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STUDY OF EXTRACTION OF GOLD IONS BY COMPLEX-FORMING IONITES BASED ON EPICHLORHYDRIN AND MELAMINE

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Abstract. In the paper a new polyfunctional ion exchanger was synthesized based on the products of the interaction of thiourea (T), epichlorohydrin (ECG) and melamine (M). They form complex compounds with gold ions. The possibility of using ion exchanger in the sorption-atomic absorption determination of gold is shown for a sample of copper concentrate. The structure and properties of the obtained ion exchangers were studied by chemical, kinetic and infrared spectroscopy (IR). It was found out that ion exchangers have a high exchange capacity (up to 5.6 mg Eq/g), increased chemical resistance in solutions of acids and alkalis, and thermal stability in water. The analyses of the gold contents were carried out by atomic absorption spectrophotometer.

1. Introduction

At present, a large number of complexing sorbents for the concentration of noble metals have been synthesized. Most sorbents contain groups of nitrogen- and sulfur-containing heterocycles (imidazole, pyrazole, thiazole, pyridine, etc.), which ensures high selectivity of sorbents with respect to noble metals. Sorbents with amidoxime, guanidine are also used. thioamide, dithizone, mercapto groups, etc. In addition to anion-exchange and complex-forming sorbents, active carbons (Cox *et al*., 2005), natural and synthetic zeolites (Guibal *et al*., 2001), modified chitosans (Chassary *et al*., 2005), biosorbents (Godlewska-Zylkiewicz *et al*., 2003), etc. are also used to concentrate precious metals. However, the low surface areas/site ratio, low adsorption capacity, low reusable rate, high cost and weak selectivity restrain the actual applicability in gold sorption. For this perspective, it is very important to develop a novel adsorbent with high capacity and selectivity. A good sorbent not only has a good reusability, but it also has a good selectivity (Xiong *et al*., 2018).

The functional groups of almost all ion exchangers are capable of not only ionization, but also other types of interactions, including coordination. The implementation of various types of interactions leads to the fact that the same polymer can serve as a molecular sorbent, ion exchanger, polymer ligand, or combine several functions (Lodeyshikov, 1993). The use of water-compatible polyglycidol grafting

products on polystyrene particles for the isolation of aqueous solutions of gold (I) and silver (I) salts was studied. The possibility of extraction of 99% of gold and silver ions was shown (Lam *et al.*, 2009; Askerov *et al.*, 2018).

A chelating melamine-formaldehyde-thiourea resin (MPT) was obtained (Aydin *et al.*, 2008) and its ability to sorb Au^{3+} ions and selectivity both by periodic and column methods was studied. The MPT resin showed an increased affinity for Au^{3+} compared to base metal ions such as Cu^{2+} and Zn^{2+}. To extract gold from thiosulfate solutions in industry, it is recommended to use carbon adsorbents (Zhuchkov & Bubeev 1992; 1988). Our studies have shown that it is possible to more efficiently use anion exchangers and amphoteric ion exchangers for sorption extraction of gold from these solutions (Kholmogorov *et al.*, 2001). The aim of this work is to study the sorption properties of ion exchangers thiourea (T), urea (U) with melamine (M), crosslinked epichlorohydrin (ECG), and the possibility of their analytical application (Eshkurbonov, 2013).

2. Experimental part

2.1. Dissolution of ore from the "Kalmakyr" Mine of the Almalyk Mining and Metallurgical Combine

Hydrometallurgical preparation of concentrates for gold dissolution was carried out by the nitric acid method (Chassary *et al.,* 2005). By decomposition of pyrite and arsenopyrite, 93-96% of gold was extracted from the concentrate into the solution, sulfur remained in the solid precipitate as elemental (5.1-5.3%), and arsenic and iron (0.4-1.2%) in this precipitate were in oxide form, and also in the form of arsenates and iron hydroxides.

Gold leaching from the product was carried out in a thermostated cell with intensive mechanical stirring of the suspension (more than 600 rpm). The gold content in the solutions was determined by the atomic adsorption method (Perkin-Elmer analyzer 3030(B)) and the solid residue was decomposed in a mixture of hydrochloric and nitric acids in a ratio of 1: 3. According to the analysis, the amount of gold recovered in the solution was calculated.

2.2. Synthesis of polymeric ion exchangers

Ionite based on diglycidylthiourea and melamine. 20 ml of 36% NaOH was added to 94 ml of diglycidylthiourea at a temperature of 60 ºC. 63 g of melamine was added to it, heated to a temperature of 105ºC and stirred for 3.5 hours. Then, it was placed in a ceramic bowl and dried in a drying cabinet at a temperature of 120ºC for 8 hours. Diglycidylthiourea: melamine ratio=1:1. Ionite yield -95%. The obtained product is washed with distilled water, 4% alkali solution and 5% chloride and sulfuric acid solution.

2.3. Characterization of polymeric ion exchangers

Ionite based on diglycidylthiourea and melamine is a solid substance in the form of light brown granules, which absorbs moisture in air, has the property of dissolving in water, d_{20}^{20}=1.08 g/cm^3.

2.4. Gold adsorption studies

Gold sorption was studied by static method. For this, the ionite sample was placed in an artificial solution of gold in "aqua regia" with a concentration of 1 g/l and kept for

24 hours. The ionite was then separated from the solution, washed in distilled water, and calcined in a muffle furnace, resulting in pure gold in the form of fine flakes. Among the ionites synthesized in this research work, those containing sulfur and phosphorus were selected separately. The results of the study are presented in Table 1.

Aqua regia (from Latin, literally "regal water" or "royal water") is a mixture of nitric acid and hydrochloric acid, optimally in a molar ratio of 1:3. Aqua regia is a fuming liquid. It was named by alchemists because it can dissolve the noble metals gold and platinum, though not all metals. Strong oxidizer.

Table 1. The sorption of gold ion on synthesized ionites

The types of ionites	SEC, for HCl mg-ekv/g	SEC, for Au, mg/g	Adsorption rate, %
DGT+ polyethylene polyamine (PEPA)	2,5	270	96,4
DGT+M	1,7	191	68,2
DGT+ Hydrolyzed polyacrylonitrile (HPAN)	3,1	276	98,8
DGT+OPA	3,0	280	100
DMT+OPA	3,1	279	98,5

1) DGT+OPA (◆); 2) DMT+OPA (■); 3) DGT+HPAN (▲).
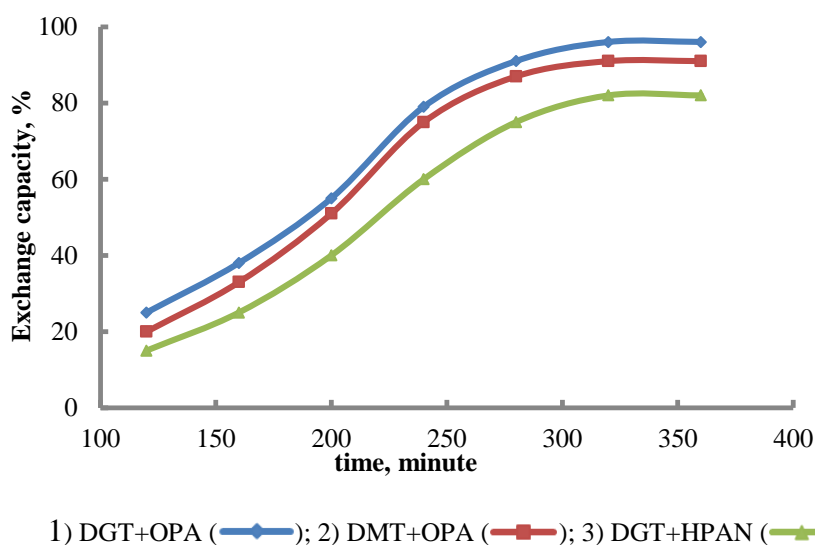
Fig 1. Time dependence of the static exchange capacity of some ionites for the gold (III) ion in solution

Fig. 1 shows the results of studying gold (III) ion sorption using some synthesized ionites. It has been shown that the ionite that forms an effective complex for the gold (III) ion is -DGT+OPA based ionite.

3. Results and discussion

3.1. Synthesis and characterization of polymeric ion exchangers

The sorption activity of nitrogen-containing polymers is related to their ability to protonate in acidic media; therefore, these compounds exhibit the properties of anion exchangers. On the other hand, the electron donor properties of the nitrogen atoms of the

hetero rings make it possible to consider them ligands capable of forming complexes with metal ions by the mechanism of donor – acceptor interaction. Interaction with metal ions occurs due to an unshared electron pair at the nitrogen atom in the 4th position of the heterocycle, which has the largest negative charge and electron density. Therefore, I1 and I2 were studied as ion exchangers with respect to the gold tetrachloride complex in a static mode (Table 1).

Table 2. Characterization of ion exchangers

Ionites	The composition of the initial mixture, mol.%	The composition of the copolymers, mol.%	The nitrogen content in the copolymer,%
I1 (T-ECG-M)	62.1: 37.5: 0.4	49.5: 50.2: 0.3	20.87
I2 (U-ECG-M)	95.0:5.0	80.7:19.3	33.25

Ionite I1 - solid white particles that are well wetted by water and swell. Ionite I2 is a white fine powder, characterized by greater swelling ($\alpha=54\%$) compared with I1 ($\alpha=9\%$).

3.2. Gold adsorption studies

The effect of the nature and concentration of acids on the extraction of the acid complex at ordinary temperature was studied. With an increase in the concentration of hydrochloric and nitric acids from 1 to 7 M, a gradual decrease in the degree of extraction of gold ion occurs, and the degree of extraction from solutions of nitric acid is lower. Further study of the sorption properties was carried out with 1M acid solutions in a static mode. The decrease in the degree of extraction of the gold tetrachloride complex is due to the competing effect of the acid anion. The obtained character of the dependence indicates the dominance of ion-exchange interaction. This is the first stage of the process, which passes into the second coordination mechanism.

The synthesized ionites were tested in the separation of gold ion from acidic solutions. When studying the dependence of gold ion sorption on the concentration of mineral acids (HCl, HNO_3, H_2SO_4), it was found that the sorption rate increased from 66% (1M HCl) to 90% (2M HNO_3). The effect of HNO_3 concentration on the extent of gold sorption is shown in Fig. 2.

As can be seen from the figure, gold can be efficiently extracted (82-99%) from 2 M solutions of nitric acid with the help of studied ionites.

The IR and Raman spectra of an ion exchanger sample (I1) treated with a 1 M HCl solution and a sample containing metal ions are studied. For the latter, metal saturation was carried out for two hours, the solid phase was separated by filtration and washed thoroughly with water until negative reaction to the chloride anion. Samples were dried on a desiccator for a day. The IR spectrum of the sample containing gold is characterized by a change in the band of 640-650 cm^{-1} compared with the initial ion exchanger sample and its form obtained by treatment with hydrochloric acid. The coordination of the metal is evidenced by a change in the absorption band responsible for the state of the nitrogen atom in the four heterocyclic position, a shift from 1500 to 1600 cm^{-1}, for a sample containing metal ions (Figs. 3 and 4) (Eshkurbonov, 2013).

But a more complete picture is provided by Raman spectra. The presence in the spectrum of the gold-saturated sample of bands 370, 340, 165 cm^{-1}, which are similar to the lines of the anion 350, 335, 165 cm^{-1}, indicates the Au - N bond.

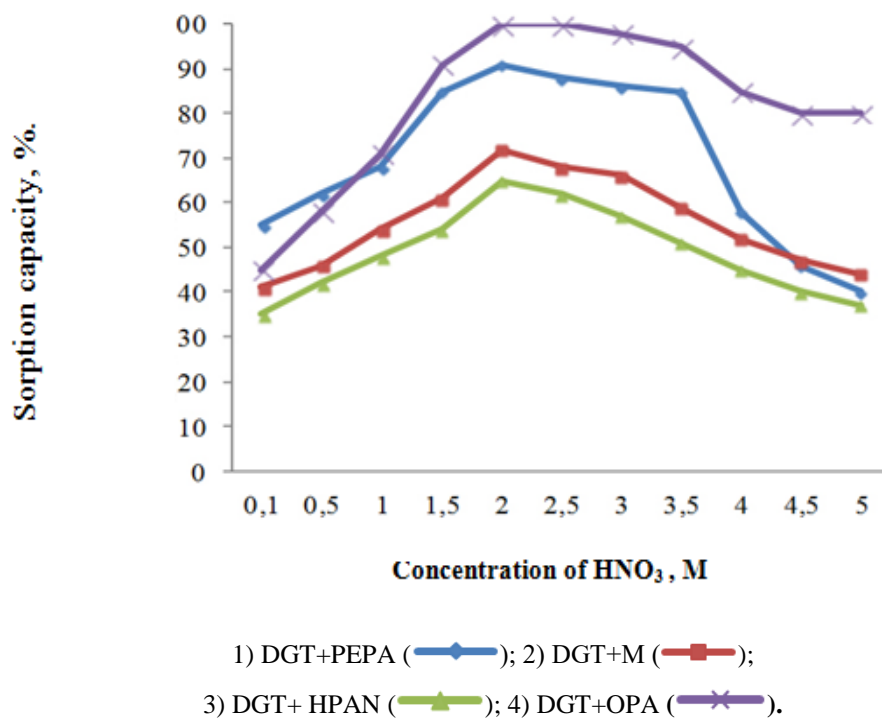1) DGT+PEPA ( ); 2) DGT+M ( );
3) DGT+ HPAN ( ); 4) DGT+OPA ( ).

Fig 2. Dependence of the degree of gold sorption on the concentration of nitric acid in the synthesized ionites
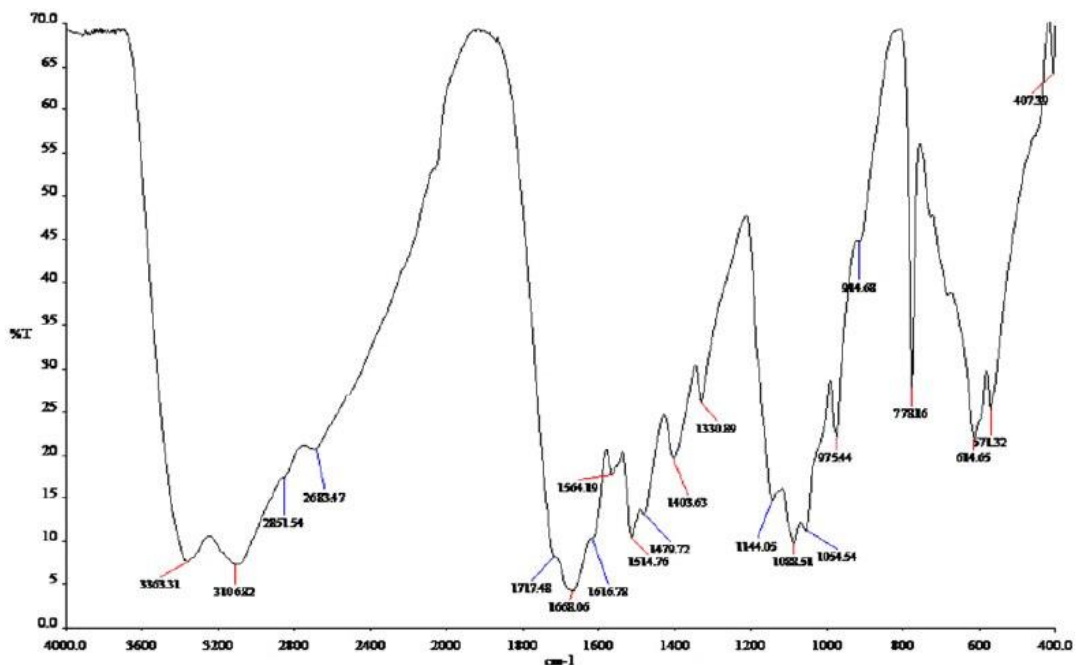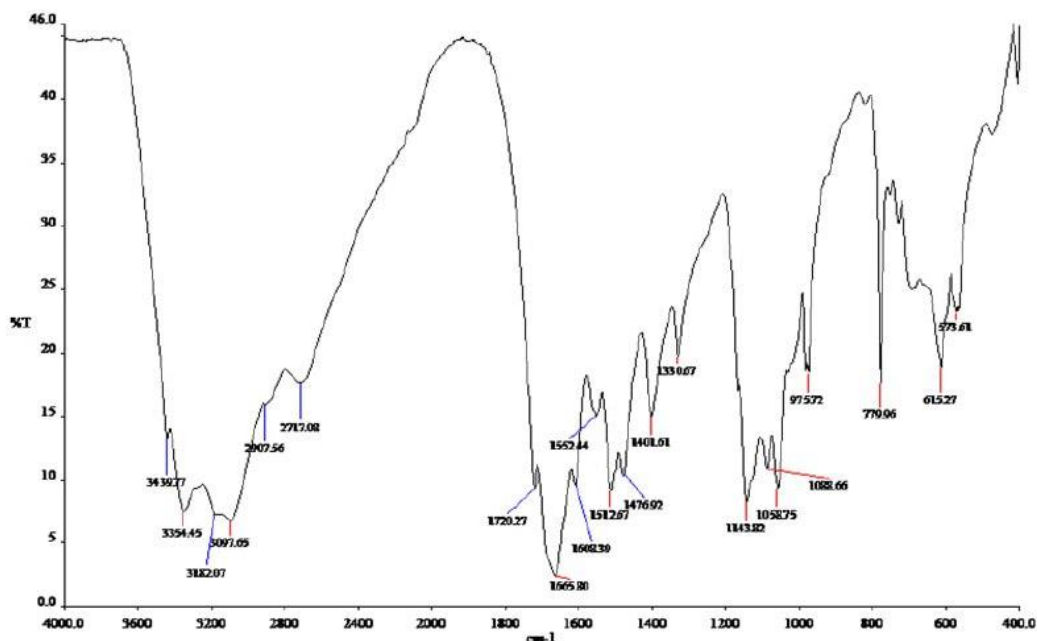

Fig 3. IR-spectrum of complex forming ionite obtained on the basis of DGT and melamine

Fig 4. IR spectrum of the complex compound of ionite obtained on the basis of DGT and melamine with gold (III) ions

The interaction of the donor atoms of the polymer under study with the gold chloride complex suggests at the first stage the formation of an ionic associate with preliminary protonation of nitrogen atoms by an electron-donor-acceptor interaction. To prove this, the filters were transferred to boxes and kept in a vacuum cycle:
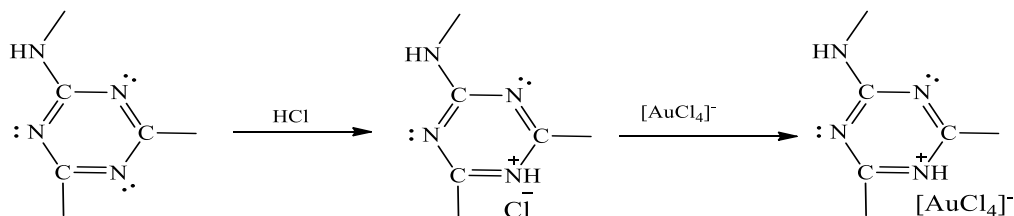
In the second stage, the destruction of the associate and the formation of a complex compound occurs:
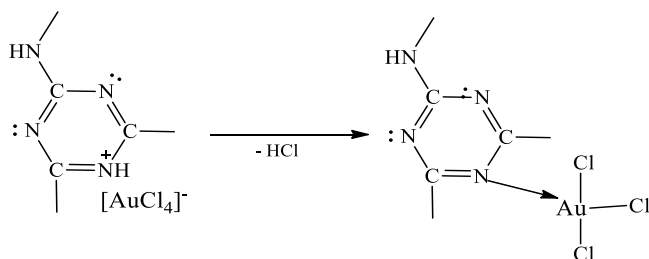
The obtained kinetic curves for the extraction of the gold tetrachloride complex indicate a high rate of establishment of sorption equilibrium, which is 35 min for polymers I1 and I2 with a half-sorption time of 12 min. To determine the type of sorption kinetics, we used the time dependence of the kinetic coefficient $B\tau$. The coefficient was calculated by the formula

$$B\tau- (F / 1,08)\,2,$$

where F is the degree of equilibrium achievement:

$$F = Q_n / Q_{max},$$

where Q_n is the sorption capacity in the saturation region,

Q_{max} is the maximum capacity.

For ion exchangers I1 and I2, a nonlinear character of the dependence is observed, which is evidence in favor of the film type of diffusion.

The calculation of the coefficients of the external and internal diffusion functions showed that the internal diffusion rate coefficient is greater than the external diffusion coefficient (Table 3). So, the rate of absorption of gold into ions can be explained by the large internal diffusion coefficient.

Table 3. Internal and external diffusion rate coefficients calculated from the experimental results

Ionites	External diffusion rate coefficient $K\cdot10^2$ sec^{-1}	Internal diffusion rate coefficient $V\cdot10^2$ sec^{-1}
DGT+ PEPA	1,75±0,46	4,85±1,7
DGT+M	1,79±0,35	5,13±1,45
DGT+ HPAN	1,56±0,58	3,92±1,03

In addition to these coefficients, the determining factor can also be estimated from the kinetic curve in the and coordinates. As a result of research, the drawn curves are depicted in Figs. 5 and 6.

1) DGT+PEPA (——◆——); 2) DGT+M (——■——); 3) DGT+HPAN (——▲——).
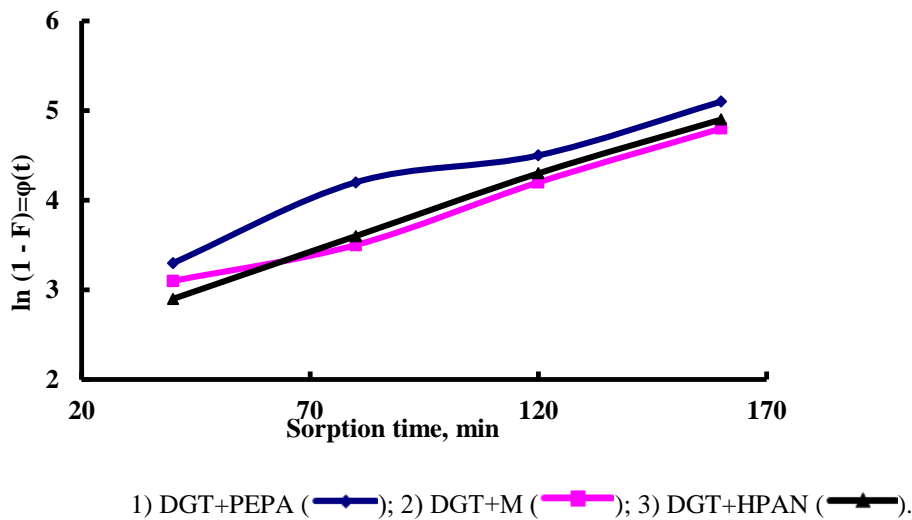
Fig. 5. Kinetic curves of gold sorption in ionites according to the coordinates of $\ln(1 - F) = \varphi(t)$

As can be seen from Fig. 5, gold sorption kinetics in the hydroxyl form DGT+PEPA, DGT+M and DGT+HPAN ions are not determined by external diffusion or chemical action, and the obtained curves are not linear.

1) DGT+PEPA (◆); 2) DGT+M (■); 3) DGT+HPAN (▲).
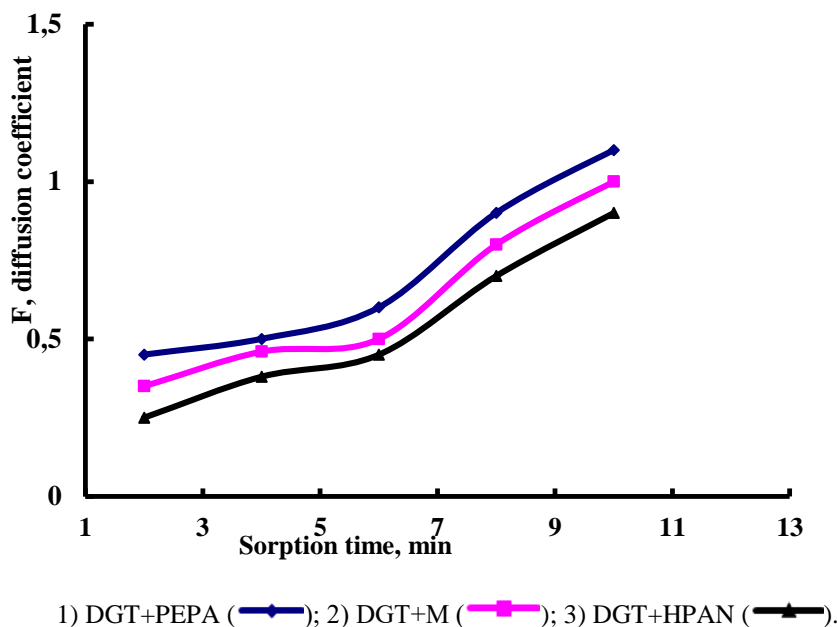
Fig. 6. Kinetic curves of gold sorption in ionites according to the coordinates of $F = \varphi(\sqrt{t})$

Fig. 6 shows the kinetics of gold sorption on DGT+PEPA, DGT+M and DGT+HPAN anionites. As many authors point out (Pimneva *et al*., 2008), in gel kinetics (internal diffusion) the dependence of F to √t has a linear change at small values of t, then bends and is reflected in the curve. This situation is also reflected in Fig. 6.

To determine the sorption capacity (SC) and distribution coefficient (D), the equilibrium distribution of gold ions between the phases was studied with increasing concentration of the latter (Fig. 7, Table 4). Comparing these values I2 with the literary ones, we can say that they are average, while I2 has a significantly higher sorption capacity, which is associated with a higher concentration of donor atoms.

The adsorption capacity of the gold ion was calculated using the following general Equation:

$$q_e = \frac{C_0 - C_t}{m} \cdot V$$

in which q_e is the amount of metal ions adsorbed at equilibrium per unit weight of sorbent (mg/g), C_0 and C_t (mg/L) are the gold ion concentrations present in the solution before and after adsorption, respectively, V is the volume of the solution (in L), and m is the amount of sorbent (in g) used in the adsorption experiment (Morcali *et al.,* 2015).

The distribution coefficient, D, is used to describe the retention of substances on the solid phase. D value is defined as the concentration ratio of the metal ions between solid and liquid phases in the equilibrium state:
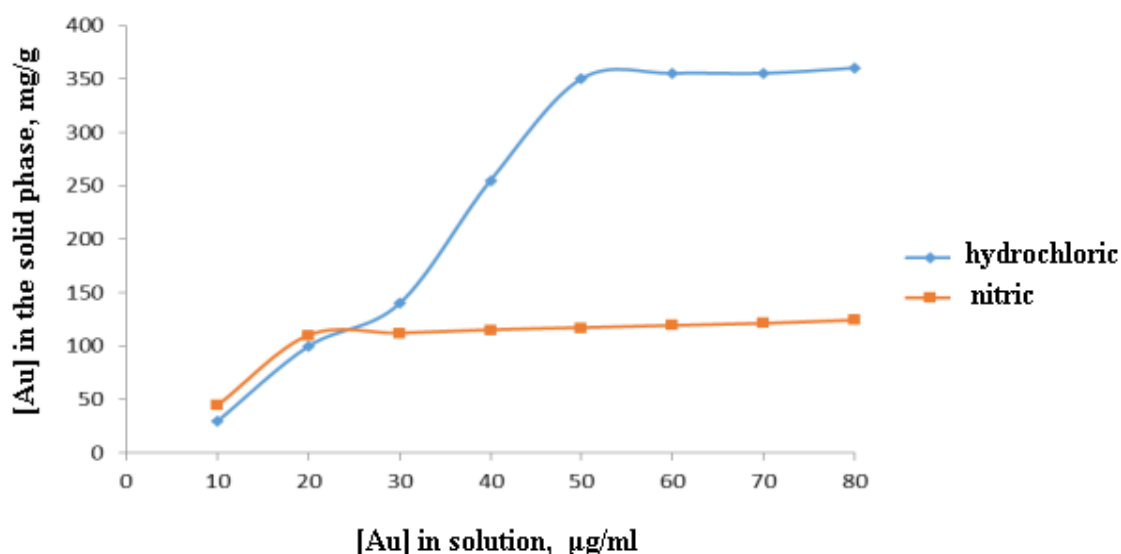
$$D = \frac{C_{M,s}}{C_{M,l}}$$

where, $C_{M,s}$ -concentration of the element in the solid phase and $C_{M,l}$ -concentration of the element in the liquid phase.

Table 4. Values of static capacity and distribution coefficient of gold ions in 1M acid solutions

Acid	Ionite I1		Ionite I2	
	SC(mg · g^{-1})	D(cm^3 · g^{-1})	SC (mg · g^{-1})	D(cm^3 · g^{-1})
HCl	122	$1.3 \cdot 10^4$	290	$5.8 \cdot 10^4$
HNO$_3$	61	$0.6 \cdot 10^4$	145	$1.6 \cdot 10^4$

Fig. 7. The curves of the equilibrium distribution of gold ions between the solution and the solid phase of ionite I2 for 1M solutions of hydrochloric (♦) and nitric (■) acids

The obtained values of the distribution coefficients, as well as the steep nature of the isotherms, indicate extraction efficiency.

2 models were used to quantitatively describe the sorption equilibrium (Guibal *et al.,* 2002) (Table 5).

Table 5. Sorption isotherm model

Model	Equation	№
Langmuir	$$q = q_\infty \frac{C_{eq} \cdot K_L}{1 + C_{eq} \cdot K_L}$$ $$\frac{1}{q} = \left(\frac{1}{q_\infty}\right) + \frac{1}{C_{eq}} \cdot \left(\frac{1}{q_\infty K_L}\right)$$	1 2
Freundlich	$$q = K_F \cdot C_{eq}^{1/n}$$ $$lnq = lnK_F + \frac{1}{n} \cdot lnC_{eq}$$	3 4

K_L and K_F in the equations presented in the table are equilibrium constants according to the Langmuir and Freundlich equations,

C_{eq} is the equilibrium concentration of components in the solution, mol/l;

q_∞ is the maximum capacity of ionite, mol/g;

n is the Freundlich isotherm constant indicating the sorption intensity.

The linear form of these models was used to determine the values of the constants derived from the Langmuir and Freundlich isotherm equations by the method of small squares (equations 2 and 4 in the table). Calculations were carried out using the LINEAR function in the Microsoft Excel 2010 office package by the method of small squares. Adequacy of the model was checked by comparison with the experimental value of F obtained from the following equation according to the F criterion.

$$F_{experiment} = \frac{nS_o^2}{S_{repetition}^2}.$$

Here S_o^2 -residual variance, $S_{repetition}^2$-repetition variance, n-the number of parallel experiments.

The F criterion value was obtained from the function *F.ОБР[P, f₁=m-2, f₂=m·(n-1)]* in the Microsoft Excel 2010 office package. *m* is the number of points on a straight line. The $F_{experiment}$ and $F_{criterion}$ values were compared and the adequacy of the equation was concluded.

It has been established that ion exchangers do not extract iron, cobalt, nickel, and zinc ions from 1M hydrochloric acid solutions; copper ions are extracted by 15% at a content of 1000 μg / 20 ml. The sorption of copper ions is explained by the ion-exchange interaction of the $[CuCl_4]^{2-}$ form and its ability to coordinate at the nitrogen atom.

One of the properties that determine the use of ion exchanger for analytical purposes is the possibility of its regeneration and reuse. Quantitative elution of gold ions occurs with a 3% solution of thiourea in 1M hydrochloric acid. It was shown that sorption extraction in the third sorption-desorption cycle is 80%, which indicates the high stability of the ion exchanger and the activity of its regenerated form.

Effective amounts of thiourea and acid solutions for desorption of sorbed metal salts are given in Table 6.

Based on the results of the research, the highest result in the sorption of metal ions contained in standard solutions with the help of obtained ionites was observed in the range of -pH=2–3 in an acidic environment.

It was observed that the yield of gold (III) ion sorption in sulfuric acid solutions increased (98.2%) with the increase of the electron-donating property of the radical derivative of the obtained ionites. A 90:1 concentration of thiourea:acid is found to be effective in desorbing metal ions from ionites.

The possibility of using ion exchanger in the sorption-atomic absorption determination of gold is shown for a sample of copper concentrate. The results of the analysis and their statistical processing are presented in table.3. The true content of the determined component is included in the confidence interval, which indicates the absence of a systematic error. The calculated value of the Student criterion ($t_{0.95: 0.01} = 1.28$) is less than the tabular ($t_{0.95: 0.01} = 2.54$), which indicates the correctness of the measurement results. Laboratory precision was evaluated with a coefficient of variation of 4.6%.

Table 6. Results of desorption of some metal ions contained in ionites using an acidic solution of thiourea

Concentration of thiourea and sulfuric acid, g/l	T⁰C	Degree of desorption, % AuCl₃
40:1	60	56
50:1	60	65
60:1	60	62
70:1	60	76
80:1	60	81
90:1	60	86

Table 7. The results of the determination of gold in a sample of copper concentrate (n = 6)

True g / t	Found, g / t	V, %
568	5.41 ± 0.25	6.2

4. Conclusion

It should be noted that the use of the sorption properties of the polyfunctional ion exchangers synthesized, based on polymers of epichlorohydrin, (thio) urea and melamine, is promising and gives reason to recommend these ion exchangers for the concentration and separation of gold ions, for removing their traces from salt solutions.

Exchange capacity, metal sorption and desorption rate of synthesized ionites with respect to metal were studied. Synthesized ionites were tested in sorption-separation of gold ions from acidic solutions. When the dependence of the gold ions sorption level on the concentration of mineral acids (HCl, HNO₃, H₂SO₄) was studied, it was found that the sorption level increased from 66% (1M HCl) to 99% (2M HNO₃).

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