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Application of Probabilistic-Deterministic Method for Experiment Planning of Hydrometallurgical Processing of Various Wastes for Gold Extraction

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This paper presents a new approach to planning experiments for hydrometallurgical processing of gold from waste printed circuit boards of cell phones by aqueous thiourea solution with and without ultrasound exposure. It is established that the use of the probabilistic-deterministic approach to the planning of experiments significantly reduces the consumption of resources and energy by reducing the number of experiments. It is shown that the models obtained using the probabilistic-deterministic approach of Malyshev V.P. allow forecasting the gold extraction from the electronic waste with sufficient accuracy. Obtained the values of gold recovery under the optimal conditions calculated by simulation which were 84.66% without ultrasound and 91.46% with ultrasound, respectively. The experimental gold recovery under optimal conditions was 79.6% without ultrasound and 88.2% with ultrasound. The correlation coefficient of the ultrasonic leaching model was R = 0.87, with a significance of the correlation coefficient tR = 12.34 > 2. The correlation coefficient of the leaching model without ultrasound was R = 0.86; the significance of the correlation coefficient tR = 11.5 > 2. Evaluating the influence of each factor individually and in aggregate to find the optimal process parameters, we built a mathematical model of the dependence of leaching and the degree of extraction of gold from e-waste.

1. Introduction

Today, e-waste recycling is a particularly pressing issue around the world. E-waste poses a threat to the environment, but with the right approach it can be useful as a source of valuable materials (Rao et al., 2021). A tonne of spent smartphones is known to contain 200 - 300 g of gold and other precious metals (Manigandan et al., 2020). The hydrometallurgical method is the most promising way to recycle e-waste (Mishra et al., 2021). The use of thiourea as a reagent contributes to the environmental friendliness of gold leaching from e-waste (Ray et al., 2022). Based on a review and analysis of studies over the past 5 y., it was found that the existing techniques for the recovery of precious metals by recycling e-waste are not scientifically valid, but are developed empirically (Ippolito et al., 2021), and/or rely on the experience and intuition of researchers (Dengetal, 2020). Probably, in order to increase the efficiency of implementation of developed methods it is necessary to understand the regularities of hydrometallurgical recycling processes. It is suggested that the use of modelling of e-waste recycling process by means of experiment planning method is promising. A complete factor experiment is usually so versatile that it does not require prior knowledge of the physical and chemical nature of the process under study. This method is fully subject to the procedure of performing certain techniques of mathematical statistics, using the criteria for assessing the reproducibility of experiments, the significance of regression coefficients, the adequacy of the regression equation, etc. However, these same advantages predetermine the main disadvantage of the full-factor planning method - the lack of possibility of unambiguous physical and chemical interpretation of the obtained regression equation as a mathematical model of the object

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under study. This is due, firstly, to the strict limitations of the limits of variation of the factors and, secondly, to the possibility of obtaining unacceptable, absurd values. In fact, the method is mainly applicable to processes with linear dependence between the parameters in question.

In this paper, based on the analysis of literature data on the physico-chemical nature of the process of gold extraction from electronic waste using thiourea, we determine the prerequisites for choosing the method of planning experiments. We take as the significant factor the degree of Au extraction. At the beginning of the process it is equal to zero (y = 0). Au recovery rate at the end of the process is ≤100% (y ≤ 100). In accordance with the theory of chemical-metallurgical processes, a non-linear nature of the dependence of Au recovery rate on such factors as concentration, temperature, rate, solid-liquid ratio and the duration of the process should be expected. Having taken into account the above, the method chosen is probabilistic-deterministic planning of experiments Malyshev, (1981). This method allows to combine purely formal (statistical) procedures with a creative approach from consideration of physical and chemical features of the process. In experiments the following main factors are taken: reagent concentration, stirring speed, solid-liquid ratio, temperature and time. Use of additional factor - ultrasonic influence (UI) was excluded from the procedure of planning of experiments, leaving as a feature of two independent series of experiments: experiments without UI and parallel experiments with UI. The present study differs from the previously known ones by attempting to create a mathematical model of the relationship between leaching and gold recovery from e-waste, assessing the significance of each of the selected factors individually and in combination in order to find the optimum process parameters.

2. Materials and methods

This paper presents a planning method for a 5-factor experiment with 5 levels of hydrometallurgical processing of e-waste to recover gold and other valuable components (Table 1).

Table 1: Plan for a five-factor experiment (x_{1-5}) at five levels

No. of experiences	x_1	x_2	x_3	x_4	x_5
1	1	1	1	1	1
2	1	3	3	3	3
3	1	2	2	2	2
4	1	5	5	5	5
5	1	4	4	4	4
6	3	1	3	2	5
7	3	3	2	5	4
8	3	2	5	4	1
9	3	5	4	1	3
10	3	4	1	3	2
11	2	1	2	4	3
12	2	3	5	1	2
13	2	2	4	3	5
14	2	5	1	2	4
15	2	4	3	5	1
16	5	1	5	3	4
17	5	3	4	2	1
18	5	2	1	5	3
19	5	5	3	4	2
20	5	4	2	1	5
21	4	1	4	5	2
22	4	3	1	4	5
23	4	2	3	1	4
24	4	5	2	3	1
25	4	4	5	2	3

Laboratory experiments of gold leaching from e-waste were carried out according to probabilistic deterministic planning according to Table 1. Where x1 - thiourea concentration g/l (12, 16, 20, 24), x2 - Stirring speed rpm (50, 100, 150, 200), x3 - temperature °C - (25, 35, 45, 60), x4 - solid/liquid ratio T/l (5, 10, 15, 20). x5 - process duration min - (30, 45, 60, 120, 240). In all cases a solution of H_2SO_4 0.2 mol/l, and $Fe_2(SO_4)_3$ 22 g/l were used. The first series of experiments were carried out without ultrasound. The second series of experiments was carried out with similar parameters but with ultrasound. The flask with the solution was placed in an ultrasonic bath for 5 minutes every 10 minutes.

Each row in the table shows the conditions of the experiment. Sampling of point dependences of gold recovery into productive solution was made by averaging the experimental results corresponding to each level (1-5). In this case there is an averaging of factors action by self-compensation of lower and upper values. Obtained private point dependences, approximated by the functions obtained by the least squares method, resulting in plots of the dependence of the extraction of gold depending on the above factors. Adequacy of the dependencies was checked by non-linear multiple correlation coefficient by the Eq(1).

$$R = 1 - \sqrt{\frac{(n-1)\sum_{i=1}^{n}(y_{эi} - y_{\tau i})^2}{(n-k-1)\sum_{i=1}^{n}(y_{эi} - y_{cp})^2}} \qquad (1)$$

where n is the number of described points; k is the number of active factors (for particular dependencies equal to one); $y_{эi}$ - is the experimental value of the result; y_{Ti} - is the theoretical (calculated) value; y_{cp} - is the average experimental value.

The significance of the correlation coefficient and, consequently, of the tested dependence (Petrov et al., 2016) is determined by the Eq(2)

$$t_R = \frac{\sqrt{n-k-1}}{1-R^2} > 2 \qquad (2)$$

The partial dependencies were combined using Protodiakonov's equation (Malyshev, 1981) described in Malyshev's works, where the partial functions are combined as factors Eq(3).Table of factor levels (Table 2) and planning matrix of experiments with obtained data of gold recovery degree UG from e-waste (Table 3) were made.

$$y_G = \frac{\Pi_{i=1}^{k} y_i}{y_{cp}^{k-1}} \qquad (3)$$

3. Results and discussion

This work is a continuation of earlier research on the recovery of gold from smartphone boards (Shoshay et al., 2021). At this stage, in addition to the extraction of sputtered gold from the board surface, the possibility of recycling electronic components separated from boards containing gold is further explored. The separated chips were crushed and subjected to leaching in aqueous thiourea solution. The leaching was carried out with agitation at a frequency of 15-40 Hz. To intensify the processes ultrasonic radiation was used, ultrasonic power, (10, 20, 40, 60, 80) %. In order to determine the average metal content of electronic components in cellular phones (Table 1), 8 boards of phone brands 2014 - 2019 were taken (Samsung GT-S5282, Samsung GT-S5360, Samsung GT-S7662, Samsung GT- S6102, Samsung GT-I8262, Samsung SM-J105 H/DS, MicrosoFt-RM-1031, LG.). The electronic components were separated from the printed circuit boards by heat treatment or thermal treatment and ground to a size of less than 0.1 mm. This material was then sampled by quarting. The average gold content of the electronic components was 86 g/t (Table 2).

Table 2: Average concentration of metals in PCB mix samples (wt. %)

Cu	Al	Sn	Ni	Zn	Pb	Fe	Ag	Au	Pd
26.4	3.9	3.2	2.3	1.2	1.7	4.2	0.2	0.0086	0.1

To obtain mathematical models of the leaching process, a table of factor levels (Table 3) is compiled, where factors x1, x2, x3, x4, x5. Values of factors from minimum to maximum are levels. In this case, if a factor does not have the fifth level, the value of the fourth level is duplicated in the fifth level. The matrix of the experiment plan (Table 4) with the resultant extraction of gold from e-waste is an experiment plan, in which each row represents a particular experiment.

Table 3: Table of factor levels of a five-factor experiment (x_{1-5}) at five levels

Factors		Levels				
x_1	C, g/l	12	16	20	24	24
x_2	V, rpm	50	100	150	200	200
x_3	T, °C	25	35	45	60	60
x_4	T/J,	5	10	15	20	20
x_5	τ, min	30	45	60	120	240

Table 4: Factor level data from a five-factor experiment (x_{1-5}) at five levels

No. of experience	x_1	x_2	x_3	x_4	x_5	Y_G
1	12	50	25	5	30	12.2
2	12	150	45	15	60	15.6
3	12	100	35	10	45	13.4
4	12	200	60	20	240	57.4
5	12	200	60	20	120	44.6
6	20	50	45	10	240	48.5
7	20	150	35	20	120	44.4
8	20	100	60	20	30	16.7
9	20	200	60	5	60	19.1
10	20	200	25	15	45	12.3
11	16	50	35	20	60	16.1
12	16	150	60	5	45	18.8
13	16	100	60	15	240	43.2
14	16	200	25	10	120	32.6
15	16	200	45	20	30	12.4
16	24	50	60	15	120	45.4
17	24	150	60	10	30	17.2
18	24	100	25	20	60	13.1
19	24	200	45	20	45	16.6
20	24	200	35	5	240	49.2

The point dependencies of gold recovery into the productive solution were sampled by averaging the experimental results corresponding to each level (Table 5).
The point dependences of gold recovery into the productive solution were constructed by averaging the experimental results corresponding to each level (Table 5). For example, the value Y_1 = 28.64 was constructed by summing Y_G values at x_1 = 12 and divided by the number of levels 5.

Table 5: Factor level data from a five-factor experiment (x_{1-5}) at five levels

Factors	Levels					Amount	Private averages	Overall average
Y_1	28.64	24.62	28.2	24.48	28.3	147.65	29.53	
Y_2	28.16	23.7	27.14	27.62	27.6	134.24	26.85	
Y_3	21.98	27.1	25.04	28.54	37.12	139.78	27.96	27.51
Y_4	26.28	26.26	25.78	26.74	26.62	131.68	26.34	
Y_5	14.18	15.94	16.7	39.82	47.6	134.24	26.85	

Using the data in Table 3 and Table 5, the graphs of partial functions have been plotted (Figure 1). The modern MicrosoftExcel function wizard (Carlberg, 2014) was used to select the type of equations and determine the regression and correlation coefficients.
Further using Protodiakonov's Eq(3), a mathematical model of the process of gold leaching from e-waste using thiourea solution without ultrasound Eq(4) was obtained.The Microsoft Excel options allowed entering the initial conditions y_i=0 as it was stated above.

$$Y_G = 0.00000175 \cdot (-0.084 \cdot x_1^2 + 3.134\, x_1) \cdot (-0.001 \cdot x_2^2 + 0.435 \cdot x_2) \cdot (-0{,}007 \cdot x_3^2 + 1.004 \cdot x_3) \cdot (-0.139 \cdot x_4^2 + 4.439 \cdot x_4)\,(-3.277 \cdot x_5^2 + 24.76 \cdot x_5) \quad (4)$$

Similarly, a mathematical model of the process of leaching gold from e-waste using a thiourea solution with ultrasound Eq(5) has been derived.

$$Y_G = 0.00000172 \cdot (-0.1 \cdot x_1^2 + 3.477\, x_1) \cdot (-0.001 \cdot x_2^2 + 0.476 \cdot x_2) \cdot (-0{,}012 \cdot x_3^2 + 1.231 \cdot x_3) \cdot (-0.148 \cdot x_4^2 + 4.751 \cdot x_4)\,(-3.811 \cdot x_5^2 + 28.34 \cdot x_5) \quad (5)$$

In order to verify the models, the values shown in Table 5 and 6 respectively were substituted in Eq(4) (without ultrasonic treatment) and Eq(5) (with ultrasonic treatment). After that, leaching experiments with these parameters were carried out. The discrepancy between practical data and calculated data was ≈3-5%.

Coefficient of correlation of the model expressed by Eq 4, R = 0.87; significance of the correlation coefficient tR = 12.34> 2. Coefficient of correlation of model expressed by Eq 5, R = 0.86; significance of correlation coefficient t_R = 11.5> 2.

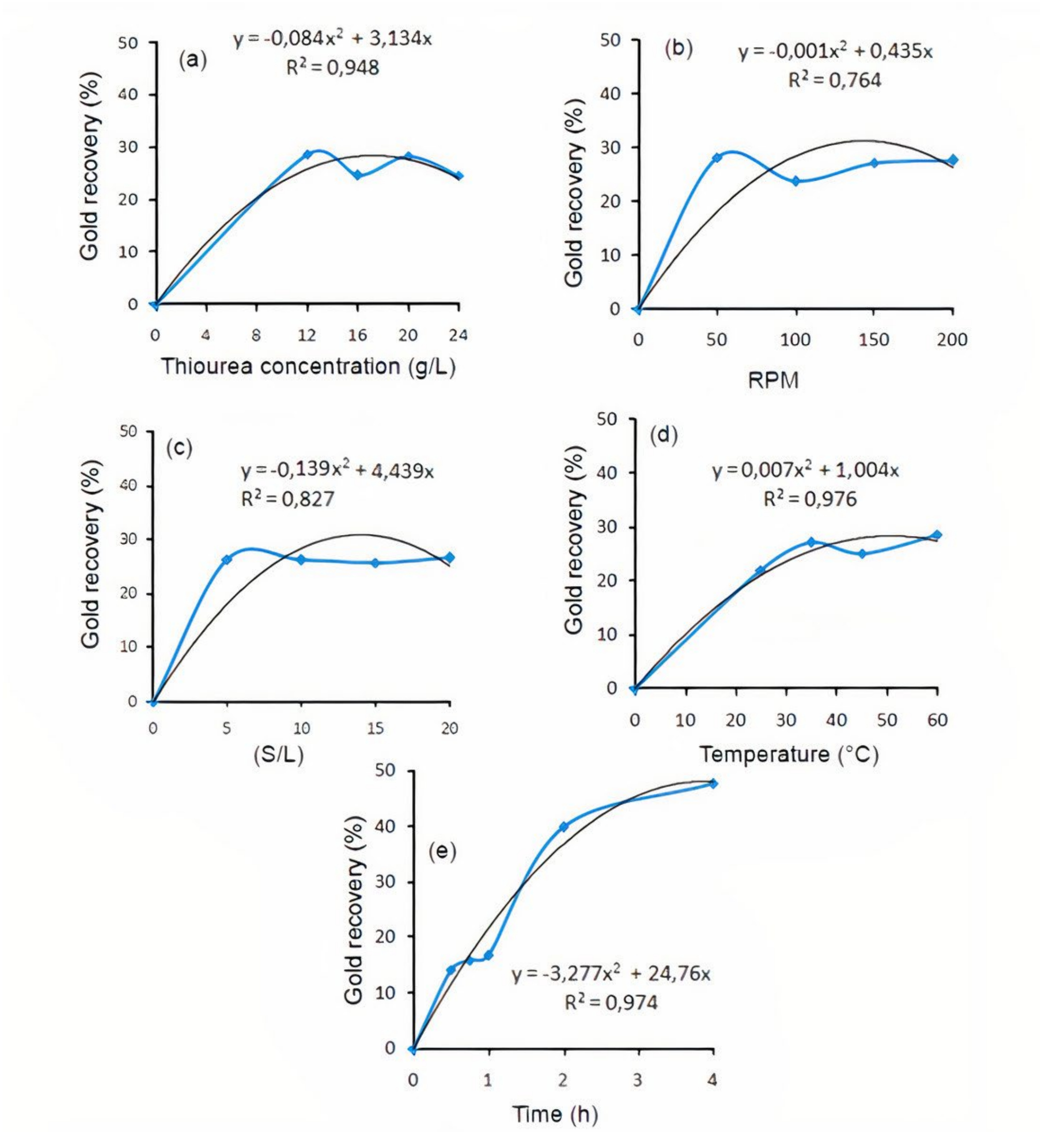

Figure 1: Partial functions of gold recovery from e-waste without ultrasound on (a) concentration; (b) stirring speed; (c) solid/liquid ratio; (d) temperature; (e) process duration

Table 5: Comparison of calculated and practical data leaching without ultrasonic influence (UI)

Factors		Calculated values						Practical data					
x_1	C, g/l	without UI			with UI			without UI			with UI		
		(24	24	24)	(24	24	24)	(24	24	24)	(24	24	24)
x_2	V, rpm	200	200	200	200	200	200	200	200	200	200	200	200
x_3	T, °C	60	60	60	60	60	60	60	60	60	60	60	60
x_4	T/J,	20	20	20	20	20	20	20	20	20	20	20	20
x_5	τ, min	90	60	30	90	60	30	90	60	30	90	60	30
Y_G	%	84.66	61.1	32.88	91.46	66.1	35.62	79,6%	59.8	29.7	88.2%	65.3	34

The calculated values showed that without ultrasonic exposure, the recovery reaches 84.66 %, with ultrasonic exposure reaches 91.46 %. The recovery rate of gold from e-waste without ultrasonic treatment depends more on concentration; stirring speed; solid-liquid ratio; temperature; and process duration. According to the model, among the factors that predominantly affect gold recovery from e-waste are concentration, time and temperature. Stirring speed (rpm) has less effect on the degree of metal recovery. Table 5 shows that ultrasound exposure increases the degree of gold recovery. It was found that the ultrasonic treatment with a duration of 90 minutes, the recovery rate is 91.46 % whereas without the ultrasonic treatment with the same duration it is possible to achieve 84.66 %.

4. Conclusions

This study demonstrated a technically feasible process to separate and recover gold from electronic components on end-of-life mobile phone circuit boards using thiourea with sulphuric acid and Fe^{+3}. The process involves separation of electronic components followed by roasting. The resulting raw material contains 0.0086% gold. By means of probabilistic-deterministic planning method mathematical models describing the dependence of gold leaching process from e-waste on various factors have been obtained. The obtained models allow to plan rather precisely the extraction of gold from electronic waste The obtained correlation coefficients and their significance (without ultrasound $R = 0.87$; $t_R = 12.34 > 2$; and with ultrasound $R = 0.86$; $t_R = 11.5 > 2$;) confirm the adequacy of the dependencies obtained. In addition, the study showed the promise of using ultrasound to intensify leaching processes. Conducted leaching showed that ultrasound increased gold recovery by 4-8 % on average in comparison with usual conditions. Using probabilistic-deterministic planning method the mathematical models describing the dependence of gold leaching process from electronic wastes on different factors were obtained

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