Adsorption of Sr^{2+} and Cu^{2+} from aqueous solutions by surface aminated nanoporous activated carbon fibers

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Objectives: Here we report on the chemical, thermal and adsorption properties of surface aminated nanoporous activated carbon fibers (ACFs). The bromination of nanoporous ACFs by using treatment with liquid bromine was followed by amination with selected amine: ethylenediamine, diethylamine, monoethanolamine, or sulfolanylethylenediamine to lead to an efficient two-step synthesis of the surface-aminated nanoporous ACFs for adsorption of contaminant ions from waters.

Methods: Nitrogen adsorption-desorption isotherms were measured on an automatic gas adsorption analyzer ASAP 2405N. Electron microscopy (SEM and TEM) observations on non-coated samples were performed on Mira 3 GMU LV-FE-SEM and JEM-2000EXII instruments equipped with EDX spectrometer from Oxford Instruments. Adsorption measurements and chemical analysis were done as earlier reported in [1].

Table 1 Elemental, textural, and TGA analyses of sorbents

Sorbent	Elemental analyses CHNS/EDX (mass%)					Texture			TGA	
	C	H	S	N	O	S_{BET} (m^2/g)	V_m (cm^3/g)	D_{avr} (Å)	C_N (mmol/g)	T_{max} (°C)
ACF	93.7	0.7	0.2	0.4	5.0	1370	0.63	19.7	–	–
ACF/Br_2	90.2	0.6	0.1	–	5.6	1070	0.50	19.1	–	–
ACF/Br_2/En	84.7	1.6	0.1	5.1	7.6	820	0.38	19.5	0.87	300
ACF/Br_2/Et_2N	87.8	1.5	0.2	2.9	7.6	880	0.41	19.4	0.62	285
ACF/Br_2/MEA	86.1	1.6	0.2	3.1	9.0	790	0.37	19.0	0.95	310
ACF/Br_2/SuEn	76.3	2.1	5.1	4.2	12.3	480	0.24	17.8	0.66	345

Table 2 Constants of the Langmuir, Freundlich, and Dubinin–Radushkevich Eqs. for adsorption of Cd^{2+} and Cu^{2+} onto на ACFs

Sorbent	Fitting parameters					
	Langmuir		Freundlich		Dubinin–Radushkevich	
	q_{max} 10^4 (mol g^{-1})	K_L (mL mol^{-1})	K_F	n	a_{micro} (mmol g^{-1})	E_{DR} (kJ mol^{-1})
ACF	1.71	3.79	0.021	1.46	2.44	14.3
ACF/Br_2/MEA	7.23	7.06	0.346	1.30	14.35	14.6
ACF/Br_2/En	5.13	10.10	0.200	1.38	10.74	14.9
ACF/Br_2/Et_2N	4.65	6.94	0.159	1.35	9.73	14.4
ACF/Br_2/SuEN	4.42	5.47	0.173	1.30	10.07	14.0

Sorbent	Fitting parameters			
	Langmuir		Dubinin–Radushkevich	
	q_{max} 10^5 (mol/g)	K_L (mL/mol)	a_{micro} 10^4 (mol/g)	E_{DR} (kJ/mol)
ACF	5.9±0.2	24±1	8.5±0.9	16.1±0.5
ACF/Br_2/En	4.89±0.07	105±6	2.3±0.2	22.4±0.7
ACF/Br_2/Et_2N	4.29±0.07	147±6	1.6±0.1	24.4±0.6
ACF/Br_2/MEA	4.92±0.08	160±5	1.7±0.1	25.4±0.3

Fig. 1. TEM/SEM image of ACFs

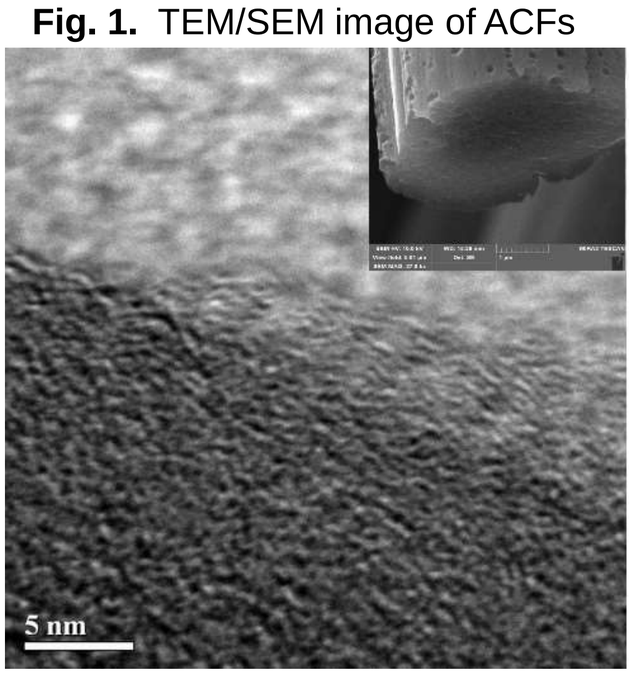
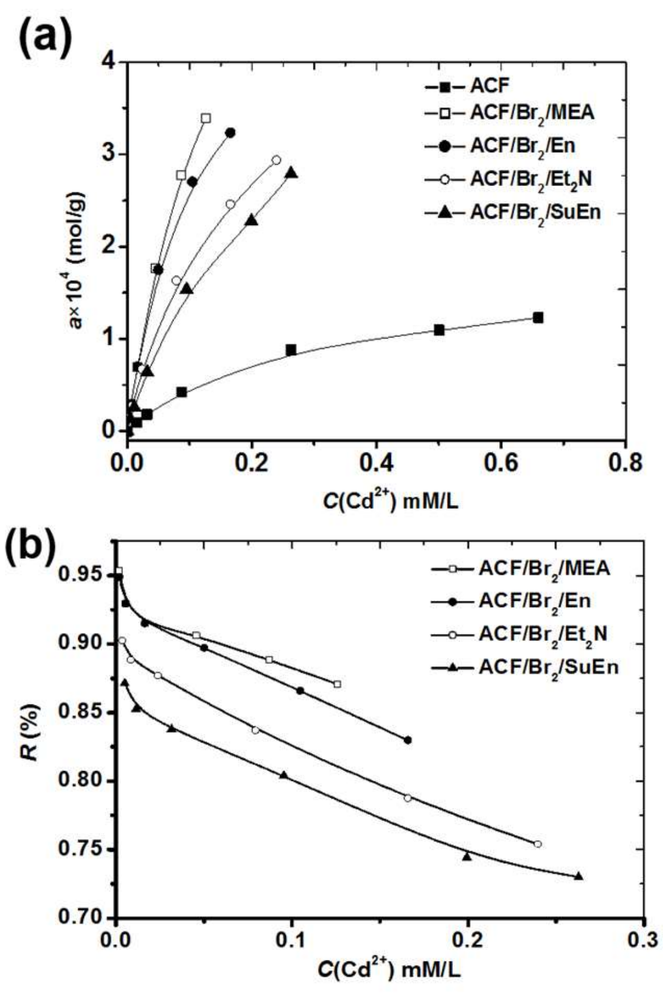


Fig. 2. (a) Adsorption isotherms and (b) recovery of Cd^{2+} against the equilibrium concentration of Cd^{2+}.



• **Results:** The most probable mechanism, according to the Dubinin-Radushkevich model, considers the adsorption of Cd^{2+} ions in micropores, and the functional amino groups are the centers of such adsorption. The presence of amino groups at the entrance to nanopores will contribute to its complete filling with Cd^{2+} ions and considerably increase the value of a_{micro}. The adsorption of copper and cadmium ions is well described by the Langmuir, Freundlich (only for Cd^{2+}), and Dubinin-Radushkevich models. By their adsorption capacity, the surface aminated ACFs can be placed, by numeric values, in the following descending series ACF/Br_2/MEA > ACF/Br_2/En > ACF/Br_2/Et_2N > ACF/Br_2/SuEn. The highest *R* recovery is observed for the ACF/Br_2/MEA; despite this sorbent has lower S_{BET} value as compared to those of ACF/Br_2/En and ACF/Br_2/Et_2N. It has been established that the main factor determining the high adsorption capacity is the presence of amino groups that form stable surface complexes with Cu^{2+} ions.

Conclusions. The surface aminated ACFs have moderate thermal stability, and thermal decomposition and detachment of amino groups pass between 170 and 460 °C. Effective adsorption of 80–90% of copper (II) and cadmium (II) metal ions from very dilute water solutions were achieved with the surface aminated ACFs. Experimental adsorption data were analyzed by fitting them to the Langmuir, Freundlich and Dubinin-Radushkevich (DR) isotherms. In this way, we proved sufficient energy homogeneity of the carbon surfaces and suggested adsorption in the micropores, correspondingly. For the aminated ACFs, the constant describing the adsorption/desorption equilibrium for each model and the E_{DR} adsorption energies have the values by 4–6 and 1.3–1.5 times higher than those found for the unmodified ACFs. The fact that supported amino groups can do effective adsorption provides unparalleled opportunities to develop innovative technologies for sustainable and greener water purification.

References: [1] L.M. Grishchenko, V.E. Diyuk, O.P. Konoplitska, V.V. Lisnyak, R.T. Maryichuk. Modeling of copper ions adsorption onto oxidative-modified activated carbons. Adsorption Sci. & Technol. 35(9–10) (2017)