

SAŠA ZELJKOVI <sup>1\*</sup>, JELENA PENAVIN ŠKUNDRI <sup>1</sup>,  
DIJANA JELI <sup>2</sup>, SLAVICA SLADOJEVI <sup>3</sup>, LJUBICA  
VASILJEVI <sup>4</sup>

<sup>1</sup>University of Banja Luka, Faculty of Science and Mathematics,  
Banja Luka, Bosnia and Herzegovina. <sup>2</sup>University of Banja Luka,  
Medical Faculty - Pharmacy department, Banja Luka, Bosnia and  
Herzegovina, <sup>3</sup>University of Banja Luka, Faculty of Technology,  
Banja Luka, Bosnia and Herzegovina, <sup>4</sup>University of East Sarajevo,  
Faculty of Technology Zvornik, Zvonik, Bosnia and Herzegovina

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## Interaction of hexavalent chromium and BSCF perovskite in water solutions

### ABSTRACT

*In this study, interaction of BSCF perovskite and hexavalent chromium in the aqueous solution was followed to provide additional useful insight in chemistry and behavior of this material.*

*Adsorption experiments were carried out systematically by batch experiments to investigate the influence of contact time, temperature and initial concentration of metal ions. The adsorption data obtained were described by the Freundlich and Langmuir adsorption isotherm model.*

*Thermodynamic study of hexavalent chromium adsorption on BSCF perovskite showed that the spontaneous adsorption process will be favored at higher temperatures (from 343 K) depending on the chromium concentration in water.*

**Keywords:** BSCF, perovskite, adsorption, chromium.

### 1. INTRODUCTION

Recently, great attention is given to investigations of intermediate temperature solid oxide fuel cells (IT-SOFCs). An integral part of the IT-SOFCs are interconnects made of metal alloys - steels with chromium contents over 20 wt% [1,2]. IT-SOFCs cathode material must be highly tolerant toward the deposition and poisoning of Cr species in order to achieve the long-term stability of the electrodes [3,4]. The Cr poisoning of the perovskite cathode material and subsequent degradation of the whole system occur as a consequence of the reaction of Cr<sub>2</sub>O<sub>3</sub> with oxygen and water to form various gaseous hexavalent Cr species under the IT-SOFCs working temperatures [5, 6].

In recent years, it was found that Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub>, as a common material for oxygen membranes and IT - SOFCs, is not

chromium-tolerant [7]. Performed study resulted in clear evidences of the chromium deposition and poisoning. The reactivity of the BSCF material toward copper and cobalt ions in the water environment was previously studied [8]. Copper and cobalt ions were adsorbed at the BSCF surface.

In this paper, we investigated the hexavalent chromium adsorption and deposition from the water solutions in order to determine and better understand reactivity of this chemical specie with BSCF perovskite. The adsorption has been described by the Freundlich and Langmuir adsorption isotherms as a mathematical calculation model.

### 2. EXPERIMENTAL

BSCF (Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub>) powder (Pra-xair) was annealed in air at 1273 K for 6 h. X-ray diffraction (XRD) was performed on a Philips SIEMENS D5000 instrument using Cu-K $\alpha$  x-ray tube ( $\lambda$  = 154nm) and  $\theta$ -2 $\theta$  configuration. Data were collected in a continuous-scan mode in the range of 20° to 100° with intervals of 0.02°, confirming the presence of single phase BSCF, Figure 1.

\*Corresponding author: Sasa Zeljkovi

E-mail: sasa.zeljkovic@unibl.rs

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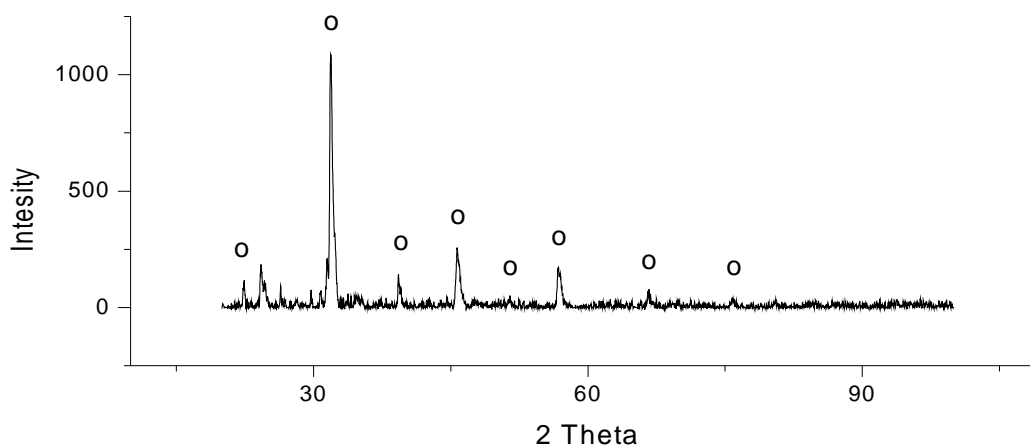


Figure 1 - XRD analysis with marked peaks of  $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-x}$  (o) perovskite.

The specific surface of  $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-x}$  perovskite determined by the Brunauer–Emmett–Teller (BET) method after four hours of annealing at 673 K was close to  $2 \text{ m}^2\text{g}^{-1}$ . The approximate pH of the BSCF perovskite samples ( $0.1 \text{ gcm}^{-3}$  water suspension) has been determined by universal paper indicator and it was about pH 5.5.

The aqueous solutions containing chromium of known concentration ( $0.01, 0.02, 0.03, 0.04, 0.05 \text{ mol dm}^{-3}$ ) were mixed with a given mass of adsorbent for a given period of time. Chromium solutions were prepared by dissolving of  $K_2Cr_2O_7$  salt (p.a. purity, Lachner).

In each experiment mass of  $0.3 \text{ g}$  of adsorbate (BSCF) was mixed with  $0.03 \text{ dm}^{-3}$  of chromium aqueous solution. The suspensions were mixed and left thermostating in a glass container at four different temperatures ( $273, 293, 303$  and  $313 \text{ K}$ ) in the duration of 1 hour. After the adsorption the solution was separated from adsorbent by filtering through the blue band filter paper. The amount of solute adsorbed by the adsorbent is summed to be the difference between the initial concentration (before contact with the adsorbent) and the solute concentration after the contact period.

The chromium concentration was determined by the AAS - atomic absorption spectroscopy (Thermo Electron Corporation S2 AA System).

### 3. RESULTS AND DISCUSSION

The batch experiments were designed to investigate the influence of contact time, temperature and initial concentration of metal ions. Prepared chromium water solutions were slightly acidic (pH 5). With this level of acidity and with regard to concentration of Cr(VI) it can be assumed that in all used solutions chromium was in anionic  $Cr_2O_7^{2-}$  form [9,10]. Figure 2 Influence of pH on the sorption was not further studied.

The amount of adsorbed chromium also depends on the contact time. The optimal time for complete sorption was specified at the temperature of  $313 \text{ K}$  in the time interval of 180 minutes, where it was determined that the optimal time for sorption is 60 minutes after which there has been no increase in adsorption. (Figure 3) The initial rapid adsorption rate may be due to the availability of positively charged active sites. Subsequent slow adsorption speaks in favor of electrostatic repulsion between negatively charged, previously adsorbed, adsorbate and anionic species present in the solution.

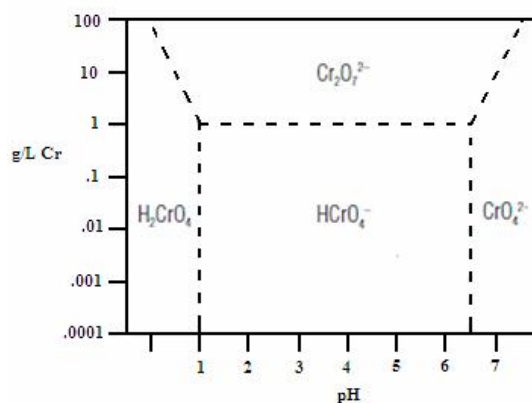


Figure 2 - Relative distribution of Cr(VI) species in water as a function of pH and Cr(VI) concentration.

The sorption of chromium onto BSCF increased with increasing temperature. The increase in the sorption efficiency indicates an endothermic process. At  $273 \text{ K}$  the sorption capacity is reached and stable at  $20 \text{ mg g}^{-1}$ , regardless of chromium concentration. At  $293, 303$  and  $313 \text{ K}$  the maximum sorption capacity does not seem to be reached as visible from the slope of the related curves. The maximum adsorption capacity was  $80 \text{ mg g}^{-1}$  at  $313 \text{ K}$ , Figure 4.

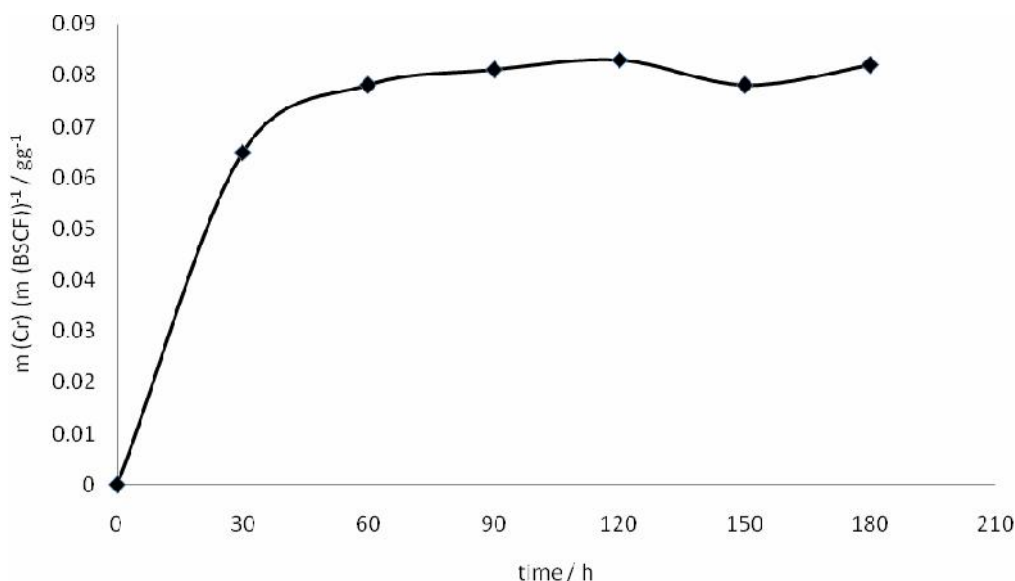


Figure 3 - Effect of contact time on removal of Cr(VI) for the Cr-BSCF system (recorded at 313 K in the time interval of 180 minutes).

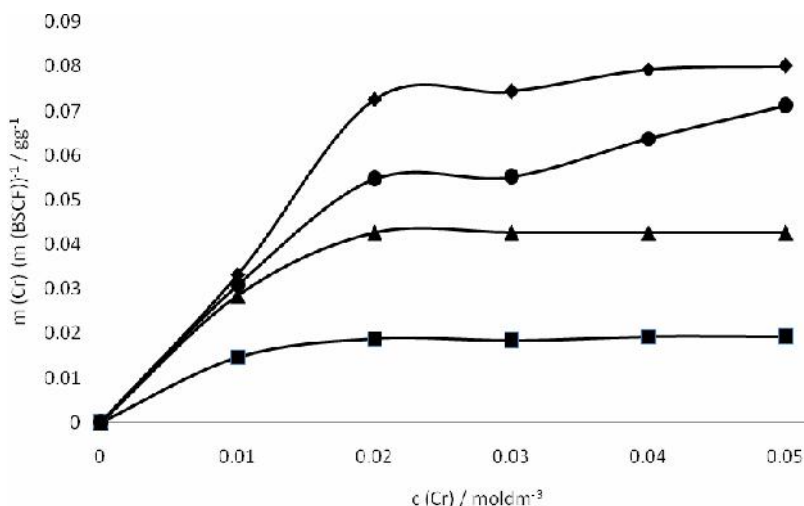


Figure 4 - Adsorption isotherms for the Cr-BSCF system recorded at 273 ( ), 293 ( ), 303 ( ) and 313 K ( ).

Chromium sorption most probably included interaction of negatively charged oxygen, in dichromate anionic molecules, and active sites at the surface of BSCF perovskite. Active sites are most probably present at the place of stoichiometrically deficient oxygen. Oxygen nonstoichiometry (as one of the BSCF characteristics) is previously explained by many authors [11-14] and proven to be highly temperature dependent. The increased presence of

oxygen defects with increasing temperature could explain the growing BSCF affinity toward chromium.

The obtained results of Cr(VI) adsorption BSCF perovskite at 273, 293, 303 and 313 K, were also analyzed using Langmuir adsorption model. The results are shown in Table 1a and 1b. Obtained positive enthalpy and entropy values indicate that the process of adsorption of Cr(VI) on BSCF is favored at higher temperatures.

Table 1 - (a and b) Overview of experimental data obtained from the Langmuir adsorption isotherm and thermodynamic functions calculated for the adsorption process of Cr(VI) on BSCF perovskite

a)

Temperature	R - Linear Correlation Coefficient	$q_m$ (adsorption capacity)	$K_L$ (Langmuir's constant)	$R_L$ ( $0 < R < 1$ ) favorable
273 K	0.99896	0.000389	436.85	0.184 for 0.0101M
293 K	0.99867	0.000856	678.80	0.127 for 0.0101M
303 K	0.98879	0.00155	152.81	0.393 for 0.0101M
313 K	0.94659	0.0017	181.17	0.353 for 0.0101M

b)

c mol/L	$H^\circ$ J/mol	$S^\circ$ J/molK	$G^\circ$ (298 K) J/mol	$G^\circ$ (423 K) J/mol	$T_{\text{spontaneously}}$ , K	R - Linear Correlation Coefficient
0.0101	26852.5	72.047	5382.5	-3622.5	372.7	0.97207
0.0192	41225.3	119.206	5702.1	-9198.7	345.83	0.99397
0.0308	33141.5	85.104	7781.5	-2857.8	389.42	0.99812
0.0403	32237.2	79.727	8519.3	-1486.8	404.34	0.99991
0.0515	31573.1	75.238	9153.5	-252.1	419.55	0.99204

The free Gibbs energies are positive up to  $T_{\text{spontaneously}}$ , after which  $G^\circ$  is negative which confirms spontaneous process. A positive enthalpy value goes in favor of an endothermic process, and increases with increasing temperature. The positive value of entropy represents an increase in the degree of disorder in the system with an increasing adsorption, ie, that there is a higher degree of freedom of the molecules in the liquid-solid boundary during the adsorption process.

#### 4. CONCLUSION

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-x}$ , (BSCF) perovskite oxide interaction with hexavalent chromium was investigated in the water environment. The influences of contact time, temperature and initial concentration of metal ions were evaluated and in final form described with Freundlich adsorption model.

Sorption of hexavalent chromium was endothermic that could indicate chemisorption.

It was found that the affinity of BSCF toward chromium increases with increasing temperature and metal ions concentration. Such behavior could be ascribed to the chemical structure of BSCF

perovskite, its active sites on the place of deficient oxygen and the bonds that could form with the sorbent.

Although in this study the reactivity of chromium was followed at low temperatures and in an aqueous environment, the present results provide further insight into the chemistry of the reaction process. Recorded affinity of the BSCF perovskite to chromium at low temperatures speaks in favor of thinking that BSCF is not chromium-deposition-tolerant material, regardless of temperature. That could lead to possible conclusion that the reduction in the SOFC operational temperature would not prevent the chromium deposition and poisoning effect

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## IZVOD

### INTERAKCIJA HEKSAVALENTNOG HROMA I BSCF PEROVSKITA U VODENOJ SREDINI

*U ovoj studiji je proučena interakcija BSCF perovskita i heksavalentnog hroma u vodenoj sredini kako bi se obezbijedile korisne informacije o hemizmu i ponašanju ovog materijala.*

*Ekperimenti adsorpcije su izvedeni sistematično i u serijama kako bi se ispitali uticaji dužine kontakta, temperature i inicijalne koncentracije metalnih jona. Podaci su opisani Freundlichovim i Langmuirovim adsorpcionim modelom.*

*Termodinamička studija adsorpcije heksavalentnog hroma na BSCF perovskitu pokazala je da je spontani proces adsorpcije favorizovan pri višim temperaturama (od 343K) zavisno od koncentracije hroma u vodenoj sredini.*

**Ključne riječi:** BSCF, perovskit, adsorpcija, hrom.

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