Copper Sorption by Coal Substances from Aqueous Solutions

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Article info

Abstract

The copper cations sorption by brown coal, humic acids and residual coal samples after the extraction of humic acid was studied by using the methods of spectroscopy FT-IR, EPR, Solid State CP/MAS ^{13}C-NMR. Samples of lignite (brown coal) of the Tisulsky deposit (TL) of Kansk-Achinsk brown coal basin (Russia), its natural-oxidized form (NOLF), as well as samples of the humic acids (HA) extracted from them, and the residual coal after the extraction of humic acids (RC) were used as sorbents. The copper cations sorption process by the investigated samples depends on contribution of several mechanisms in varying degrees. It may be an ion exchange; complexation with the functional groups of the electron donor; complexation to form the bond Me^{z+} – HA due to the presence of the free π-electrons on the surface. The quantity of adsorbed copper cations depends on the functional and structural composition of the investigated samples. The copper cations sorption by the coals, humic acids and residual coals reduces the number of paramagnetic centers in the samples and the intensity of the NMR spectra. The copper cations sorption by HA from TL is determined by the significant contribution of the ion exchange process. HA from NOLF; initial TL and NOLF; RC TL and RC NOLF sorb copper cations mainly due to the formation of complexes with individual functional groups and the negatively charged surface portions. The data of ^{13}C-NMR and EPR studies have shown that the aromatic structures make the main contribution to the complexation.

1. Introduction

The sorbents obtaining is one of the basic direction of humic acids using [1-2]. The sorption of cations Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Fe^{2+}, Mn^{2+}, Ca^{2+}, Mg^{2+}, Pb^{2+} from aqueous solutions by the humic acids extracted from brown coal and peat has been investigated in [3-6]. During the metals sorption by the humic acids several sorption mechanisms can be realized. It can be the ion exchange; the complexation with electron-donor functional groups; the complexation with forming of a bond Me^{z+} − HA due to the free π-electrons on the surface; redox reduction reaction of a metal cation to an elemental form. It assumed that the metal cations interact with humic acids by the first and the second mechanisms, i.e. complexation as an addition to the ion exchange [7-8]. The disappearance or decreasing of the HA IR spectra intensity bands of stretching vibrations of the C=O (1710-1720 cm^{-1}) and deformation vibrations of O-H (1220-1270 cm^{-1}) of carboxyl groups, as well as the emergence of symmetrical bands (1380-1400 cm^{-1}) and asymmetrical (1560-1600 cm^{-1}) stretching vibrations of the carboxylate ion indicate the realization of the ion exchange process of sorption humic acids [3, 9]. According to its ion-exchange properties HA are close to the weak acid cation exchangers. Due to the presence of the carboxyl and phenolic hydroxyl ion-exchange groups sorption properties of humic acids depend on the pH and the HA nature.

When cations sorption takes place for the formation of coordination compounds it is necessary that there are free orbitals of the metal ions and free electron pairs of a donor, which are a part of the sorbent functional groups. In the sorbent structure there are electron-donating functional groups such as $>C=O$, $–COOH$, $–C–OH$, $Ar–OH$, $= N–H$, $\equiv N$ etc. in various combinations, these groups have to

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support the formation of complexes with metal cations in the solid phase. In [10] copper sorption by carboxyl cation exchanger has been studied by EPR and it has been shown the formation of mononuclear complexes in which each cation is connected with two copper carboxylate ions, –COO⁻, as well as the formation of binuclear and polynuclear complexes. It has been assumed [6] that the interaction of metal cations with humic acids is realized through the two mechanisms – micro- and macrocoordination. During microcoordination metal cations are associated with individual functional groups, during macrocoordination metal cations interact with the negatively charged surface portions of humic acids and form the macromolecular complexes. The ability of humic acids to the ion exchange and complex formation produces great prospects for the separation and recovery of metal cations from various environs, for wastewater treatment. However, the structure complexity of these natural compounds results in some difficulties for the investigation and interpretation of its properties.

The purpose of this work has been investigation of the copper cations sorption from aqueous solutions by the brown coals, humic acids and residual coals after the HA extraction.

2. Experimental

As sorbents samples of lignite (brown coal) of the Tisulsky deposit (TL) of Kansk-Achinsk brown coal basin (Russia), its natural-oxidized form (NOLF), samples of the humic acids (HA) and the residual coal (RC) synthesized according to the scheme (Fig. 1) have been used.
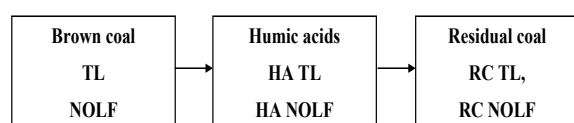

Fig. 1. The scheme of the samples obtaining from the Tisulsky deposit brown coal and its natural-oxidized form.

Humic acids were extracted from the coal by treating the samples by sodium hydroxide solution and by hydrochloric acid deposition [11]. Characteristics of the samples are listed in Table 1.

The high-resolution solid-state ^{13}C-NMR spectra were recorded by "Bruker Avance III 300WB" at 75 MHz and sample rotation 5 kHz with using of the cross-polarization technique and "magic" angle spinning (CP/MAS).

The samples EPR spectra were recorded by the EPR spectrometer "Bruker EMX-m40X" at 9.86 GHz and at the room temperature. For all samples the EPR spectra recording conditions were identical: the power level was 1.8-1.9 mW, modulation frequency was 100 kHz. As a standard the Mn^{2+} ions in magnesium oxide MgO was used. The known concentration standard imidazolinon nitroxyl radical $C_{13}H_{17}N_2O_2$ was used for determination of organic paramagnetic centers (PMC) quantity. Characteristics of EPR spectra were calculated by using the Bruker WinEPR.

IR spectra were recorded by the spectrometer with Fourier transform "CFT Infralyum-801" in tablets with KBr.

After sorption of the copper the samples X-ray diffractions were obtained by X-ray diffractometer "Bruker Avance A25" according to the polycrystal method at the room temperature.

For protons determination initial and equilibrium solutions were analyzed by using the pH meter "Sartorius PP-50".

To determine the investigated samples sorption capacity 1 g of the sample was taken and placed in a conical flask, then it was filled with the aqueous solution of the copper nitrate (V = 25 ml, C = 0.1 mole/l, pH = 4.13) and allowed to establish equilibrium during three days at T = 298 K. The copper cations content was determined in the initial solutions and equilibrium ones by the trilonometric titration. The absorbed cations Cu^{2+} quantity was calculated by the concentrations difference in the initial and equilibrium solutions per 1 g of a dry sample.

Table 1
Characteristics and elemental composition of brown coals and products, (%)

Sample	W^a	A^d	V^{daf}	C^{daf}	H^{daf}	$(O + N + S)^{daf}$ by difference	$(HA)_t^{daf}$
TL	8.04	6.11	48.14	64.34	4.69	30.97	21.33
HA TL	4.92	9.16	-	59.05	4.88	36.07	-
RC TL	8.96	11.39	47.82	51.91	4.24	43.85	-
NOLF	13.5	46.64	90.84	55.08	2.66	42.26	60.91
HA NOLF	6.99	15.15	-	61.58	5.35	33.07	-
RC NOLF	2.20	72.18	66.88	49.07	3.88	47.02	-
$(HA)_t^{daf}$ — output of the humic acid calculated by a coal dry ash-free weight [11]							

3. Results and Discussion

The investigated coals, humic acids and residual coals are characterized by the IR typical absorption bands of varying intensity that corresponds to the results of the previous studies [12]. There is a broad band with the absorption maximum ~3400 cm⁻¹ in the spectra of the coal, humic acids and residual coals samples and it indicates to the existence of hydrogen bound hydroxyl groups. The bands 2940-2920 cm⁻¹ and 2860-2840 cm⁻¹ are the stretching vibrations of –CH₃ and –CH₂ groups; the band 1620-1600 cm⁻¹ is the stretching vibrations of the conjugated double bonds C=C and aromatic parts; in the region 1370-1450 cm⁻¹ there are deformation vibrations of C–H bond in the aliphatic groups –CH₃ and –CH₂; the band 1280-1240 cm⁻¹ illustrates the bonds of the C–O carboxylic acids, esters, O–H-phenols; the

band 1100-1030 cm⁻¹ does the same for the C–O cyclic and aliphatic ethers and alcohols. The band of the C=O bond stretching vibrations in the carboxylic groups (1720-1710 cm⁻¹) exists in the HA spectra extracted from all coals. The absorption bands intensities comparison in the region 1620-1600 cm⁻¹ to the intensity of the absorption bands of 2940-2920 cm⁻¹ and 2860-2840 cm⁻¹ allows us to estimate the degree of aromaticity of the investigated coals. For coal NOLF the aromaticity degree is 3.3; for TL it is 1.92. The oxidized coal NOLF has the lower content of carbon and hydrogen (Table 1); this is an indirect evidence of a higher degree of aromaticity.

The samples of NOLF, HA from NOLF are highly aromatic as it can be seen from the Table 2. Besides the NOLF coal sample has a relatively high content of carboxyl groups in comparison with the TL coal.

Table 2
Relative abundances of different carbon types assessed by ¹³C NMR, (%)

Sample	Chemical shift rang, ppм						
	220-187 C=O	187-165 COOH	165-145 C_{ar}-O	145-108 C_{ar}	108-90 $C_{O-alk-O}$	90-48 C_{alk}-O	48-5 C_{alk}
TL	4.4	4.7	4.2	19.1	3.5	7.5	55.6
HA TL	4.4	7.3	5.4	17.9	3.6	10.8	50.7
RC TL	5.9	8.0	6.9	39.6	4.9	15.0	20.5
NOLF	2.6	6.0	8.9	31.9	5.7	12.7	30.3
HA NOLF	3.5	7.4	8.2	31.7	6.3	14.8	26.8
RC NOLF	3.1	7.5	7.9	31.2	5.2	15.0	28.3

The sorption capacity (E) of the samples and the pH of the equilibrium solutions are given in Table 3. It can be seen that not only humic acids, but the initial coals and the residual coals have the sorption capacity for the copper cations.

The presence of the active acidic carboxyl groups in the samples results in the process of ion exchange and it is confirmed by the acidity increasing for the equilibrium solution in comparison with the initial one. In this case, the carboxyl groups' protons are exchanged to the copper cations from the external solution in accordance with the equation:

$$2R\text{-}COOH \text{ (solid)} + Cu^{2+} \text{ (solution)} \rightarrow (R\text{-}COO)_2Cu \text{ (solid)} + 2H^+ \text{ (solution)}.$$
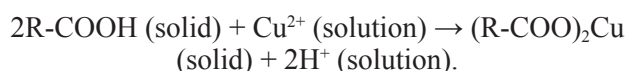
We calculated the Cu²⁺ portions involved in the ion exchange from the total amount of adsorbed cations (Table 3) according to the equation:

$$\frac{C_H^+ - C^0_H{}^+}{C^0_{Cu}{}^{2+} - C_{Cu}{}^{2+}} \times 100\%,$$

where: C_H^+, $C_{Cu}{}^{2+}$ is the equilibrium concentrations of protons and cations of copper, g-eq/l g;
$C^0_H{}^+$, $C^0_{Cu}{}^{2+}$ – the initial concentrations of protons and cations of copper, g-eq/l g.

For the sample HA TL there is observed the maximum contribution of ion exchange to the process of copper sorption (50%). It is also confirmed by the appearance of the band 1390-1380 cm⁻¹ (symmetric vibrations of carboxylate-ion) in the IR spectra of the samples containing sorbed copper cations. The higher capacity for HA NOLF (2.62) compared to HA TL (0.99) is realized with the minimum contribution of ion exchange 2%, i.e. almost all sorbed copper cations are involved in the formation of coordination compounds. By comparing the Table 3 data we can assume that the investigated samples of original and residual coals sorb copper cations by the complex formation way. Tables 2 and 3 data analysis does not allow identifying the dependence between the content of functional groups and the sorption capacity of the samples. On the one hand, it is probably connected to the ability of carboxyl

and hydroxyl groups to the association through the formation of hydrogen bonds [13]; as a result a part of the functional groups, capable of reacting with the cations, is shielded and sterically inaccessible; from the other hand, it is connected with the various reactive ability of the functional groups of aromatic and aliphatic fragments.

Table 3
The sorption capacity (E) of the investigated coals and its derivatives per Cu^{2+}

Sample	E, mg-eq/g	pH equilibrium solution	Share of the ion exchange,%
TL	0.87	3.20	2
HA TL	0.99	2.13	50
RC TL	3.60	4.73	<1
NOLF	1.79	3.55	<1
HA NOLF	2.62	2.89	2
RC NOLF	1.67	4.67	<1

There are high sorption characteristics to the copper cations for residual coal RC TL and RC NOLF that may be associated with the increasing of hydrophilicity of the samples surface. The possibility of different structural groups' participation in the process of copper cations sorption through the macrocoordination mechanism should not be excluded also.

In the study of the copper cations interaction with peat humic acids by the EPR method it has been shown [14] that there is no the formation of diamagnetic compounds of copper in the sorption process, i.e. copper cations save its original oxidation state. We have carried out X-ray diffraction study of copper-containing samples and the Cu^0 was not detected. On the other hand, the agreement of the copper cations quantity after sorption and desorption by hydrochloric acid indicates also to the absence of Cu^0 in the solid phase.

In the region of g-factor = 2.003-2.004 spectra were registered during the EPR analysis of the samples of coal, humic acids and residual coal, which corresponds to the radicals of coals organic compounds [15]. For almost all samples signals of organic radicals are symmetrical or slightly asymmetrical singlets, which is typical for the coal and solid polyaromatic compounds with semiquinone-type radicals [16]. The singlet is a superposition of two EPR signals of the various width and intensity.

Table 4 lists the EPR spectra parameters of the investigated samples. The line width of the signals for coal TL, as well as for humic acids and residual coal extracted from it, is $\Delta Hpp \geq 4\text{-}6$ G, which is in agreement with the literature data [17, 18]. For the samples of the series NOLF EPR spectra differ in its parameters from the similar ones of TL samples. The EPR signal of organic singlet of NOLF coal and RC NOLF residual coal is narrower and has the width $\Delta Hpp = 2.5\text{-}3.6$ G. It may be due to the higher content of aromatic fragments and oxygen-containing functional groups [18]. The increasing of the polyconjugation links degree can also result in the narrowing of the signal [19]. For the humic acids of the series TL samples the signal is the least intensive one. Among the samples of the NOLF series RC NOLF ones demonstrate the higher intensity of the signal. The decreasing of the g-factor (TL – 2.00334, NOLF – 2.00316) and (RC TL – 2.0039 and RC NOLF – 2.00337) may be associated with the increasing of condensation degree of oxygen-containing radicals [19].

Table 4
Characteristic parameters of EPR spectra of the investigated samples

Sample	g-factor	Line width ΔHpp,G	Organic free radical content (PMC) $\times 10^{-19}$, spins/g	$Cu^{2+} \times 10^{-21}$, spins/g
TL	2.00363	6.520	36.7	-
TL – Cu	2.00319	4.176	2.99	1.3
HA TL	2.00364	4.981	2.69	-
HA TL – Cu	2.00352	6.611*	0.5	1.7
RC TL	2.00397	6.740	5.29	-
RC TL – Cu	2.00324	4.162	0.4	1.6
NOLF	2.00316	2.564	1.1	-
NOLF – Cu	2.00314	2.491	1.07	1.5
HA NOLF	2.00364	7.590	0.27	-
HA NOLF – Cu	2.00321	6.243*	0.02	3.3
RC NOLF	2.00337	3.663	6.4	-
RC NOLF – Cu	2.00314	2.784	1.1	1.1

* – the EPR signal is very weak one

Against the broad signal from the copper cations there is a signal of the organic paramagnetic centers (PMC) which is lower considerably in comparison with the signal for the samples without Cu^{2+}. Figures 2 and 3 show the spectra of HA TL and RC NOLF before and after the copper cations sorption. The decreasing of the EPR signal intensity, as well as reducing of the number of paramagnetic centers in several times (Table 4), indicates the interaction between cations Cu^{2+} and polyaromatic compounds through the donor-acceptor mechanism.
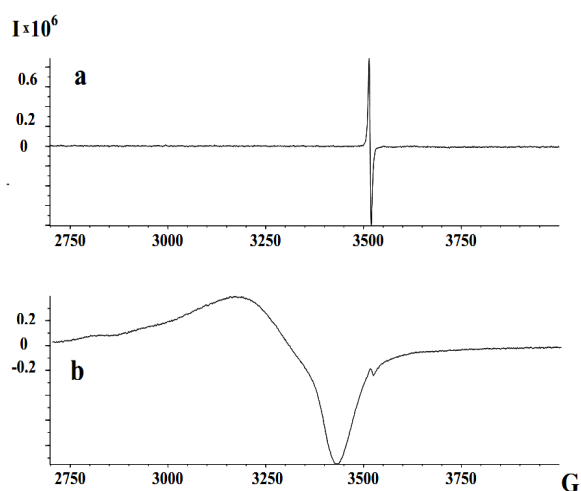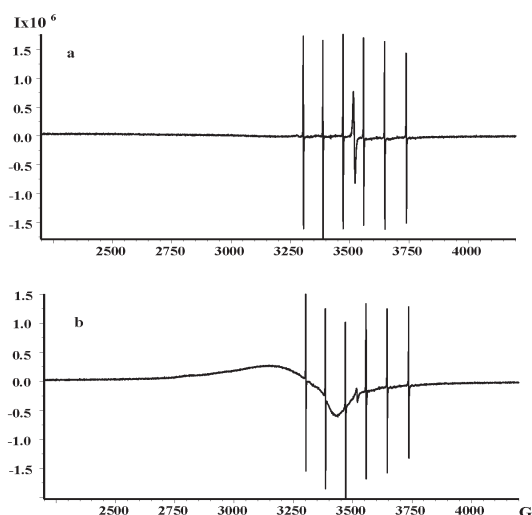

Fig. 2. EPR spectra of HA TL (a), HA TL - Cu^{2+} (b).

Fig. 3. EPR spectra of RC NOLF (a), RC NOLF - Cu^{2+} (b).

For all samples of the coal, humic acids and residual coals EPR spectra of adsorbed copper cations are similar. There are narrow signals (various intensity) of organic PMC on the right slope of the copper anisotropic signal.

The spectra of adsorbed copper cations consist of the superposition of the two signals: isolated copper ions and copper associates (a singlet signal). The EPR parameters of the isolated ions ($A_\parallel$ = 130 MHz, $g_\parallel$ = 2.35) indicate the octahedral symmetry of the oxygen environ of copper cations with the strong tetragonal distortion. The singlet signal (g_0 = 2.15-2.16) corresponds to dehydrated associates of copper cations with the weak interaction between the ions. For copper cations signals the same intensities values were obtained approximately for all samples (Table 4); the maximum value is 3.3×10^{21} spins/g (a sample RC NOLF – Cu^{2+}).

Introduction of the copper cations to the substance of the coal, HA and RC should also be reflected in the ^{13}C-NMR spectra. It is known that the inclusion in the structure of the investigated substances paramagnetic compounds leads to the intermolecular exchange of unpaired electron and electron density distribution upon the conjugated bonds that results in the broadening of the NMR signals [20]. With the increasing of the paramagnetic centers concentration signals can shift and broaden and it may be unobservable. For an example, the interaction of the lanthanide with β-diketones it has been shown [20] that the reason for the broadening and shifting of the NMR signals is the formation of complexes in which the paramagnetic cation has a free coordination vacancy. By NMR, EPR, exclusion chromatography methods it has been shown [21], that the interaction of iron (III) cations with humic substances is mainly realized through the participation of the carboxyl groups of aliphatic chains; for copper cations it is realized through the phenolic, substituted phenolic groups and the oxygen-containing alkyl groups in the side chains of substituted aromatic rings.

The ^{13}C-NMR spectra of the samples NOLF, RC NOLF and spectra of the same samples containing copper cations are shown in Figs. 4 and 5. When there is the cations copper sorption by NOLF and RC NOLF samples it can be seen decreasing of the intensity and broadening of the signals in the regions 48-5 ppm (C_{alk}), 145-108 ppm (C_{ar}), 165-145 ppm (C_{ar}-O). In the region 187-165 ppm (COOH) the signals almost disappear. It can be assumed that the change in the NMR signal intensity is due to the fact that the various structural units of the investigated samples take part in the copper cations sorption. When the sorption is realized by RC NOLF samples it is most likely that the carboxyl groups as well as the aromatic and aliphatic fragments take part in the complexation; by the NOLF samples oxygen-containing group $C_{O-alk-O}$, carboxyl groups and aromatic fragments play the main role in the process. For TL and HA TL samples during the copper cations sorption in the

intensity of the NMR signals insignificant changes are observed. The greatest changes are observed in the region for the chemical shifts 145-108 ppm (C_{ar}), 220-187 ppm (C = O), 187-165 ppm (COOH) for the RC NOLF sample. The higher content of the carbonyl groups, carboxyl ones and aromatic fragments in RC NOLF samples (Table 2) in comparison with the content of these groups in TL and HA TL results in the higher sorption capacity value due to the interaction of the copper cations with these functional groups.
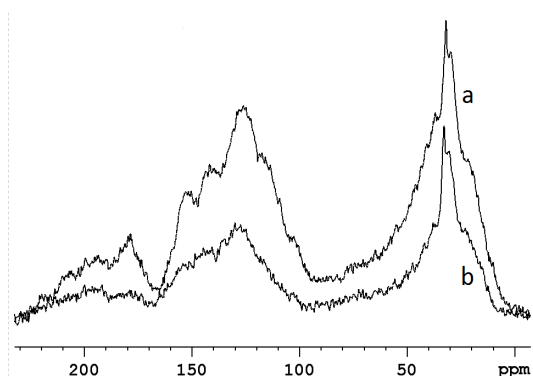

Fig. 4. ^{13}C CP/MAS NMR spectra of NOLF (a) and NOLF - Cu^{2+} (b).
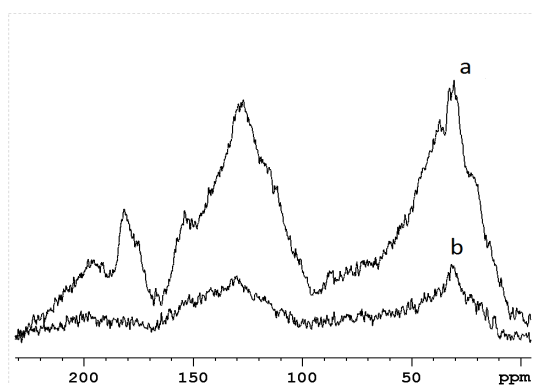

Fig. 5. ^{13}C CP/MAS NMR spectra of RC NOLF (a) and RC NOLF - Cu^{2+}(b).

4. Conclusions

The following conclusion can be done from the results analysis.

Not only humic acids extracted from different coal types exhibit sorption capacity, but also the initial and residual coals. The quantity of the adsorbed copper cations depends on the functional and structural composition of the investigated samples. The copper cations sorption by the coals, humic acids and residual coals reduces the number of PMC in the samples and reduces the intensity of the NMR spectra. The sorption process of the copper cations by the investigated samples depends on contribution of the several mechanisms in various degrees. The sorption of the copper cations by the humic acids extracted from the brown coal of the Tisulsky deposit is determined by the significant contribution of the ion exchange process. The humic acids extracted from the oxidized coal, and all initial and residual coals sorb copper cations largely due to the formation of the complexes as with the individual functional groups and with the negatively charged surface portions. The results of ^{13}C-NMR and EPR investigation have shown that aromatic structures make the main contribution to the complexation. It may act as polydentate ligands having several types of active sites which differ in strength of binding copper cations.

Acknowledgments

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