

SORPTION ACTIVITY OF UKRAINIAN SALTY COALS TOWARD POLYVALENT METALS

T.G. Shendrik, V.V. Simonova, S.B. Lyubchik and V.I. Saranchuk

Institute of Physical Organic and Coal Chemistry, National Academy of Sciences,

R. Luxemburg Str. 70, 340114 Donetsk, UKRAINE

Introduction

The problem of environmental protection in Ukraine is extremely important. Therefore search of cheap adsorbents for different pollutants is very actual. Some kinds of natural fuel can be efficient sorbents.

Basic factors, which influence on sorption capacity of brown coals were established. They are petrographic composition, content of acid functional groups, microporosity, seam moisture of coal and ionization potential of adsorbates [1, 2]. Electron transfer between contacting phases plays an important role in adsorption processes [3].

The low grade coals of Ukraine with high content of sodium chloride (5–15% in ash) – *salty coals* (SC) were considered as sorbents for some heavy metals. Salty coals have some peculiarities of structure and properties, such as high content of oxygen groups in H^+ - and cation-substituted forms, different kind of microelements (30–32), large size of polyarene packets (15–35Å) in coal organic mass (COM). Combination of these factors can provide different types of sorption by SC. The objective of this work were: to estimate the sorption capacity of SC toward Cu and Cr -ions, to detail the mechanism of the ions sorption by salty coals.

Experimental

Coal characteristics of Western Donbass deposit are following: $W^a=5\div 8\%$, $A^d=10\div 20\%$, $C^{daf}=68\div 72\%$, $H^{daf}=4.9\div 5.2\%$, $(O+N)^{daf}=18.0\div 22.0\%$, Na_2O content in ash – $4\div 16\%$, chlorine content – $0.4\div 0.8\%$ in coal.

Sorption ability of SC toward Cu^{2+} , $Cr_2O_7^{2-}$ was examined. In order to detail the sorption capacity of SC, sorption process (from $Cu(Ac)_2$ and $Na_2(Cr_2O_7)$ solutions) was carried out for a long time, i.e. during 40 days. Coal:solution ratio was 1:100, initial concentration of copper was 0.01M; and of chromium—the same. Equal aliquots (30ml) were taken daily. Equilibrium concentration of copper has been determined by photocolourimetry at $\lambda=590$ nm, chromium—at $\lambda=440$ nm. Structural transformation of coal organic mass (COM) and forms of adsorbed substances were examined by X-ray analysis and IR-spectroscopy [4].

Results and Discussion

It has been established that copper sorption has periodical character with maximum in 4, 12, 28 and 36–37 days and minimum in 9, 15–16, 24, 32 and 40 days. In maximum points Cu sorption achieved 70% (4 days) and 85% (28 days) that corresponds to 40–45 mg/g of coal. These results are closed to analogical results for natural brown coals of Angren [1].

It should be noted, that pH-parameter varies antipathetic to sorption capacity (Fig.1), that shows ion-exchange character of Cu sorption.

The FTIR spectra of samples confirmed the ion-exchange mechanism of copper sorption and allowed to suppose Cu-coals complexes formation (Table1). It has been established:

1. Substitution of H^+ of carboxylic group by Cu^{2+} -cation: peak at ca. 1700 cm^{-1} , which can be ascribed to non-ionic COOH groups, disappears, whereas there is appearance or increasing of band intensity at 1590 cm^{-1} and 1380 cm^{-1} , that is typical for ionic carboxylic group in salts.

2. Destruction of natural helat complexes of coal (wide band at $2500\text{--}2100\text{ cm}^{-1}$ disappears) and formation new helat substances with central Cu-ion (appearance of well defined band at 3210 cm^{-1} in maximum points of Cu sorption).

3. Abrupt change in IR-absorption at the range of low frequency ($470\text{--}850\text{ cm}^{-1}$). Decreasing or disappearance bands at 755, 470, 545 cm^{-1} could be attributed to degradation of caolinit and Fe-organic substances. Whereas for bands at 825, 635, 470 cm^{-1} , these could be related to destruction of illite (Fe-containing mineral) [5] or difficulty of deformative fluctuation of C–H-bonds in aromatic-circles.

4. Change at ca. 1250 cm^{-1} could be assigned to decreasing of asymmetric C–O–C and symmetric stretching.

More in depth investigation of resulted crystalline phases (after 40 days of Cu-sorption) by X-ray analysis have shown, that some new substances with $d = 10.91; 5.70; 2.71, 2.18; 1.87, 1.67, 1.63\text{ \AA}$ are formed. Reflexes with $d = 5.70, 2.18, 1.87\text{ \AA}$ can be attributed to crystalline $CuCl_2$, with $d = 2.71, 1.87, 1.63\text{ \AA}$ – to CuS

form, with $d = 1.67 \text{ \AA}$ to CuCl and with $d = 10.91 \text{ \AA}$ – to Cu-O-C complexes.

Sorption of $\text{Cr}_2\text{O}_7^{2-}$ by SC have stepped character: It is possible to divide several stages: 1 stage, (upto 6 days) sorption process closes to Freinlich-law; 2 stage (from 7day to 18 day) sorption capacity upto 35%; 3 stage (from 19day to 40 day) sorption capacity reaches its maximum, i.e. ca. 50%. After 40 days the new form of Cr-containing compounds are formed: Cr_2O_3 with reflexes at $d = 1.82, 2.49, 1.67, 2.18 \text{ \AA}$; and other form with $d = 5.88, 5.38, 2.33 \text{ \AA}$, which we have to identify in the future.

So, this fact illustrates the reduction of Cr^{6+} to Cr^{3+} followed by Cr_2O_3 formation. It can be explained as the result of electron transfer from coal matrix to chromium ion. In the same time the periodic restructurization of COM takes place (1 stage- the disordering, 2 stage- high regulation of COM) [5].

Conclusions

Salty coals are polyfunctional natural carbon sorbents, thanking their reach content of O-active groups and well organized π - conjugated system of COM, which has been formed under see water influence. Different mechanism for sorption of Cu^{2+} and $\text{Cr}_2\text{O}_7^{2-}$ -ions by SC

(ion-exchange, complex formation and reduction sorption) were established.

Therefore such sorbents can have potential practical usage as a efficient sorbent for wide metals.

References

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Table 1. IR data of initial SC and after copper sorption

References	$D \frac{3390}{470}$	$D \frac{3210}{470}$	$D \frac{2920}{470}$	$D \frac{1700}{470}$	$D \frac{1680}{470}$	$D \frac{1600}{470}$	$D \frac{1430}{470}$	$D \frac{1395}{470}$	$D \frac{1375}{470}$	$D \frac{1260}{470}$
Initial SC	1.15	-	0.85	1.80	1.85	2.75	2.15	-	2.05	1.95
SC, after 28days of sorption	2.00	1.88	1.88	-	-	2.63	1.83	-	1.95	1.76
SC, after 40days of sorption	4.36	4.00	3.58	-	-	4.52	3.01	3.24	3.24	2.67
SC, after 585days of sorption	2.05	-	0.95	-	1.81	3.29	2.24	-	2.43	1.95

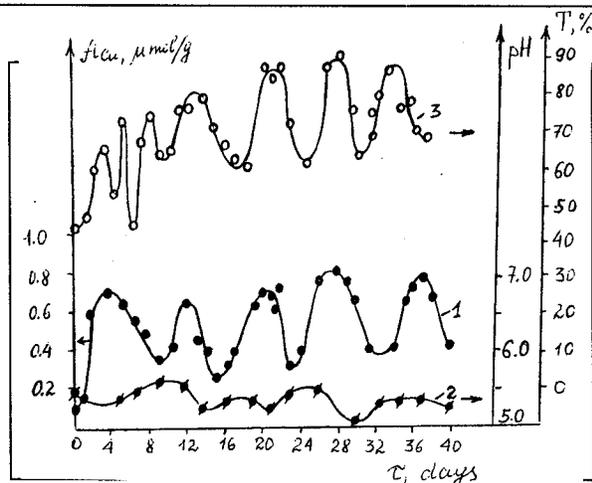


Figure 1. pH-parameter and sorption capacity and transmission vs. time of copper sorption process

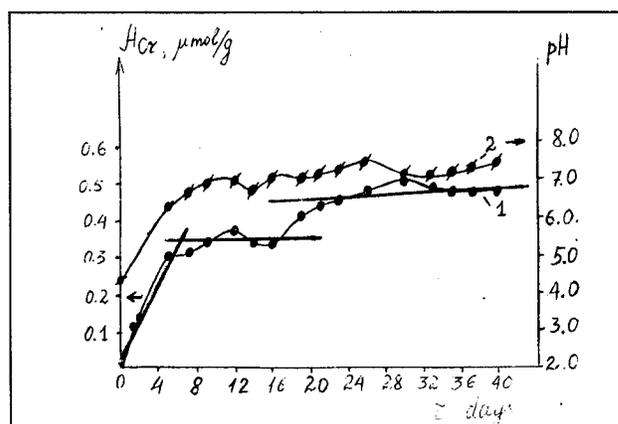


Figure 2. Sorption capacity vs. time of chromium sorption