

SORPTION OF GOLD BY CARBONIZED SORBENTS ON THE BASIS OF VEGETATIVE RAW MATERIAL

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Introduction

Activated carbons are being widely used for extraction, separation and concentration of gold [1-5]. Materials of plant origin (apricot stones, grape stones, walnut shells) synthesized by carbonization are of special interest [6-7]. This paper presents the results of investigation on one of such carbonized materials JPY with the aim to determine its sorption capacity to the chloride complex of gold (III).

Experimental

Carbonized materials JPY were synthesized from agricultural raw materials under different conditions according to the methods described in [8]. Investigations of sorption activity of the carbonized material JPY were carried out by a common chemical method under statistical and dynamic conditions [9] by the decrease of gold (III) content in a sorption system. In this case, the content of gold (III) in the solution was determined by the method of atom-absorption spectroscopy (AAS).

Adsorption of gold (III) was also studied by the electrochemical method by recording J, t – curves at constant potential corresponding to limiting current for electroreduction of gold (III) on the platinum electrode. J, t – curves were recorded automatically by KСП-4 recorder on the potentiostat П-5848. The procedure of experiments on adsorption by the electrochemical methods was as follows. The cell was connected with the reference chlorine-silver electrode and an auxiliary electrode with the help of salt bridges filled with a saturated KCl solution. An indicator platinum electrode was placed into an electrochemical cell.

Fig. 1 presents the results of experiments on sorption of gold (III) on sorbents JPY in 0.25 n HCl solution using a common method. As it is seen, JPY-1 has the best 100 % sorption of gold (III). Sorbent JPY-2 sorbs about 60 % of gold (III) during 1 hour, and sorbent JPY-3 sorbs only 20 % of gold (III) during the same period of time. In case of sorbent JPY-1, complete, practically 100 % sorption proceeds 4 minutes. The form of the kinetic curves also shows the decrease in the rate of gold (III) sorption as follows: JPY-1 > JPY-2 > JPY-3. During sorption of gold (III) the grains of JPY-1 sorbent are covered by a film of yellow color which is metallic gold according to electron-microscopic pictures and diffractograms.

The reducing ability of JPY sorbents was verified by the measured values of stationary potentials of these sorbents. Measurements of stationary potentials were carried out with the help of an electrode of special construction. This electrode is a fluoroplastic casing with the diameter of 20 mm with a thread at the end face. On which a platinum electrode with the diameter of 19 mm is fixed. A platinum current collector is brought out from the platinum electrode through the center of the casing. The platinum disk is compressed by a fluoroplastic clutch with a perforated face. When measuring the potential, an ashless filter is placed on the perforated face, the sorbent being studied is poured onto the filter. Then the clutch with the sorbent is applied by winding on the fluoroplastic casing, thereby providing an intimate contact of the substance being studied with the platinum electrode.

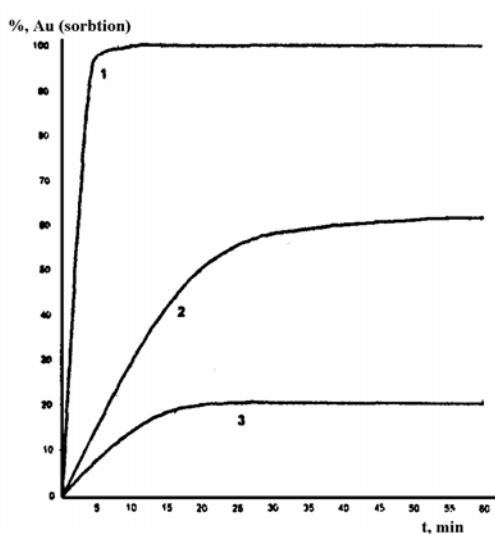


Figure 1. Kinetic curves of sorption of gold (III) on different sorbents in 0.25 n HCl solution.

Mass of the sorbent is 0.2 g, the amount of gold (III) is 0.6 mg, the volume of the solution is 25 ml. Sorbent: 1 – JPY 1; 2 – JPY 2; 3 – JPY 3.

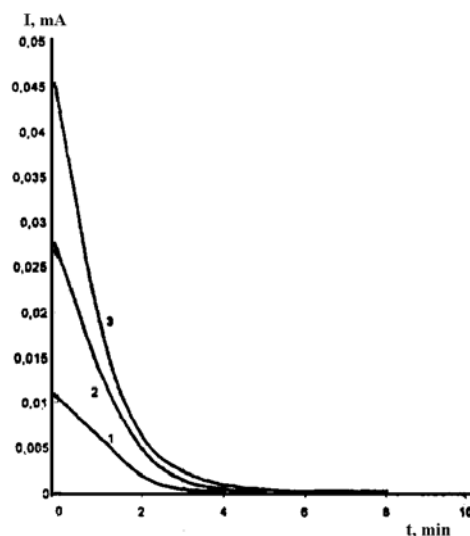


Figure 2. Kinetic curves of sorption of gold (III) on sorbent JPY-1 in 0.25 n HCl solution.

Concentration of gold (III): 1 – 5.97 mg/l; 2 – 11.95 mg/l; 3 – 23.9 mg/l. The volume of gold (III) is 25 ml, the mass of the sorbent is 0.2 g.

The results of the measurements showed that the sorbents of JPY series have quite a low redox potential. For sorbents JPY-1, JPY-2, JPY-3, stationary potentials are 0.23 V, 0.36 V, 0.38 V, respectively. Therefore, sorbents JPY have reducing properties. These reducing properties are likely to be conditioned by the presence on the surface of the carbonized sorbents of reducing carbon groups: aldehyde, ketone, alcohol groups. Besides, carbon itself must possess reducing properties, the more so, as it is in the form of nanocarbon tubes [7,8].

Hence, carbonized sorbents JPY are not only ion-exchange sorbents [7], but at the same time they are redox sorbents. The real potential of the system $\text{AuCl}_4^- / \text{Au}^0$ in 0.25 n HCL solution is 0.74 V (XCЭ) /10/. From the data on potentials it follows that the potential difference between the oxidizer – gold (III) and the reducing agent – sorbents JPY-1, JPY-2 and JPY-3 makes up 0.51 V, 0.38 V, respectively. The required difference of real (stationary) potentials for practically complete (99%) procedure of any redox reaction must be equal to 0.24 V [10]. Therefore, there are preconditions for reduction of gold (III) to a metal by sorbents JPY. In case of JPY-1, the potential difference is the greatest, owing to which this sorbent readily reduces gold (III). It is interesting to note that potential of JPY-1, after sorption of gold – (JPY-1) Au^0 on it has the value of 0.50 V (XCЭ), i.e. has an intermediate value between the potentials of AuCl_4^- and JPY-1.

On the basis of the above-mentioned data, two schemes of the chemism of gold (III) sorption on JPY sorbents may be suggested. With the aim to obtain a displayed characteristics of sorption capacity of jpy-1 in relation to gold (III) in the hydrochloric acid medium we have studied the effects of different factors: concentration of gold (III), acidity of the hydrochloric acid medium, the influence of impurities of metal ions. Fig. 2 presents the obtained by the electrochemical methods kinetic curves of gold (III) sorption at its different concentrations. As it is seen, within the studied range of gold (III) concentration (5.97-23.9 mg/l) a complete sorption of gold (III) takes place during 4 minutes, regardless of its concentration. The slope of I, t-curve of the decrease in the amount of gold (III) in the solution, and hence, of its sorption rate, increases with the increase of gold (III) concentration. To determine the numerical values of gold (III) sorption, a well-known in chemistry method of initial sites was used. For calculations according to this method, an initial segment of the curve is used, when the surface of the sorbent is still free of the reaction products and the mass of the reaction products changes quite insignificantly against the initial concentration of the active sites of the sorbent and the initial concentration of gold (III). The sorption rate (W) was calculated by the formula:

$$W = \frac{\Delta C \cdot V}{\Delta t \cdot m \cdot 1000}$$

where ΔC is the change in the amount of gold (III) which passed from the solution onto the sorbent (mg/l) during the time Δt (sec): V is the volume of gold (III) solution, ml: Δt is the time during which the change of ΔC takes place: m is the mass of the sorbent, g: 1000 is the conversion factor from a litre to milliliters.

To find Δt , a line tangent, which cut off the value of Δt on the abscissa axis, was drawn to the initial segments of the kinetic curves. If the data in Fig. 2 are converted into relative values – percent of gold (III) sorbed with time, it appears that kinetic

curves for different amounts of gold (III) practically merge into one curve. The adsorption time of the half $\tau_{1/2}$ of the initial amount of gold (III) does not depend on its initial concentration and makes up 1.1 min. Independence of $\tau_{1/2}$ sorption indicates the fact that for the studied range of gold (III) concentrations the kinetics of the sorption process obeys the equation of the first order:

$$K_s = \frac{2,3}{\tau} \lg \frac{C_0}{C}$$

By plotting the coordinates of $\lg C - \tau$, the sorption rate constant was found. The obtained values of W , $\tau_{1/2}$ and K_s are given in table 1.

Table1
Kinetics of gold (III) sorption on JPY-1 sorbent in 0.25 n HCl solution

№	Concentration of Au (III), mg/l	W, mg/c·g (of the sorbent)	$\tau_{1/2}$, min	K_s , $s^{-1}g^{-1}$
1	5.97	$0.54 \cdot 10^{-2}$	1.18	$7.35 \cdot 10^{-2}$
2	11.95	$1.08 \cdot 10^{-2}$	1.10	$7.15 \cdot 10^{-2}$
3	23.90	$2.26 \cdot 10^{-2}$	1.12	$7.45 \cdot 10^{-2}$

$(7.32 \pm 0.22) \cdot 10^{-2}$

The dynamic capacitance of JPY-1 sorbent was determined, i.e. the capacitance before passing of gold (III) ions through the adsorption column. The passage rate of gold (III) solution with the concentration of 23.9 mg/l was 2.5 ml/min, the amount of the taken sorbent was 0.5 g. The experiments showed that passing of gold (III) ions took place after passing of 220 ml of gold (III) solution that corresponds to the sorption capacity of this sorbent – 10.5 mg of gold / 1 g of sorbent. In case of sorbents JPY-2 and JPY-3, when passing the first portion of gold (III) solution of 25 ml, the passing of 60-70% of the initial amount of gold (III) is observed. The sorption capacity of these sorbents is lower by two orders of magnitude than that of the sorbent JPY-1.

Investigations on the effect of acidity of hydrochloric acid medium on gold (III) sorption on the sorbent JPY-1 showed that gold practically quantitatively (98%) sorbed in a wide range of acidity of hydrochloric acid solution, from pH 5.6 to 4m HCl. A quantitative 100% sorption takes place at the acidity from pH=2 to 2m HCl. At higher values of pH (2-5.6) and concentration of HCl (2-4m) sorption decreases to 98-97%. With the increase in acidity, not only some decrease in sorbability, but also the decrease of the sorption process rate constant is observed (table 2).

Table 2

Constants of gold (III) sorption rate on the sorbent JPY-1 in hydrochloric acid medium.

Concentration of gold is 11.95 mg/l

No	Concentration of HCl, n	$K_s, s^{-1}g^{-1}$ (of the sorbent)
1	0.25	$7.15 \cdot 10^{-2}$
2	1.00	$7.00 \cdot 10^{-2}$
3	2.00	$6.20 \cdot 10^{-2}$
4	3.00	$5.40 \cdot 10^{-2}$
5	4.00	$3.87 \cdot 10^{-2}$
6	5.00	$3.32 \cdot 10^{-2}$

The effect of the pressure of the salts of the different metals: Fe (III), Ni (II), Co (II), Zn (II), Cu (II), Hg (II) As (V), Pt (IV) on the sorption of gold (III) was determined. All the mentioned above metals in considerably predominating amounts (100-800 times) do not interfere in the sorption of gold (table 3). These metals, judging by literature data [7] must be sorbed by carbon sorbents. That they do not interfere in the sorption of gold (III) indicates the fact the rate of gold (III) sorption is significantly higher than that of metals-impurities. Moreover, Ni, Co, Cd, Zn, Cu, As ions have a less positive redox potential than the stationary potential of JPY-1 sorbent. Therefore, these metals can not enter the redox interaction with this sorbent, and their sorption must be of ion-exchange character. The rate of electrochemical process is known to be always higher than that of ion-exchange process. This may account for the fact why these metals do not interfere in the sorption of gold (III).

The effect of iron (III) salts should be noted. In the presence of iron (III) the rate of gold (III) reduction considerably increases and complete sorption of gold (III) takes place during 1.5 min, while in the absence of iron (III) – during 4 min. Such increase of gold (III) sorption rate should be related to the catalytic effect.

Table 3

The influence of metal impurities on the sorption of gold

Concentration of Au (III), mg/l	Concentration of the impurity, g/l	Sorption time of Au (III), 98%, min	Sorption percent of Au (III) in ten minutes, %
11.95	Ni (II)-10 g/l of NiSO ₄	5	99.2
11.95	Cd (II)-10 g/l of CdSO ₄	5	99.2
11.95	Co (II)- 10 g/l of CoSO ₄	5	99.2
11.95	Zn (II)-10 g/l of ZnCl ₂	5	99.2
11.95	Fe (III)-1 g/l of FeCl ₃	1	99.2
11.95	Cu (II)-7 g/l of CuSO ₄	5	99.2
11.95	As (V)-1 g/l of Na ₃ AsO ₄	5	98.0
11.95	Pt (IV)-5 g/l of H ₂ PtCl ₆	10	98.0
11.95	Hg (II)-0.5 g/l of Hg(NO ₃) ₂	7	99.2

Conclusion

The carbonized materials JPY have a low redox potential and exhibit the properties of redox sorbent in relation to gold (III) ions in hydrochloric acid medium. During sorption of gold (III) it deposits on the surface of JPY in a metallic state. The process of gold (III) sorption is an electrochemical one with separate cathode and anode sites on the sorbent grains. The difference in real potentials of gold (III) and sorbents JPY ($\Delta E = E_{Au(III)} + E_{JPY}$) increases in the series JPY-3 < JPY-2 < JPY-1. The rate and completeness of gold (III) sorption as well as the dynamic capacitance of these sorbents increase accordingly.

The best sorbent is JPY-1. The quantitative (99-100 %) extraction of gold (III) on this sorbent takes place during 3.5–4 min regardless of the initial content of gold (III) in the solution. The sorption time of the half of the initial content of gold (III) - $\tau_{1/2}$ is 1.1 min irrespective of its initial concentration, the sorption rate obeys the equation of the first order. This order of the reaction is characteristic of the electrochemical process limited by the substance to the surface of the electron donor.

The dynamic capacitance of the sorbent JPY-1 as regards to gold is 10.5 mg/g of the sorbent. The capacity of sorbents JPY-2 and JPY-3 is less by two orders of magnitude. The presence of predominant quantities of Ni (II), Co (II), Cd (II), Zn (II), Cu (II), Fe (III), Pt (IV), Hg (II), As (V) does not interfere in the sorption of gold (III).

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