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Enhancement of anions removal *via* adsorption-induced deformation of hydrated xerogels [ZrYb]O_2–Al_2O_3 prepared at different temperatures

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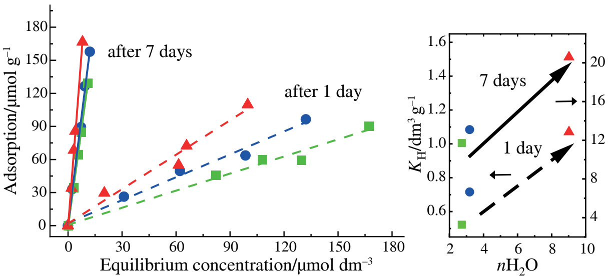
Alumina–zirconia doping ytterbia xerogels with an atomic ratio Al/Zr(Yb) = 1/3(0.3) prepared *via* sol–gel process at temperatures of 10, 25 and 60 °C were examined by TGA/DSC, SAXS and SEM methods and tested as sorbents of hexavalent chromium and methyl orange dye. A twenty-fold increase in the Henry's law constant for dichromate ion sorption was observed after 7 days of sorption. This allows one to assume that the adsorption process induces self-formation of the xerogel porous structure resulting in the substantial enhancement of its sorption performance.



Keywords: alumina, zirconia, hydrophilicity, adsorption, xerogel expansion.

Water pollution by the wastes of various enterprises has a negative impact on the environment, therefore, the wastewater purification is currently a key goal. Textile and electroplating companies are the main sources of wastewater contaminated with toxic dyes and heavy metal ions.[1,2] Adsorption is an effective method of various pollutant ions removal from aqueous solutions, *e.g.*, sorption of anionic dyes Congo red by porous ZrO_2 and methyl orange sorption process on modified carbons.[3,4] As an alternative to carbon materials, zirconium and aluminum oxides and hydroxides, which are precursors of ceramic materials fabrication, appear to be the promising sorbents owing to their high porosity, specific surface area and concentration of the active adsorption centers.[5]

In alumina–zirconia (AZ) system, the addition of aluminum oxide to zirconium oxide reduces the particles growth; their average size decreases and the specific surface area of such mixed oxides powders increases.[6,7] Addition of 3 mol% of the oxides of rare earth elements results in the formation of a solid solution with zirconium oxide, stabilizing tetragonal phase ZrO_2.[8,9] To reduce the agglomeration of particles during sol–gel synthesis, polymers and surfactants, so-called structure-forming agents, are often introduced into the reaction mixture.[10]

The most suitable method for the synthesis of mixed AZ systems due to its simplicity and accessibility is the sol–gel technique. By varying the conditions of sol–gel process, the properties of the sorbent can be controlled. The temperature of sol–gel synthesis affects the rate of sol–gel transition: an increase in temperature significantly reduces the sol–gel transition time.[11,12] It is obvious that the reaction rate strongly affects the growth rate of particles and their maturation, which entails a change in morphology, porosity and crystalline structure, that in turn affects the adsorption properties.

The fundamental understanding of the thermodynamic and mechanical aspects of adsorption-induced stress and solids deformation (silica, zeolite granules, coal, shale and cement) has been reviewed earlier,[13] though the Bangham's theory described there considers adsorption on a surface and not in pores.

There are very few studies of the effect of sol–gel synthesis temperature (SGT) on the adsorption characteristics of AZ. In our previous work, hydrated xerogels of mixed alumina and zirconia AZYb were prepared by sol–gel method at temperatures of 10 (sample 1), 25 (sample 2) and 60 °C (sample 3) and characterized by IR, XRD and BET/BDJ methods. The results confirmed the hydrophilic properties of AZYb powders, amorphous shape of all AZYb xerogels with the values of the specific surface area decreased from 427 (sample 1) to 2.3 $m^2\ g^{-1}$ (sample 3) and pore volume decreased from 0.326 to 0.004 $cm^3\ g^{-1}$.[14]

The aim of this work was to determine the adsorption capacity of AZYb xerogels depending on the temperature of sol–gel synthesis.[†]

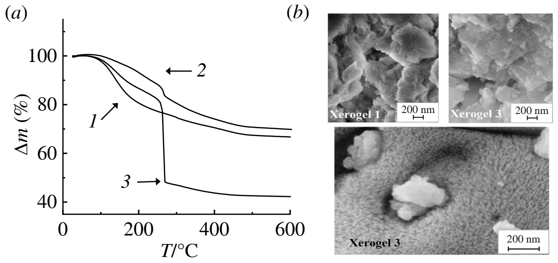


Figure 1 (*a*) TG curves of AZYb xerogels obtained by sol–gel synthesis at temperatures of 10 (curve *1*), 25 (curve *2*) and 60 °C (curve *3*) and dried at 180 °C; (*b*) SEM images of AZYb xerogel powder.

[†] Hydrated xerogels of mixed alumina and zirconia AZYb were prepared by sol–gel method at temperatures of 10 (sample 1), 25 (sample 2) and 60 °C (sample 3) in our previous work.[14]

The obtained xerogels were studied by TG-SCA (Netzsch STA 409 PC/PG), SEM (SUPRA 40-30-87 Microscope) and SAXS (AMUR-K) methods.

Kinetics of sorption and long-time sorption were studied by photometric method (Ecoview UV1200) at the analytic wavelength λ_m of 352 nm (DCH) and 462 nm (MOD). The durations of long-time sorption of $Cr_2O_7^{2-}$ anions were 1 day and 7 days.

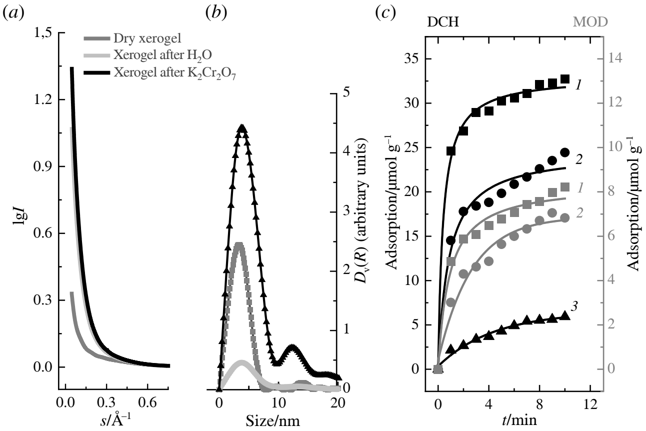


Figure 2 SAXS data: (*a*) scattering curves and (*b*) distribution functions of heterogeneities of xerogel (sample 3). (*c*) Kinetic data of dichromate and methyl orange ions sorption on AZYb xerogels obtained by SGS at temperatures of 10 (curve *1*), 25 (curve *2*) and 60 °C (curve *3*).

Figure 1(*a*) demonstrates the thermogravimetry results. The mass loss has almost stopped at 500 °C. Index *n* of xerogel AZYb·*n*H$_2$O, calculated from TGA data, changed as follows: 3.19 (sample 1), 2.73 (sample 2) and 9.02 (sample 3), thus the sample 3 having higher SGM possessed the highest hydrophilicity. Noteworthy, the t-ZrO$_2$ crystallization in binary system occurs at 895–903 °C and α-Al$_2$O$_3$ at 1305–1340 °C (according to SCA data).

The pores in the samples were of the same diameter (4 nm) but the sample 3 also contained macropores. SEM images show the morphology of sample 3 [see Figure 1(*b*)]. In this work, the size distributions of pores as inhomogeneities in the material were characterized by the method of small-angle X-ray scattering (SAXS) for dried and wet samples after being in water and in K$_2$Cr$_2$O$_7$ solution.

Scattering curves are shown in Figure 2(*a*). The main fraction has a pore radius of *ca.* 4–7 nm (wet, in K$_2$Cr$_2$O$_7$ solution) with increased content of such pores. The fraction with large pores *R* = 12–17 nm [Figure 2(*b*)] has been also observed.

Dichromate ions (DCH) and methylene orange dye (MOD) were selected for adsorption tests as model inorganic and organic anionic pollutants.

Kinetics of adsorption data and long-time sorption characteristics are shown in Figures 2(*c*) and 3 and summarized in Table 1. Kinetic curves of DCH and MOD sorption [Figure 2(*c*)] were well treated by a pseudo-second order for two-fold adsorption model.[15] The DCH adsorption capacity tended to increase as follows: sample 2 < sample 1 < sample 3. The initial rate of chemisorption (W_0) and maximum quantity of adsorbed molecules ($A_{\max}$), calculated from kinetic data, decreased in the same row. The opposite result was obtained for the long-term sorption data. The sorption values *A*(1) MOD correlate with *A*(1) DCH. It is notheworthy that the sample 3 (SGT temperature of 60 °C) has swelled forming a globule upon contact with MOD solution, therefore, even in kinetic experiments the dye removal was not observed.

The duration of Cr$_2$O$_7^{2-}$ ions sorption was 24 h (1 day) and 7 days. Henry constants of DCH sorption K_H increased as follows: sample 2 ≈ sample 1 < sample 3; and dramatic rise of AZYb sorption capacity was found for 7 days [Figure 3(*a*)]. The correlation between K_H and AZYb hydrophilicity for both isotherm measurements is shown in Figure 3(*b*). A twentyfold increase in K_H values after 7 days of sorption can be explained by xerogel framework self-formation in DCH aqueous solution. Therefore, a well-known phenomenon of structure expansion of mesoporous material and/or structure reconstruction due to sorption was also observed for hydrated xerogel AZYb.

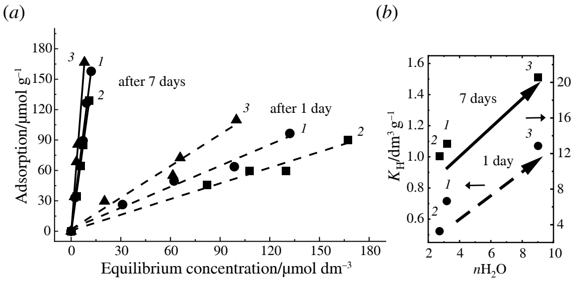


Figure 3 (*a*) Lasting 1 day and 7 days isotherms of dichromate ions sorption for AZYb xerogels obtained by sol–gel synthesis at temperatures of 10 (*1*), 25 (*2*) and 60 °C (*3*); (*b*) correlation between the hydrophilicity of AZYb xerogels obtained by varying of sol–gel temperatures and the Henry constant K_H (1) and K_H (7) of dichromate ions sorption lasting 1 day and 7 days.

Table 1 Results of adsorption experiments with dichromate ions (DCH) and methyl orange dye (MOD) at room temperature.

Sample	Sorption kinetic data				Long-term sorption				
	W_0[a] DCH	$A_{\max}$[b] DCH	W_0[a] MOD	$A_{\max}$[b] MOD	*A*(1)[c] MOD	*A*(1)[c] DCH	*A*(7)[d] DCH	K_H(1)[e] DCH	K_H(7)[f] DCH
1	19	24	3.7	8.4	11.6	63.6	163	0.716	13.1
2	53	30	7.5	8.8	10.4	59.7	157	0.522	11.7
3	1.7	7.5	not registered		12.5	76.7	167	1.07	20.6

[a] Initial rate W_0/μmol g^{-1} min^{-1}. [b] Maximum surface coverage $A_{\max}$/μmol g^{-1} according to pseudo second-order kinetic model of DCH adsorption. [c,d] The amount of sorbate *A*(1), *A*(7) in μmol g^{-1} and [e,f] the Henry constants K_H (1), K_H(7) in dm^3 g^{-1} after 1 day and 7 days of DCH sorption.

Thus, the variation of the sol–gel synthesis temperature made it possible to obtain xerogels with different textural and structural properties. Adsorption activity correlates with the rate of hydration: an increase in the amount of water in AZYb sorbent results in the decrease of the kinetic characteristics of chemisorption, while the values of pseudo equilibrium sorption and Henry constants K_H obtained from linear isotherms of DCH increased. Also, these systems are characterized by the phenomenon of xerogel self-formation. For the adsorption of anionic pollutants in the kinetic mode, it is preferable to synthesize AZYb xerogels at a temperature of 25 °C, while for the long-term adsorption, the optimal temperature is 60 °C.

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