PECULIARITIES OF CHROMIUM(VI) IONS REMOVAL USING SILICA SORBENTS WITH QUATERNARY AMMONIUM GROUPS

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Chromium pollution poses a significant threat to the environment. Toxic Cr(VI) enters water bodies with emissions from steel mills, chemical industries, cement and textile production, and motor vehicles. Cr(VI) can leach into groundwater from chromite mines, as well as through improper waste disposal. The presence of toxic Cr(VI) residues in fresh water bodies and soil negatively affects plant growth, animal health, and causes various health problems in humans [1]. According to WHO, the maximum permissible concentration of Cr(VI) in drinking water is 0.05 mg/L [2]. One of the current methods for removing anionic forms of chromium from water is adsorption using nitrogen-containing organosilicon materials.

Therefore, the current study focuses on the preparation of materials with quaternary ammonium functional groups. Trimethylaminopropyl-functionalized silica particles (Fig.1a) were synthesized via the hydrolytic co-condensation of TMPAC (Fig.1b) and different structuring silanes (Fig.1c, d, e). The silane-based synthesis applying ethanol and ammonia allowed the one-pot non-grafting preparation of the organosilicas. Different structure-forming agents were used to obtain three types of materials, differing in porous structure and the number of functional groups. As summarized in Fig.1 polysiloxane samples (**TN1**, **TN2**) were synthesized with TEOS, while polysilsesquioxane materials were synthesized with BTESE (**EN1**, **EN2**) and BTESB (**BN1**, **BN2**). Indices 1 and 2 denote the 2:1 and 4:1 structuring-to-functionalizing Si ratios in the samples. Their detailed properties are given in Table 1.

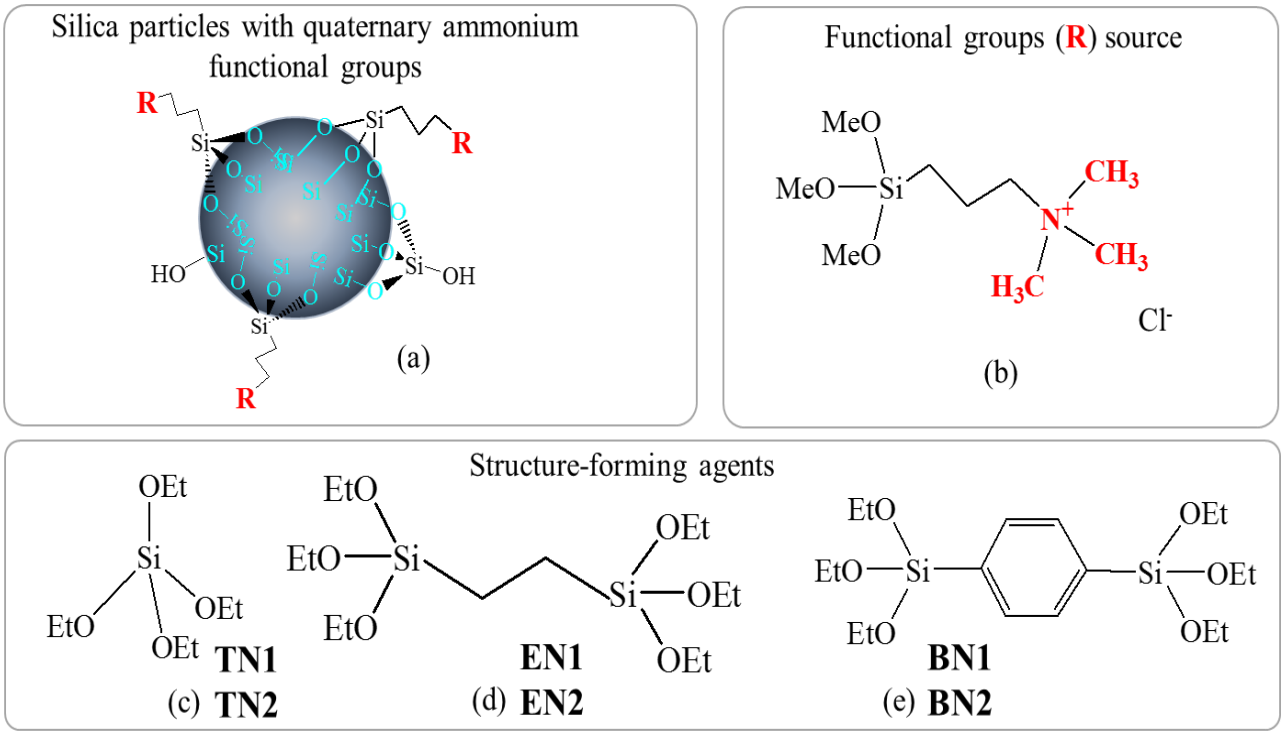

Fig.1. Sol-gel derived silica samples (a) prepared using the following structural components: (b) N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride (TMPAC), (c) tetraethyl orthosilicate (TEOS), (d) 1,2-bis(triethoxysilyl)ethane (BTESE), and (e) 1,4-bis(triethoxysilyl)benzene (BTESB).

The attachment of the targeted quaternary ammonium groups, R-N(CH_3)$_3$, was confirmed by Fourier-transform infrared spectroscopy of the materials with a Thermo Nicolet Nexus FTIR spectrometer. Their presence is evidenced by N-C_4 skeletal vibrations in the range of 980-900 cm^{-1} and CH_3 bands observed at 3020, 1485 and 1415 cm^{-1} in the IR spectra of all synthesized samples. In addition, the content of the groups ($C_{f.g}$) was quantified based on the analysis of CHNS elements performed with the elemental analyzer Vario MACRO cube (Elementar Analysensysteme GmbH, Germany) (Table 1). As expected for the series of samples, samples **TN1**, **EN1** and **BN1**, which were synthesized applying a higher content of functionalizing silane in the reaction mixture, have higher number of attached groups.

Table 1

Composition and some characteristics of the functional composite samples

Sample	Structuring ligament	$C_{f.g}$, mmol/g	S_{BET}, m^2/g	V_{tot}, cm^3/g	$SSC_{(Cr)}$, mg/g
TN1	-$SiO_{3/2}$	2.5	136	1.47	45.3
TN2	-$SiO_{3/2}$	1.8	178	1.19	23.6
EN1	$_{3/2}$OSi-C_2H_4-$SiO_{3/2}$	2.2	6	-	45.3
EN2	$_{3/2}$OSi-C_2H_4-$SiO_{3/2}$	1.4	268	0.43	42.4
BN1	$_{3/2}$OSi-C_6H_4-$SiO_{3/2}$	1.8	13	-	37.7
BN2	$_{3/2}$OSi-C_6H_4-$SiO_{3/2}$	1.2	285	0.23	23.6

The structural characterization of the materials was performed using a Costech Sorptometer Kelvin1042 and the NOVA 1200e Surface Area & Pore Size Analyzer (Quantachrome Instruments, USA). The isotherms were used to calculate the sorption pore volume (V_{tot}), while the BET specific surface area (S_{BET}) was assessed using the relative pressures (P/P_0) range of 0.05-0.35.

The isotherms of polysiloxane samples **TN1** and **TN2** belong to Type II, with a small hysteresis loop in the region of high relative pressures (Fig. 2). Usually, this type of isotherm is characteristic of non-porous or macroporous materials. During the synthesis of **TN2**, a larger amount of structure-forming silane was added, which slightly affected the porous structure of the resulting sample. Both samples, **TN1** and **TN2**, have similar S_{BET} (136 and 178 m^2/g) and the pore volumes (1.47 and 1.19 cm^3/g).

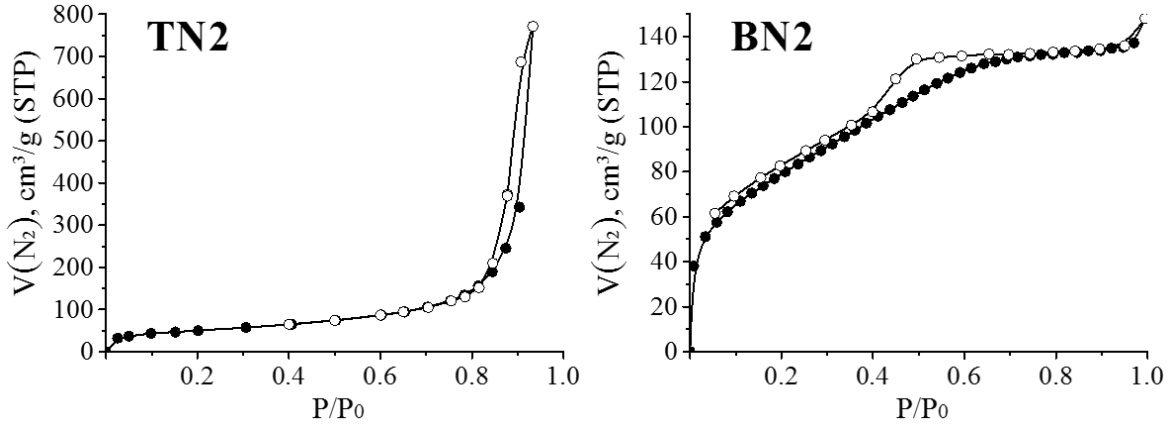

Fig.2. Low-temperature nitrogen adsorption-desorption isotherms for some samples.

The isotherm of polysilsesquioxane sample **BN2** belongs to TypeIV(a) with a slight hysteresis loop at medium values of relative pressures. It has a well-developed porous structure (S_{BET} = 285 m^2/g and V_{tot} = 0.23 cm^3/g) and the nature of the isotherm indicates that the sample is mesoporous. Meanwhile, **BN1** is likely non-porous has a small specific surface area, 13 m^2/g.

Similar to BTESB-based materials, BTESE-based polysilsesquioxane **EN2** has S_{BET} = 268 m^2/g and V_{tot} = 0.43 cm^3/g), while **EN1** is likely non-porous with specific surface area of 13 m^2/g. Thus, a higher content of structuring silane contributes to the formation of well-developed porosity in the mesoporous range.

The study of adsorption properties of materials opens up prospects for their new applications. The materials were tested for the removal of Cr(VI) ions. One of the key parameters determining the efficiency of the adsorbents is the speed of establishing adsorption equilibrium between the adsorbent and the solution. The kinetics of Cr(VI) ions sorption was studied under static conditions (Sample batch m = 10 mg, solution volume V = 10 mL, $C(K_2Cr_2O_7)$ = 0.1 mmol/L, pH = 2, T = 25°C). For isothermal studies, contact time *t* was 24 h and concentrations $C(K_2Cr_2O_7)$ were varied from 0.1 to 2.0 mmol/L. Concentration of Cr(VI) ions in the solution was determined by colorimetric diphenylcarbazide method (λ = 540 nm).

The corresponding kinetic curves and isotherms are presented in Fig. 3. The results show that sorption equilibrium in such systems is established quite quickly. The values of correlation coefficients R^2 indicate that all the kinetic curves are better fitted by pseudo (II) order kinetic model, assuming that the rate-limiting step of the adsorption process is chemisorption. Thus, comparing the rate constants k_2, the highest sorption rate is observed for polysilsesquioxane samples **EN1** and **BN1**, followed by **EN2** and **BN2**; whereas adsorption on polysiloxane samples is slower.

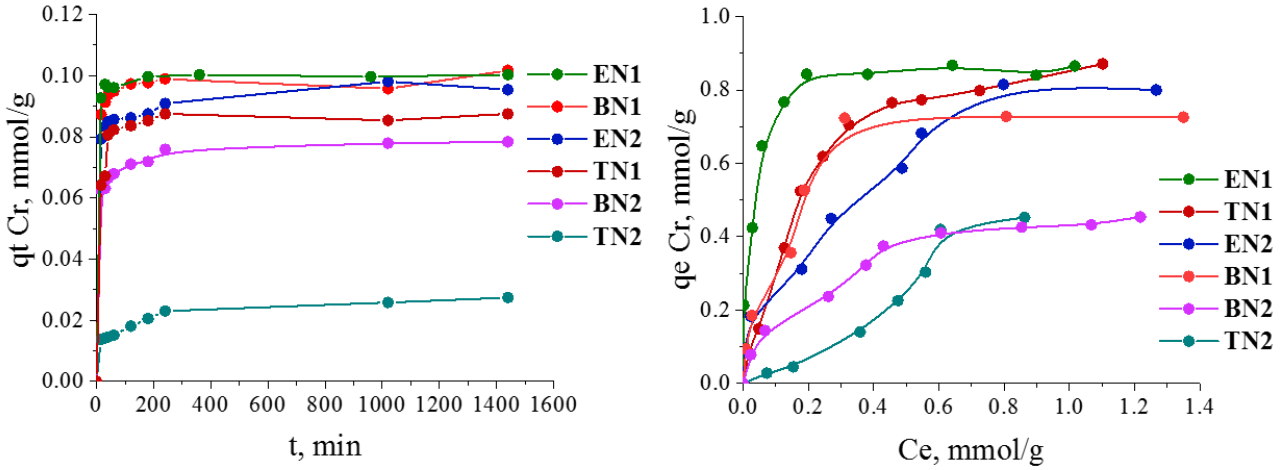

Fig.3. Kinetic curves and isotherms of Cr(VI) adsorption by the samples.

Table 2

The kinetic parameters of Cr(VI) ions sorption by the synthesized samples with quaternary ammonium functional groups.

Sample	Pseudo (I) order kinetic model $q_t = q_e(1 - e^{-k1t})$			Pseudo (II) order kinetic model $q_t = k_2 q_e^2 t/(1 + k_2 q_e t)$		
	q_e, mmol/g	k_1, 1/min	R^2	q_e, mmol/g	k_2, g/(mmol min)	R^2
TN1	0.09	0.08	0.975	0.09	1.91	**0.988**
TN2	0.02	0.03	0.799	0.03	1.52	**0.908**
EN1	0.10	0.19	0.997	0.10	8.27	**0.999**
EN2	0.09	0.13	0.972	0.09	3.54	**0.987**
BN1	0.10	0.15	0.992	0.10	4.73	**0.997**
BN2	0.07	0.11	0.956	0.08	3.05	**0.986**

q_e and q_t are values of equilibrium adsorption and adsorption at time t, mmol/g; t is contact time, min; $k_1$and k_2 are rate constants of pseudo (I) and pseudo (II) order kinetic models.

In decreasing order of static sorption capacity (SSC), the samples can be arranged in the following sequence*:* ***EN1***=***TN1***>***EN2***>***BN1***>***BN2***=***TN2***. Thus, polysiloxane sample **TN1** and polysilsesquioxane sample with an ethylene bridge **EN1** are characterized by the highest uptake of Cr(VI) ions, 0.87 mmol/g. However, it is worth noting that contrary to **TN1**, the isotherm of the sample **EN1** has a sharp rise in the initial section, apparently associated with the high affinity of the surface for the adsorbate. The lower sorption by the **EN2** sample, compared to **EN1**, is most likely associated with the smaller number of functional groups. A similar dependence of sorption on the number of groups is observed for polysiloxanes (0.87 mmol/g and 0.45 mmol/g) and polysilsesquioxane samples with a phenylene bridge **BN1** and **BN2** (0.73 mmol/g and 0.45 mmol/g).

The adsorption isotherm data were fit to the Langmuir and Freundlich isotherm models (Table 3). It is clear that for polysilsesquioxane adsorbents with a phenylene bridge (**BN1** and **BN2**) the obtained experimental data are described by the Langmuir equation more reliably than by the Freundlich equation, as indicated by the higher value of the correlation coefficient R^2. This may indicate the formation of a sorbate monolayer on the surface of the particles due to the interaction of Cr(VI) anions with homogeneous adsorption centers on the surface.

For polysiloxane adsorbents, at a high content of groups (sample **TN1**), the adsorption surface is more homogeneous and the results are better approximated by the Langmuir equation. However, with a decrease in the content of functional groups (sample **TN2**) and an increase in the specific surface area, the heterogeneity of the surface increases, so the correlation coefficient for fitting the experimental data to the Freundlich equation is higher. A similar relationship is observed for polysilsesquioxane adsorbents with an ethylene bridge.

The value of *1/n* from the Freundlich isotherm equation varies depending on the heterogeneity of the adsorbent and indicates the favorability of the adsorption process. For all studied samples, the value of *1/n* lies in the range of 0.1 to 1, therefore the surfaces of all adsorbents are favorable for the adsorption of Cr(VI) anions.

Table 3

Parameters of Cr(VI) ions sorption in the Langmuir and Freundlich equations

Sample	***SSC, mmol/g***	**Langmuir equation** $q_e = Q_m K_L C_e/(1 + K_L C_e)$			**Freundlich equation** $q_e = K_F C_e^{1/n}$		
		K_L, **L/mmol**	Q_m, **mmol/g**	R^2	K_F, **mmol/g) (L/mmol)$^{1/n}$**	***1/n***	R^2
TN1	0.87	5.28	1.05	**0.987**	0.94	0.39	0.925
TN2	0.45	0.01	92.06	0.919	0.58	0.87	**0.933**
EN1	0.87	45.61	0.89	**0.968**	0.95	0.19	0.896
EN2	0.81	2.79	1.08	0.950	0.79	0.41	**0.962**
BN1	0.73	9.08	0.82	**0.945**	0.75	0.30	0.875
BN2	0.45	4.40	0.54	**0.977**	0.45	0.38	0.963

q_e - equilibrium adsorption, mmol/g; K_L - a Langmuir constant; C_e - equilibrium concentration of Cr(VI) ions in the solution, mmol/L; Q_m- maximal adsorption capacity; K_F - a Freundlich constant; 1/n *- parameter characterizing adsorption intensity.*

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1. McNeill L., McLean J., Edwards M and Parks J., State of the science of hexavalent chromium in drinking water (D.: WRF. 2012).

2. Guidelines for drinking–water quality. Incorporating the First Addendum, fourth edition. World Health Organization, (G.: WHO. 2017.).