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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Sorption of Heavy Metals in Cationic and Anionic Forms by SKS Synthetic Carbons Modified with Nitrogen and Sulfur

S. S. Stavitskaya, V. M. Vikarchuk, S. V. Zhuravskii, N. N. Tsyba, and V. V. Strelko

Institute of Sorption and Endoecology Problems, National Academy of Sciences of Ukraine, Kiev, Ukraine

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Abstract—Data on the sorbability of ions of heavy metals (lead, cobalt, cadmium, zinc, copper, nickel) from Ringer's solution with complex composition by untreated SKS synthetic carbons and those modified with nitrogen and sulfur were obtained. Exploratory studies of the sorption of complex anions of copper and iron with complexing ligands (Cl and CN) were performed. Selectivity series of toxic metals were determined on the basis of their calculated distribution coefficients. It was shown that the best sorption effect is due to the presence of nitrogen atoms and strongly acidic SO_3H groups in the carbon structure.

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The increasing role of adsorption in various technological processes, including the adsorption of heavy metals, favors continued search for carbon materials with improved physicochemical properties and performance characteristics.

Frequently, the sorption properties of carbons are affected by the presence in their structure of atoms of oxygen, hydrogen, nitrogen, sulfur, phosphorus, and other elements because of their electronegativities different from that of carbon. Of considerable interest are, in particular, nitrogen-containing carbons that have long been manufactured and studied [1–8].

Nitrogen atoms in a carbon structure behave as polar centers: a nitrogen-containing carbon has a higher surface polarity than a nitrogen-free carbon. Nitrogen atoms raise the negative (pyridine nitrogen [1, 7]) or positive (nitrogen atoms substituting carbon atoms in the graphite lattice) charge on the carbon surface. It is commonly believed [1, 3, 4, 8] that nitrogen enhances the basicity of the carbon structure and thereby enables its use in catalysis. It is known that carbons containing chemically bound nitrogen have an increased anion-exchange capacity that is one of the most interesting properties of nitrogen-containing carbons [1, 3–5, 8, 9].

For example, it can be seen from Fig. 1 [1] that, in contrast to the ordinary carbon sorbent composed of a formaldehyde resin and having almost zero anion-exchange capacity at pH ~6–8, a nitrogen-containing carbon can absorb about 0.5 mg-equiv g^{-1} of Cl^- ions under these conditions. The increased anion-exchange capacity of nitrogen-containing carbons opens up prospects for their use in sorption of complex anions of

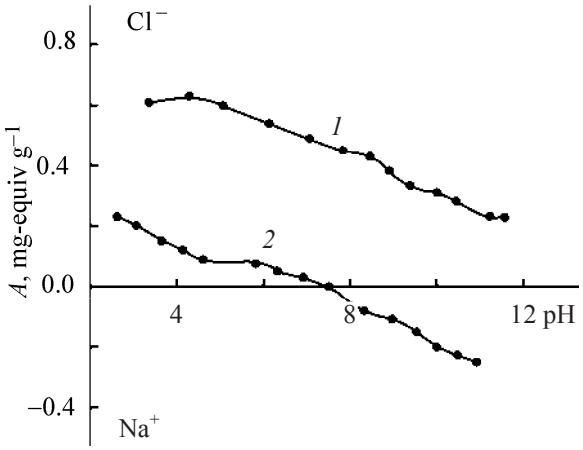


Fig. 1. Ion-exchange capacity A vs. the pH value of the equilibrium solution for (*1*) nitrogen-containing activated carbon SKN and (*2*) ordinary carbon prepared from phenol-formaldehyde resin. (A) Adsorbed amount of Cl^- and Na^+.

transition metals, commonly formed in large amounts in industrial recovery of metals by extractive methods.

The surface chemistry of these adsorbents, different from that of classical activated carbons, can strongly affect the results of their use in, e.g., sorption of toxic substances and heavy metals. Therefore, synthesis and study of new carbon sorbents with increased anion- and cation-exchange capacities, which enable a more differentiated approach to problems of absorption of noxious substances, are topical and worthwhile tasks.

The aim of this study was to examine the sorption properties of synthetic carbons of the SKS type (both activated and oxidized forms [2]), composed of styrene-divinylbenzene resin and modified with nitrogen or sulfur atoms to raise their absorption capacity for toxic metals.

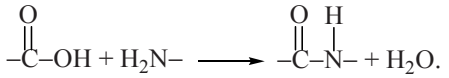
The presence of nitrogen atoms in the carbon structure favors a firmer binding of cations being sorbed (e.g., copper ions [3]) because of the coordination interaction of the complex-forming cation with, simultaneously, the nitrogen and oxygen of surface groups [1, 2, 5].

It should be noted that there is almost no published evidence about sorption of heavy metal ions on carbons of the SKN and SKS types and on their modified forms.

EXPERIMENTAL

The known SKN nitrogen-containing carbons are produced by carbonization of an expensive and ecologically unsafe nitrogen-containing product, 2-methyl-5-vinylpyridine [1]. The closest in porous structure and mechanical properties to SKN carbons are carbons of the SKS type, produced from porous styrene matrices; however, these carbons contain no nitrogen.

We chose for our study SKS carbons obtained from a chloromethylated copolymer of styrene and divinylbenzene after a thermal treatment of their oxidized forms impregnated with nitrogen-containing compounds [6, 10] (SKS-N sample). As a nitrogen-containing additive served urea, a readily available compound with a high content of nitrogen and a presence of amino groups. The presence of amino groups is necessary for chemical binding of urea molecules with the surface functional groups of an oxidized carbonizate of the chloromethylated copolymer (mostly carboxy and phenol groups):



The SKS-N sample we synthesized contained 3.6% of nitrogen according to elemental analysis data [6]. In addition to this sample, we obtained from the starting SKS porous carbon an oxidized sulfur-containing carbon by its sulfonation in conc. H_2SO_4 at a temperature of 180°C for 4 h [11] (SKS-S sample).

Table 1. Acid groups of the synthetic carbons modified with nitrogen and sulfur

Carbon	CEC, mg-equiv g^{-1}		Amount of groups, mg-equiv g^{-1}		
	for 0.1 N HCl	for 0.1 N NaOH	I[a]	II[a]	III[a]
SKS-N	0.75	0	0	0	0
SKS-S	–	4.8	3.2	0.0	1.6

[a] I, strongly acidic carboxy; II, weakly acidic carboxy; and III, phenolic.

Table 1 lists the results of a chemical analysis of surface groups of the carbons under study by the known procedure [12] of titration of the carbons with bases of varied strength. It can be seen in Table 1 that SKS-N carbon is an anion-exchanger with a high exchange capacity for 0.1 N HCl, and SKS-S sample is a cation exchanger with a capacity of 4.8 mg-equiv g^{-1} (for 0.1 N NaOH), where strongly acidic carboxy and phenol groups were found.

Because the porous structure parameters of the sorbent enable prognostication of its efficiency under real conditions, we employed commonly accepted methods [13] to obtain structural-sorption characteristics of both the starting carbonizates and nitrogen- and sulfur-containing samples we synthesized (Table 2).

The following parameters were determined: adsorption of Methylene Blue, AMB, from the sorption of a benzene vapor by the desiccator method [13]; specific volume of sorption pores, W_s; a NOVA-2200E Quantochrome high-speed low-temperature gas analyzer was employed to determine the adsorption of nitrogen at T = 77 K, *AN*; volume of micro- and mesopores, V_{mi} and V_{ms}; their surface areas S_{mi} and S_{ms}; total specific surface area for nitrogen, S_{sp}; and pore radius r (Å) distribution (Table 2, Figs. 2a and 2b).

Table 2. Structural-sorption properties of the starting carbon SKS_c and SKS carbon modified with nitrogen and sulfur

Sample	S_{sp}	S_{ms}	S_{mi}	W_s for C_6H_6	V_{tot}	V_{ms}	V_{mi}	A_N	A_{ms}, mg g^{-1}	r, Å
	$m^2\ g^{-1}$			$cm^3\ g^{-1}$						
SKS_c	299	453	105	0.103	0.573	0.453	0.044	370	155	38
SKS-N	827	227	599	0.876	0.924	0.685	0.239	600	367	22
SKS-S	521	121	340	0.740	0.660	0.503	0.157	470	258	25

This was done using various calculation procedures (BJH, DFT) [14].

We performed sorption experiments under static conditions by continuous agitation of a weighed portion of the sorbent (commonly 0.1 g) in a salt solution (20 ml) with various initial concentrations on the background of a standard Ringer's salt solution (NaCl 0.8, KCl 0.42, $CaCl_2$ 0.024, $NaHCO_3$ 0.01%) imitating biological media of a living organism. The initial (c_0) and equilibrium (c_{eq}) concentrations of metal ions were determined by atomic-absorption spectroscopy on a KAC-120.1 spectrometer.

To study the adsorption of complex ions of transition metals and to elucidate the role of nitrogen- and sulfur-containing functional groups in anionic processes on synthetic carbons, we chose aqueous solutions of the salts $K_3[Fe(CN)_6]$ and $H_2[CuCl_4]$ (solution of the $CuCl_2 \cdot 2H_2O$ salt in conc. HCl) with various concentrations (0.5 to 15 mM).

Figures 3a, 3b, and 3c shows sorption isotherms of metal ions (Pb^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}) on SKS-N and SKS-S carbons and the starting SKS carbon, respectively.

The curves are described by a Freundlich equation at equilibrium concentrations of 0.1–1.5 mM. The absolute amounts of adsorption of the ions are rather close in a wide range of concentrations and reach the maximum values of 0.8–1.6 mmol g^{-1}.

It should be noted that these values are approximately 4 times those for the adsorption of the same ions, previously obtained [15] under similar conditions ($s : l = 1 : 200$, Ringer's solution, 4 h of contact with the solution) on an oxidized carbon fabric having high sorption properties as a result of its specific structural-geometric characteristics [16].

The nitrogen- and sulfur-containing carbon sorbents synthesized in this study far better absorb heavy metal ions because their structure contains basic complexing nitrogen groups (despite the absence of strongly acidic groups necessary in this case [2], Table 1) and sulfur in the form of SO_3H groups (Figs. 3a–3c).

The results obtained can be used to compose selectivity series of sorption of heavy metal ions by the sorbents under study in the concentration range 0.5–4 mM: $Ni^{2+} > Pb^{2+} > Co^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+}$ for SKS-N and $Ni^{2+} > Co^{2+} > Zn^{2+} > Cu^{2+} > Pb^{2+} > Cd^{2+}$

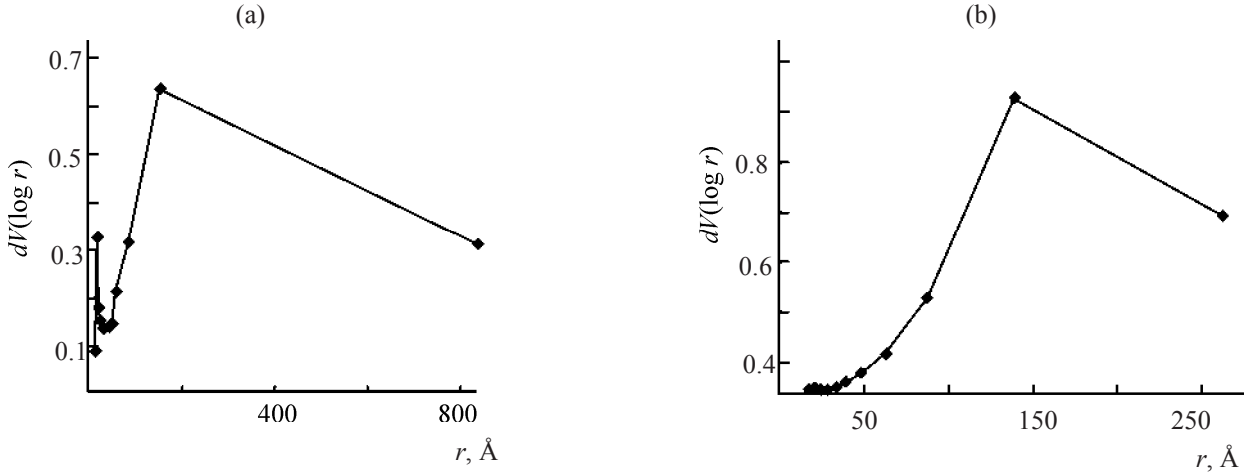


Fig. 2. Distribution of pore volumes V over radii r on (a) SKS-N and (b) SKS-S carbons.

for SKS-S. These series are typical of most of oxidized carbons [2], except for the high values of sorption for nickel ions.

The experimental values of adsorption were used to easily calculate the distribution coefficients K_d for each of the ions, reduced to standard conditions (concentrations of ions in solutions, 1 mM) and to trace the manner in which K_d (volume of the equilibrium solution containing the same absolute amount of a substance under study as that in adsorbed state in 1 g of the adsorbent) varies in a wide range of equilibrium concentrations c_{eq} of ions in solution. The results obtained are shown in Figs. 4a and 4b. Table 3 lists values of K_d for the ions, calculated for different sorbents at the same c_{eq} of 1 mM (for comparison).

These data characterize the sorbents we synthesized as a sufficiently highly selective material with respect to heavy metal ions, and especially Co^{2+}, Pb^{2+}, Cu^{2+}, and Ni^{2+}. In fact, such a sorption material can effectively diminish increased concentrations of these metals in a living organism (in the case of the so-called metalosis) to a required (physiological) level.

To elucidate the role of nitrogen and sulfur in adsorption of complex anions of transition metals, where the ligands Cl and CN were complex-forming agents, we obtained isotherms of sorption of copper and iron ions from aqueous solutions of the salts H_2CuCl_4 and $K_3[Fe(CN)_6]$, respectively. The solid: liquid ratio was 1 : 200, the solution concentrations were varied within the range 0.5–10 mM. First trial experiments demonstrated (Fig. 5) that the synthetic SKS carbons modified with nitrogen and sulfur differently sorb these ions from anionic complexes. For example, copper and iron were best absorbed on the SKS-S and SKS-N samples and worst absorbed on nitrogen- and iron-containing carbons, respectively.

Probably, the complexing agent Cl forms (in the case of copper) firmer complexes with sulfur-containing surface functional groups, compared with nitrogen-containing groups. At the same time, in the case of the anionic complex of iron with CN, the complex with nitrogen is, by contrast, firmer than that with sulfur (Fig. 5, curves *3* and *2*).

Table 3. Distribution coefficients K_d of the heavy metal ions under study on SKS-N and SKS-S carbons[a]. Weighed portion of a sample m = 0.1 g, solution volume V = 20 ml, T = 20°C, 4 h of contact between the carbon and the solution

Sorbed ion	K_d, ml g^{-1}	
	SKS-N	SKS-S
Cd^{2+}	1960	60
Co^{2+}	1200	2100
Zn^{2+}	900	100
Ni^{2+}	1200	480
Cu^{2+}	1000	3000
Pb^{2+}	1700	270

[a] Values of K_d are given (for comparison) for identical equilibrium concentration c_{eq} = 1 mol l^{-1}.

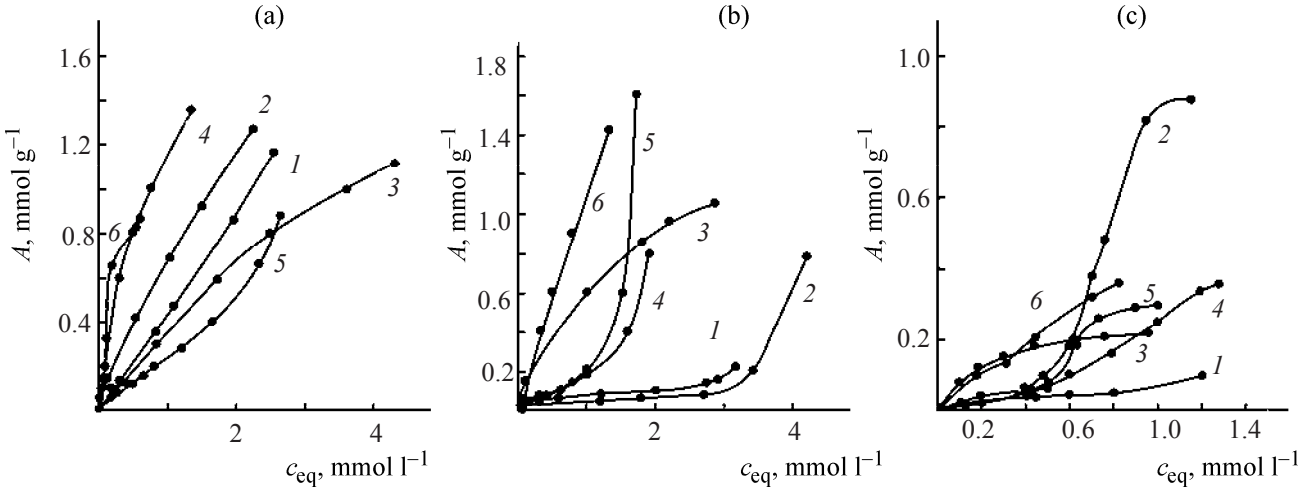


Fig. 3. Isotherms of ion adsorption A from Ringer's solution on (a) SKS-N and (b) SKS-S carbons and (c) unmodified SKS carbon. (c_{eq}) Equilibrium concentration; the same for Fig. 5. (a) (*1*) Cd^{2+}, (*2*) Co^{2+}, (*3*) Zn^{2+}, (*4*) Ni^{2+}, (*5*) Cu^{2+}, and (*6*) Pb^{2+}; (b) (*1*) Pb^{2+}, (*2*) Cd^{2+}, (*3*) Co^{2+}, (*4*) Cu^{2+}, (*5*) Zn^{2+}, and (*6*) Ni^{2+}; (c) (*1*) Zn^{2+}, (*2*) Pb^{2+}, (*3*) Cd^{2+}, (*4*) Cu^{2+}, (*5*) Co^{2+}, and (*6*) Ni^{2+}.

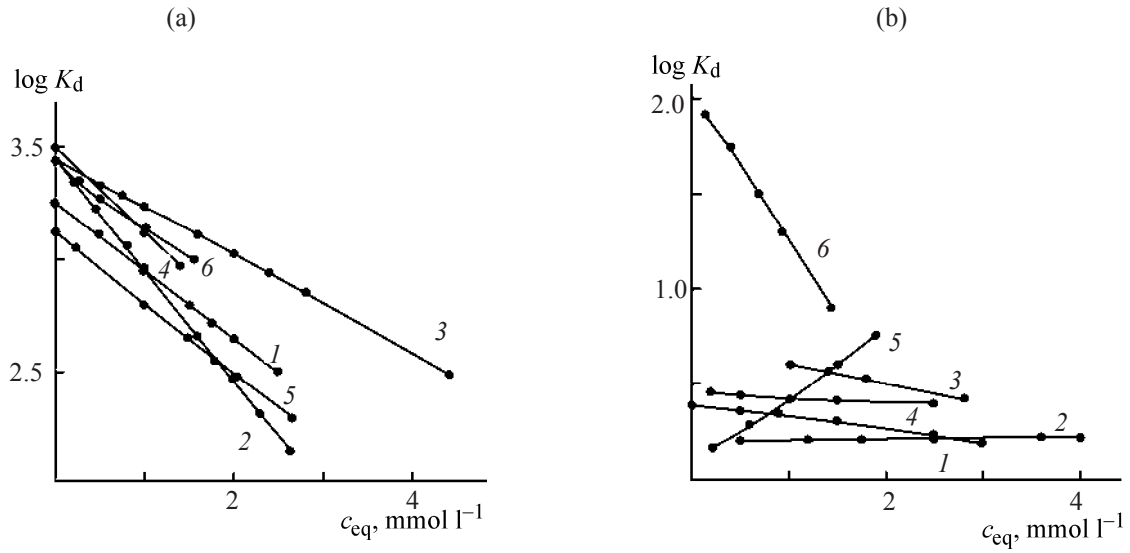


Fig. 4. Distribution coefficients K_d of ions vs. c_{eq} on (a) SKS-N and (b) SKS-S carbons. (a) (*1*) Cd^{2+}, (*2*) Co^{2+}, (*3*) Zn^{2+}, (*4*) Ni^{2+}, (*5*) Cu^{2+}, and (*6*) Pb^{2+}; (b) (*1*) Pb^{2+}, (*2*) Cd^{2+}, (*3*) Co^{2+}, (*4*) Cu^{2+}, (*5*) Zn^{2+}, and (*6*) Ni^{2+}.

Previous results [17] and the data obtained in the present study confirm that SKS carbon has a flexible, easily controllable structure (Table 2). Synthetic SKS carbons are micro-mesoporous adsorbents. Even raw carbon (carbonizate) SKS_c can be used as an adsorbent without additional activation.

In the course of steam-gas activation (activated SKS), the slit halfwidth of SKS micropores changes from 0.3 to 0.96 nm [17], with the volume of micropores possibly reaching a value of 0.24 cm^3 g^{-1} and the uniformity of the microporous structure increasing. This enables purposeful development of sorbents for particular technologies.

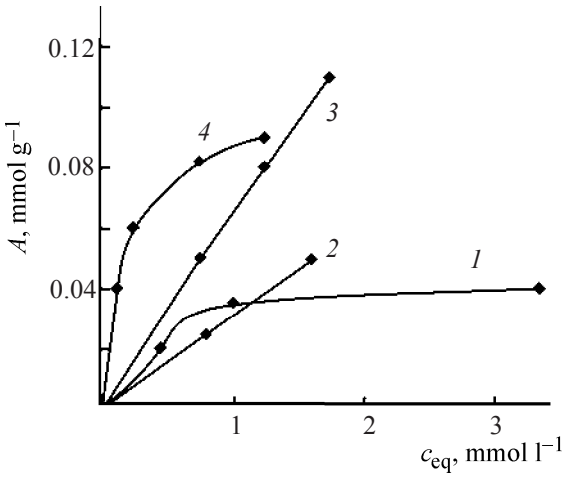


Fig. 5. Isotherms of sorption A of (*1, 4*) copper and (*2, 3*) iron in the anionic form (complexing agents, Cl and CN, respectively) on (*1, 3*) SKS-N and (*2, 4*) SKS-S carbons.

For example, it was found (Figs. 3a and 3b) that synthetic activated carbons SKS-N and SKS-S with small micropores show an increased adsorption capacity for heavy metal cations. With allowance made for its high strength and lower cost [9], compared with synthetic SKN carbon, SKS carbon is a promising sorbent for application to various technologies.

CONCLUSIONS

(1) A sample of a nitrogen-containing carbon sorbent SKS-N was obtained by thermal treatment of oxidized modifications of a carbon produced from styrene-divinylbenzene resin, by their impregnation with a nitrogen-containing compound, urea. An SKS-S sorbent with high cation-exchange properties was synthesized by sulfonation of the starting carbon with concentrated sulfuric acid at $T = 180°C$.

(2) It was found that synthetic SKS carbons are micro-mesoporous adsorbents with micro- and mesopore volumes of 0.157–0.239 and 0.453–0.685 cm^3 g^{-1}, respectively; specific surface area S_{sp} = 300–830 m^2 g^{-1}; and pore radius $r \approx$ 20–22 Å.

(3) It was shown that, owing to the presence of modifying additives, the sorbents under study have an increased adsorption capacity for heavy metal cations (Pb^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}) and also can absorb complex anions of copper and iron with various ligands (Cl and CN).

(4) It was demonstrated that the absolute values of ion adsorption are sufficiently close in a wide range of

concentrations and 4 times those obtained for these cations on oxidized carbon sorbents.

(5) Sorption selectivity series were determined for toxic metals from the distribution coefficients calculated for standard conditions.

(6) It was suggested that the sorbents synthesized can be used for removal of heavy metals in both cationic and anionic forms in water treatment and for fairly effective reduction of increased concentrations of these metals in a human organism to the required (physiological) level.

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