by the statement of being “greater than the sum of parts”. It is known that standard methods do not allow characterization of the entire composites, which often consists of both crystalline and amorphous phases, which requires both attracting more precision tools (such as EXAFS/XANES) and application of several spectroscopy approaches.

Contamination of drinking water with toxic anions has been a growing which resulted in dramatical (>5 times) lowering of their maximum permissible concentrations (MPC) in drinking water and in a society demand for new materials/technologies. Inorganic anion exchangers based on metal oxides are the class of adsorptive materials which, due to their chemical nature, are capable to achieve the newly established MPCs to toxic anions. Superiority of complex materials (here, metal oxides) over individual compounds is also true for adsorptive removal of toxic substances from water solutions. However, to date, both commercially available inorganic anion exchangers are individual metal oxides (of Al and Fe), Activated Alumina (AA) and Granular Ferric Hydroxide (GFH). Arrival of next generation inorganic sorbents in water market depends on deepening the knowledge of materials chemistry at synthesis and in the final products.

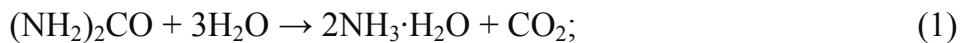
Addressing the society demands for the next generation inorganic sorbents with high affinity to aqueous toxic anions such as arsenate, **the tasks of this work were to:**

- Synthesize a series of new inorganic adsorbents based on oxides of two metals (Fe and Ce) with various ratios of Fe-to-Ce by an advanced, yet relevant to adsorption application, preparation method.
- Characterize the structure of new inorganic composites by several spectroscopy tools (including XANES linear combination fitting and EXAFS simulation) and by measurements of their porous structure.
- Assess adsorptive properties of Fe/Ce complex oxides towards several toxic anions (H_2PO_4^- , H_2AsO_4^- , F^- , Br^- and BrO_3^-).
- Improve the knowledge about relationship between the structure of metal oxides and their anion removal performance using EXAFS simulation.

RESULTS AND THEIR INTERPRETATION

Materials. Using urea supported hydrothermal precipitation we have produced ten composites based on Fe/Ce oxides (with Fe-to-Ce ratio in precursor 2:1; 1:1; 1:2; 0:1; 1:0)

each of which was thermally treated at 80 and 300°C which resulted in ten samples in total [1,2], denoted here accordingly as Fe, Fe₂Ce₁, Fe₁Ce₁, Fe₁Ce₂, Ce following by the respective temperature. For material preparation, we used inorganic salts of Fe and Ce (chlorides) in their lower oxidation states, +2 and +3, respectively. Coprecipitation of Fe/Ce hydroxides was caused via reactions of urea decomposition in accordance with (1) and (2):



Methods. New composites were characterized by x-ray diffraction patterns (XRD), Fourier-transform infra-red spectroscopy (FTIR), x-ray photoelectron spectroscopy (XPS), N₂ adsorption/desorption. Chemical composition was defined by sample dissolution in acid and in solid state by CHNS elemental analyzer. Fe K-edge (7112 eB) and Ce L₃-edge (5723 eB) EXAFS spectra for ten samples were recorded on Dutch-Belgian (DUBBLE) beamline-BM26A equipped by monochromator MSN(111) [1,2] at ambient temperature in transmission mode. In addition, we collected the spectra of reference materials (Ce₂(CO₃)₃, CeO₂, Ce(OH)₄, FeOOH, Fe₂O₃, FeCO₃, Fe(II)/Fe(III) oxide) for XANES linear combination fitting (LCF). For EXAFS simulation of Fe/Ce local environment, feff.inp files were generated using crystallographic information of reference materials available in the literature: α-Fe₂O₃ (Hematite), β-iron oxide, guildite (layered Fe(II)/Fe(III) oxide) and butlerite (Fe(II)/Fe(III) green rust), CeO₂, Ce₂(CO₃)₃, Ce(OH)CO₃, and Ce(OH)SO₄.

Anion removal properties of Fe/Ce composites were assessed in batch sorption experiments at pH=6.7±0.2 (adjusted with 0.1N HNO₃ and 0.1N NaOH) at the initial anion (H₂PO₄⁻, H₂AsO₄⁻, F⁻, Br⁻ and BrO₃⁻) concentration of 200±15 mg/L, measured by major chemical element, such as mg[As]/L for H₂AsO₄⁻.

Structure versus anion removal performance.

It was defined by XRD that crystalline phases of Fe component in 80°C-composites mainly consisted of Fe oxides (maghemite-γ-Fe₂O₃, magnetite-Fe₃O₄) with minor presence of FeCO₃ while Ce component was solely grounded on several phases of Ce carbonates (Ce₂O(CO₃)₂·H₂O, Ce(OH)CO₃). Calcination at 300°C resulted in transformation of Fe compounds into different Fe oxide phases (majority of which was Hematite, α-Fe₂O₃) while Ce carbonates were converted into ceria (CeO₂). Spectra XANES (Fig. 1), their derivatives and linear combination fitting for Fe/Ce composites dried/calcined at 80/300°C using reference materials (Table 1) helped to define both the oxidation state of Fe and Ce and the ratios between the main chemical substances composed Fe- and Ce-components in the entire samples regardless of their crystallinity.

Researchers in adsorption science use to classical rule about interdependence between surface area of adsorptive material and its removal which is always true for activated carbon. So, there had been an expectation also in this work to find out the same regularity (the more porous material the greater adsorption), however, the data on porous structure (by N₂ sorption) and crystalline phases (XRD) in ten experimental samples were in disagreement with their removal properties to five aqueous anions. Moreover, the samples with higher porosity (Fe-80, Fe-300 i Fe₁Ce₂-300) (Fig. 2A) had lower sorption capacities (Fig. 2B) than the less porous materials (which contradicted the expected/well-known positive correlation).

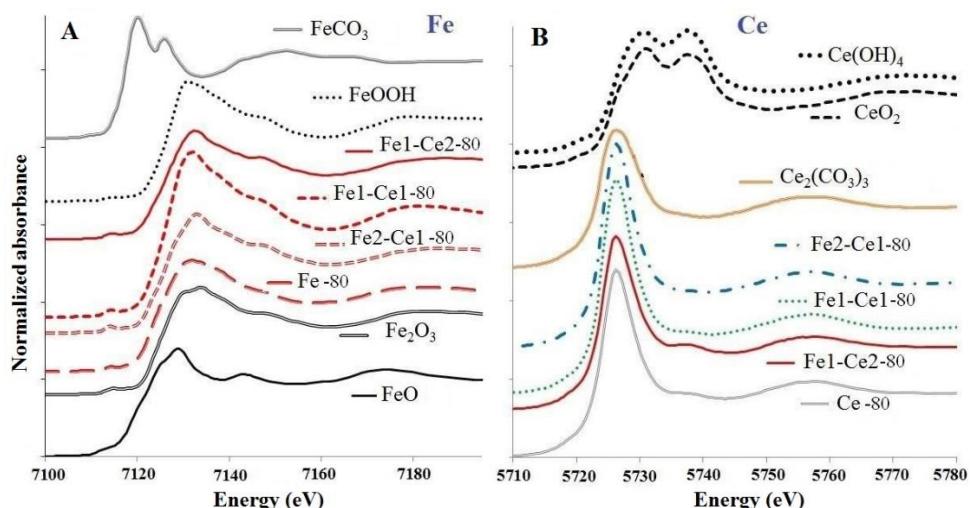


Fig. 1. XANES of Fe K-edge (A) and Ce L₃-edge (B) EXAFS in composites based on Fe/Ce oxides dried at 80°C, and the respective references [1]

Table 1. Phase composition of Fe and Ce components (in upper and lower parts, respectively) in ten Fe/Ce oxide-based composites resulted from linear combination fitting of XANES spectra (for Fe and Ce, respectively) using reference materials, % of particular reference [2]

Reference	Fe component							
	Fe		Fe2-Ce1		Fe1-Ce1		Fe1-Ce2	
	80°C	300°C	80°C	300°C	80°C	300°C	80°C	300°C
FeCO ₃	20.6	9.5	4.7	-	-	-	-	-
FeOOH	40.6	-	95.3	75.0	57.9	9.9	55.8	17.6
Fe ₂ O ₃	34.9	-	-	25.0	14.2	87.9	36.2	5.6
Fe(III) oxide		87.7		-		2.2		76.8
FeO	-	-	-	-	-	-	8.0	-
Fe(II)Fe(III)oxide	3.9	-	-	-	27.9	-	-	-
Unknown compound		2.8		-	-	-	-	-

Reference	Ce component							
	Ce		Fe1-Ce2		Fe1-Ce1		Fe2-Ce1	
	80°C	300°C	80°C	300°C	80°C	300°C	80°C	300°C
Ce ₂ (CO ₃) ₃	95.6	18.3	92.9	4.8	100	2.1	100	6.6
Ce(OH) ₄	4.4	36.4	7.1	48.9	-	63.8	-	64.1
CeO ₂	-	45.3	-	46.3	-	34.1	-	29.3

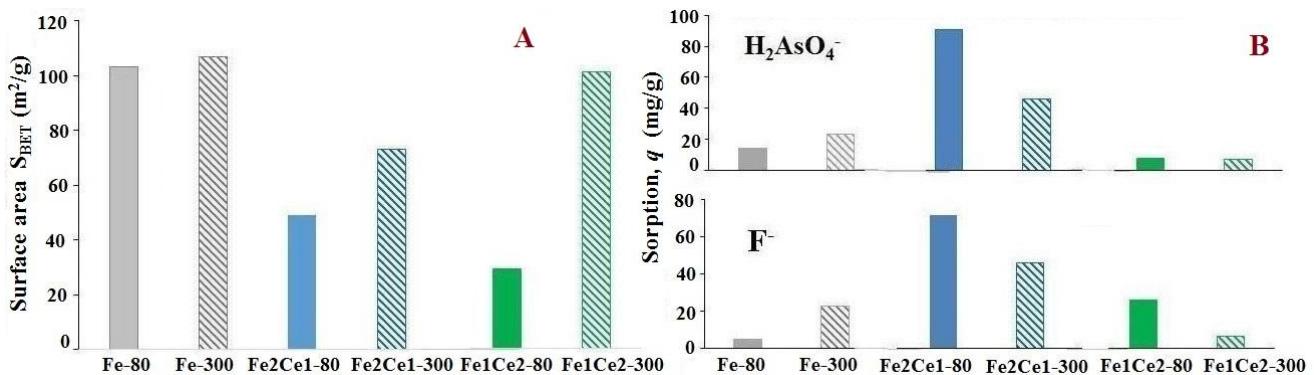


Fig. 2. Surface area (A) of some samples of ten Fe/Ce-oxide based composites and their sorption capabilities to two anions, H_2AsO_4^- and F^- (B) [3]

An absence of classical relationship between the structure of composites established by standard techniques and their adsorptive characteristics required in-depth characterization of these materials using more precision tools. To deepen the knowledge on ten composites, simulation of local structures around Fe and Ce has been done using Fe K-edge (7112 eB) and Ce L₃-edge (5723 eB) EXAFS spectra, respectively, which allowed to determine their structures at the atomic scale. Results of EXAFS calculations were presented in four tables [1,2] (for Fe and Ce components in five samples treated at 80 and 300 °C) one of which is shown in table 2, for Fe local structure since Fe substances were dominating on the surface.

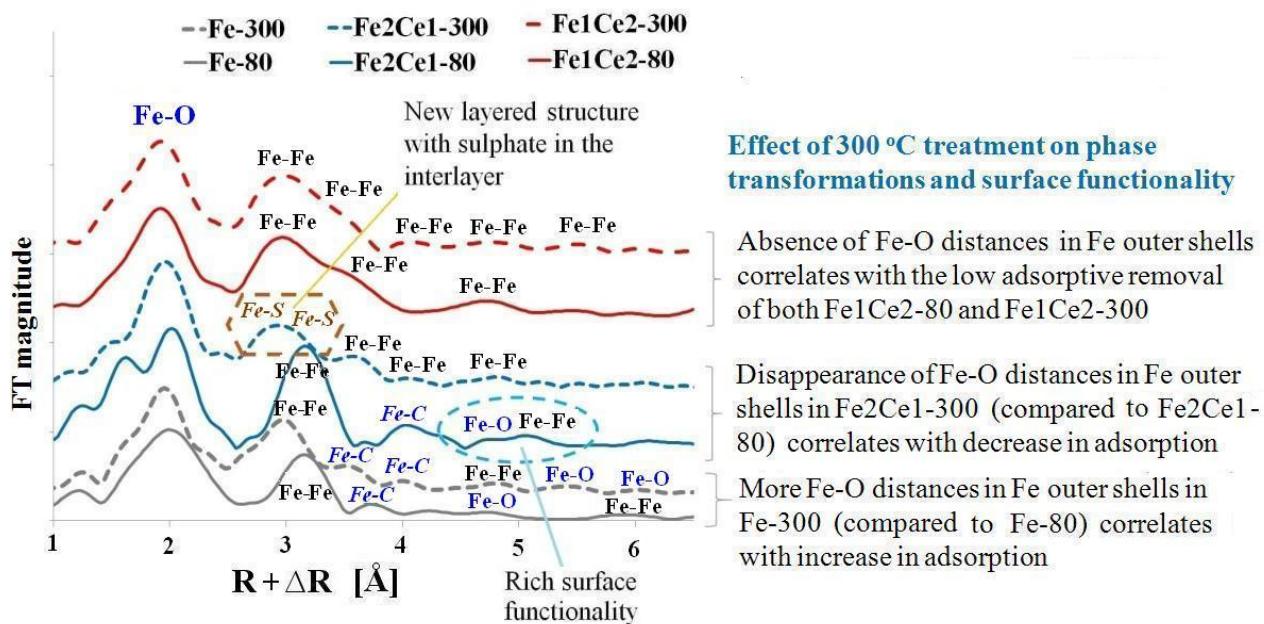


Fig. 3. Radial structure around Fe obtained based on Fourier transforms of $k^3\chi(k)$ Fe K-edge EXAFS oscillations in six composites and some results of EXAFS simulation [3]

Table 2. Cluster structure data for Fe component of 80°C-samples resulting from Fe K-edge EXAFS simulation and some crystallographic data (paths) used for the fitting. R—interatomic distance, CN—coordination number, σ^2 —the Debye–Waller mean square disorder factor, ΔE_0 —energy shift parameter, R-factor—goodness of fit [1]

Sample	Path (<i>computed from a particular reference</i>)	R, Å	CN	σ^2 (Å ²)	ΔE_0 (eV)	R-factor
Fe-80	Fe-O (β -iron oxide)	1.99	7.3	0.0168	-6.11	0.0026
	Fe-Fe (β -iron oxide)	3.06	3.6	0.0099	4.20	
	Fe-C (Siderite)	3.71	4.0	0.0028	-6.62	
	Fe-Fe (Siderite)	4.79	6.0	0.0168	4.72	
	Fe-O (β -iron oxide)	4.91	6.0	0.0105	-3.05	
	Fe-Fe (β -iron oxide)	5.88	6.0	0.0170	10.0	
Fe2-Ce1-80	Fe-O (β -iron oxide)	1.99	6.1	0.0094	-3.10	0.0032
	Fe-Fe (β -iron oxide)	3.09	6.0	0.0066	-0.05	
	Fe-C (Siderite)	3.75	6.0	0.0146	10.0	
	Fe-O (Siderite)	3.98	6.0	0.0154	10.0	
	Fe-O (Hematite)	4.44	3.0	0.0002	0.55	
	Fe-Fe (Hematite)	5.02	6.0	0.0150	10.0	
	Fe-Fe (Hematite)	6.02	6.0	0.0097	0.30	
Fe1-Ce1 -80	Fe-O (β -iron oxide)	1.98	6.0	0.0119	-7.32	0.0038
	Fe-Fe (β -iron oxide)	3.08	6.0	0.0105	0.30	
	Fe-Fe (Hematite)	4.04	3.6	0.0250	1.18	
	Fe-O (Hematite)	4.94	2.0	0.0001	7.81	
	Fe-O (Siderite)	5.26	6.0	0.0194	8.93	
	Fe-Fe (Akaganeite)	6.10	1.5	0.0026	10.0	
	Fe-O (Akaganeite)	6.49	2.0	0.0016	2.34	
Fe1-Ce2-80	Fe-O (Hematite)	1.95	6.0	0.0174	-10.0	0.0030
	Fe-Fe (Hematite)	3.04	3.0	0.0135	4.86	
	Fe-Fe (Hematite)	3.56	3.0	0.0108	4.86	
	Fe-Fe (Akaganeite)	4.72	2.0	0.0120	5.32	

EXAFS simulation allows to calculate distances between atom-absorber of x-rays (Fe or Ce), in order to determine its environment as well quantity of surrounding atoms called coordination number. To refine the structure of a material, it is sufficient to do EXAFS simulation of the local structure around major atoms (x-ray absorbers) in the first and the second coordination shells for which is used the information about oscillating atoms at distance <4Å. However, EXAFS fitting technique permits us to simulate extended x-ray absorption fine structure until 6 Å which is much difficult task than fitting 1st and 2nd shells. However, if both the preliminary information on complex material sample obtained by traditional methods and the atomic coordinates of respective (relevant) references are available in the literature, we can also simulate local environment of the main atoms until 6Å. Theoretically, such data might be useful, however, until this work was published [1,2], none was ever attempted to apply EXAFS simulated extended fine structure in outer shells for any characterization of materials. In this paper (based on [1,2]), we refined the local structure around Fe and Ce in ten Fe/Ce oxide-based composites by EXAFS simulation at until 6 Å and carefully reviewed all collected data including sorption tests which resulted in a discovery of interdependence between Fe outer shell composition and anion removal performance. It turned out that those composites (Fe2Ce1-80) whose Fe outer shells were modelled with Fe and O atoms simultaneously oscillating at >4-6Å (see Fig. 3) were the

best anion removers (see Fig. 2B). It was logical to anticipate that {Fe+O} atoms oscillating from outer shells reflect an abundance of material surface (anion exchange) OH^- groups, exchange of which with aqueous anions is the leading mechanism of anion removal by metal oxides. Disappearance of such EXAFS features in outer shells due to 300°C calcination (Fe2Ce1-80 vs Fe2Ce1-300 in Fig. 3) resulted in considerable worsening of sorption properties (see Fig. 2B, samples Fe2Ce1-80 vs Fe2Ce1-300). Based on this discovery we proposed a methodological suggestion [1,2] which for the first-time correlates EXAFS simulated local structure with a focus on outer shells with the material (adsorptive) performance.

CONCLUSIONS

Atomic scale structure and phase composition of ten (hydrothermally precipitated) Fe/Ce-oxide based composites have been established in entire volume of the materials regardless of their crystallinity due to utilization of several spectroscopy methods (EXAFS/XANES/XPS/XRD/FTIR), linear combination fitting of XANES spectra, EXAFS simulation and measurements of porous properties by N_2 adsorption/desorption.

The later technique, however, has not revealed a traditional (always true for activated carbon) positive correlation between the material surface area and its adsorptive performance. In particular, there has not been an interdependence between porous properties of ten Fe/Ce oxide-based composites and their removal of toxic anions (H_2PO_4^- , H_2AsO_4^- , F^- , Br^- , BrO_3^-) which proved that porosity of *inorganic* anion exchangers based on metal hydrous oxides is not a major characteristic which defines their sorption capabilities.

However (instead), we discovered a correlation between anion exchange properties of Fe/Ce oxides and local structure around Fe/Ce, simulated using EXAFS oscillations. Improved sorption performance was inherent in those samples whose Fe outer shells were formed due to backscattering oscillations from Fe and O atoms simultaneously.

Consequently, we proposed an idea (methodological suggestion) which allows anticipating the anion exchange properties of metal oxides (which, to a great extent, are predetermined by the presence of anion exchange centers, OH^- , on the material surface) from availability of developed local structure around the main atoms (such as Fe/Ce) resulted from simultaneous oscillations from both atoms, one heavy Fe/Ce and oxygen, backscattering from outer shells. The concept above has received a confirmation in the next manuscript [under review] in which was also made an additional observation which for the first time links the presence of physi-sorbed water in Fe-oxide based material with the local structure around Fe, whose outer shells were simulated using O atoms only.

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