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APPLICATION OF CHITOSAN-ZINC OXIDE NANOPARTICLES FOR LEAD EXTRACTION FROM WATER SAMPLES BY THE COMBINED OF ANT COLONY OPTIMIZATION-ARTIFICIAL NEURAL NETWORK^{**}

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Chitosan-zinc oxide nanoparticles (CZPs) were developed for solid-phase extraction. Combined artificial neural network-ant colony optimization (ANN-ACO) was used for the simultaneous preconcentration and determination of lead (Pb^{2^+}) ions in water samples prior to graphite furnace atomic absorption spectrometry (GF AAS). The solution pH, mass of adsorbent CZPs, amount of 1-(2-pyridylazo)-2-naphthol (PAN), which was used as a complexing agent, eluent volume, eluent concentration, and flow rates of sample and eluent were used as input parameters of the ANN model, and the percentage of extracted Pb^{2^+} ions was used as the output variable of the model. A multi-layer perception network with a back-propagation learning algorithm was used to fit the experimental data. The optimum conditions were obtained based on the ACO. Under the optimized conditions, the limit of detection for Pb^{2^+} ions was found to be 0.078 µg/L. This procedure was also successfully used to determine the amounts of Pb^{2^+} ions in various natural water samples.

Keywords: lead, zinc oxide nanoparticles, chitosan, Artificial neural network, ant colony optimization, water samples.

ПРИМЕНЕНИЕ НАНОЧАСТИЦ ОКСИДА ЦИНКА С ХИТОЗАНОМ ДЛЯ ИЗВЛЕЧЕНИЯ СВИНЦА ИЗ ОБРАЗЦОВ ВОДЫ МЕТОДОМ, СОЧЕТАЮЩИМ МУРАВЬИНЫЙ АЛГОРИТМ И ИСКУССТВЕННЫЕ НЕЙРОННЫЕ СЕТИ

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Для твердофазной экстракции свинца из воды разработан метод получения наночастиц оксида цинка с хитозаном (CZPs). Муравьиный алгоритм в сочетании с искусственными нейронными сетями применялся для определения ионов свинца (Pb²⁺) в предварительно обогащенных образцах воды. Затем использовалась атомная абсорбционная спектрометрия в графитовой печи; pH раствора, масса адсорбента CZP, количество 1-(2-пиридилазо)-2-нафтола (PAN), которое использовали в ка-

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честве комплексообразующего агента, объем элюента, его концентрация, скорость потока образца и элюента служили входными параметрами модели муравьиного алгоритма, а процент выделенных ионов Pb²⁺ — как выходная переменная модель. Для согласования с экспериментальными данными использовалась многослойная система восприятия с алгоритмом обучения, основанным на обратном распространении. В оптимизированных условиях, которые найдены на основе муравьиного алгоритма, предел обнаружения ионов Pb²⁺ равен 0.078 мкг/л. Разработанный метод успешно использован для определения содержания ионов Pb²⁺ в различных образцах естественной воды.

Ключевые слова: свинец, наночастицы оксида цинка, хитозан, искусственная нейронная сеть, муравьиный алгоритм, образцы воды.

Introduction. Excess heavy metals such as lead in water are well-known sources of potential harm to aquatic life and human health. The extraction of toxic heavy metals from various samples (i.e., water samples) at trace amounts is therefore extremely important [1–4]. Lead is a toxic heavy metal with no known positive physiological role in the human body. It causes a range of diseases and has undesired effects on health. The main sources of lead exposure are water, smoking, food, contaminated air (mainly from tetra-ethyllead used as a motor fuel additive), soil, and consumer products. Occupational exposure of lead in the workplace is one of the most common causes of lead poisoning in adults, particularly in the scrapping, smelting, printing, pigment production, battery manufacture, plastics, and chemical industries, as well as in mining and among metalworkers [3, 4]. Accordingly, it is essential to develop methods for the separation and analysis of trace amounts of lead in water samples.

Chitosan is a natural biopolymer with an excellent capacity for adsorbing a wide variety of contaminants, including heavy metals and dyes, because it contains hydroxyl and amino groups. However, raw chitosan has a tendency to agglomerate in aqueous media [5–7]. To overcome the drawbacks of chitosan and improve its applicability to environmental water treatment, we investigated chemical crosslinking of chitosan with zinc oxide nanoparticles in the present study. The aim of nanotechnology is to generate nanoarrays/nanostructures with special chemical and physical properties that are not shown by their single particles or bulk states. The surface atoms of nanoparticles are unsaturated and have high chemical activity, which enables them to bind with other atoms. In this study, chitosan-zinc oxide nanoparticles (CZPs) were used as adsorbents for preconcentration of Pb²⁺ ions from water samples. This procedure is beneficial because of its simple design, low cost, and use of a nontoxic adsorbent with high extraction efficiency [7–10].

An artificial neural network (ANN) is a useful tool in mathematics that can be used for modeling highly complex systems with many variables. The ANN does not require any detailed information about the physical parameters of the system, and instead uses available data for predicting the relationship between input and output variables. Among different types of ANNs, back-propagation neural networks are usually used because of their excellent robustness and fault tolerance, as well as their ability to estimate any continuous function [2, 11].

Ant colony optimization (ACO) is a technique for optimization of problems. In nature, a colony of ants uses its swarm intelligence and capability to obtain the shortest path between the colony and food sources. This concept can also be used to identify and optimize a route length in a network or a graph [2, 12, 13]. The ACO technique can therefore be used for a variety of combinatorial optimization problems.

This study evaluated the extraction ability of CZPs as an adsorbent for preconcentration of lead from water samples. The effects of different variables, including the solution pH, mass of adsorbent CZPs, amount of 1-(2-pyridylazo)-2-naphthol (PAN), eluent volume, eluent concentration, and sample and eluent flow rates were also investigated. The aims of this study were to (i) identify a good model based on the ANN system for predicting the efficiency of lead extraction, (ii) optimize the lead-extraction capability by using a hybrid of ANN and ACO techniques, and (iii) develop a rapid and simple method for extraction of lead.

Experimental. PAN, ZnO powder, ethanol, reagent grade $Pb(NO_3)_2$, and all acids were purchased from Merck (Darmstadt, Germany). A stock solution containing 1000 mg/L of lead was prepared by dissolving the appropriate amount of $Pb(NO_3)_2$ in double-distilled water. Working solutions were prepared by diluting an appropriate amount of stock solution with double-distilled water.

Lead was determined using a Varian atomic absorption spectrometer (model SpectrAA-20 Plus) equipped with a graphite furnace (GTA-96). Details of the graphite furnace temperature program used for the determination of Pb are shown in Table 1. The solution pH was determined using a pH meter (model 630 Metrohm) with a combined glass-calomel electrode.

Wavelength	283.3 (0.5 nm)		
D ₂ Lamp	On		
Temperature pro	ogramming (°C – s)		
	85 - 5		
Drying	95 - 40		
	120 - 10		
Ashing	600 - 5		
Ashing	600 - 5		
Atomization	2100 - 2		
Atomization	2100 - 0.8		
Cleaning	2300 - 2		

TABLE 1	Optimum	GF-AAS	Operating	Conditions	for the	Determinati	on of Pb
TIDDD I.	opuniani	01 11110	operating	Contaitionio	101 0110	Determination	011 01 1 0

CZPs were synthesized using a previously reported method [14, 15]. Briefly, ZnO powder (1 g) was dissolved in 1% CH₃COOH (100 mL). In this step, ZnO molecules were changed to zinc cations. Chitosan (1.0 g) was added to this solution. The mixture was then sonicated for 30 min, after which 1 mol/L NaOH was added dropwise to the solution until the pH was 10. The solution was then heated in a water bath at 60°C for about 3 h. Finally, this solution was filtered and the residue was washed several times with deionized (DI) water, and then dried at 50°C for 1 h in an electrical oven. A representative scanning electron microscopy (SEM) image of the CZPs is shown in Fig. 1.



Fig. 1. The SEM image of chitosan-zinc oxide nanoparticle.

An empty solid-phase extraction cartridge was packed with different amounts of CZP adsorbent, treated with 5 mL of HNO_3 and methanol, and washed with DI water.

Next, a sample solution (50 mL) containing 0.2 mg/L of Pb^{2+} ions was prepared and the pH was adjusted to between 7 and 10 with 0.1 mol/L NaOH. This solution was subsequently passed through the cartridge at a flow rate of 2–8 mL/min. In this step, the lead ions were retained on the adsorbent. The sorbent was then eluted with 1–3 mL of nitric acid as the eluent. Next, the lead concentration in the nitric acid was determined using graphite furnace atomic absorption spectrometry (GF AAS). For each sample solution, the extractions were conducted in triplicate and the average was reported.

In this study, Neural Network Toolbox V7.12 of MATLAB mathematical software was applied to identify the optimum extraction efficiency of lead from water samples. An ANN is a combination of neurons (processing elements) that are linked together in a specified way based on the network type. The feedforward (FF) structure provides weighted connections between two adjacent layers of neurons, which obtain information from the previous layer of neurons, and send their output to the next layer. The neurons between the input and output layers are considered to be hidden neurons. The overall output of neurons can be calculated as follows:

$$\operatorname{net}_{j} = f\left(\sum_{r=1}^{N} w_{jr} + b_{j}\right), \tag{1}$$

where b_j and net_i are the bias and output of the *j*th neuron, and w_{jr} is the weight from neuron *r* to neuron *j*.

As shown by Eq. (1), x_r is strengthened or weakened through multiplication by weights and summing with bias coefficients. The biases are activation thresholds that add to the multiplication of inputs and their particular weight coefficients. The net output of each neuron passes through an activation or transfer function (*f*). Various transfer functions such as linear (*purlin*), radial basis, log-sigmoid, and tan-sigmoid (*tansig*) have been considered for ANNs [15, 16]. In this study, the transfer functions used are defined by the following equations:

$$Purelin (sum) = sum, \tag{2}$$

Tansig(sum) =
$$(1 - e^{-sum})/(+e^{-sum})$$
, (3)

where tansig is used between the input and hidden layers, and purelin is used between the hidden and output layers.

The ACO algorithm was first presented by Dorigo et al. [17] as a multi-agent technique for complicated problems in combinatorial optimization. In nature, ants work by themselves, independently from other colony members. However, they can solve difficult problems by acting as a community. The path selection model is defined as follows:

Each ant chooses the next independent state. The probability of the k^{th} ant moving from state *i* to a new state *j* is $P_{ij}^{k}(t)$, which can be determined using the following probability rule [13]:

$$P_{ij}^{k}(t) = \begin{cases} \frac{[\tau_{ij}(t)]^{\alpha}[\eta_{ij}]^{\beta}}{\sum_{k \in \text{allowed}_{k}}[\tau_{ik}(t)]^{\alpha}[\eta_{ik}]^{\beta}} & \text{if } j \in \text{allowed}_{k}, \\ 0 & \text{otherwise} \end{cases}$$
(4)

where τ_{ij} refers to the pheromone density of the edge (i,j), $\eta_{ij} = 1/C_{ij}$ is the heuristic function, C_{ij} refers to the cost of production for that particular stage to occur, α and β are the relative importance of pheromone trails and visibility values, respectively (α and $\beta \ge 0$), and "allowed_k" are the available states that the k^{th} ant can choose from the i^{th} state to the j^{th} state.

Updated ant pheromone trails are a key element in adaptive ACO learning. They help to ensure further improvement of solutions. Pheromone trails are updated by reducing the amount of pheromones on all links to simulate the evaporation of pheromones and ensure that no single path becomes dominant. This is accomplished using the following equation [13]:

$$\tau_{ij}^{\text{new}} = \rho \tau_{ij}^{\text{old}} + \sum_{k}^{K} \Delta \tau_{ij}^{k}, \quad \rho \in (0, 1),$$
(5)

where τ_{ij}^{new} refers to the pheromone on link (i,j) after updating, τ_{ij}^{old} is the pheromone on link (i,j) before updating, ρ refers to the parameter that controls the speed of evaporation, k is the number of the route, K is the number of the route in the solution, and K > 0 and $\Delta \tau_{ij}^{k}$ are the increased amounts of pheromones on link (i,j) of route k found by the ant. This updating encourages the use of shorter routes.

The mutation process refers to a genetic algorithm (GA) that alters each child with a predefined probability. Operators are able to help the ACO attain more solutions in the search space. Here, the mutation operator is considered to progress to the convergence speed.

Results and discussion. *Optimization of CZP solid-phase extraction.* Based on preliminary tests, seven parameters, i.e., solution pH, adsorbent CZP mass, amount of PAN (used as a complexing agent), eluent volume, eluent concentration, and eluent and sample flow rates, were selected. Table 2 shows the main variables and lead recoveries.

The number of neurons in the output and input is equal to the number of output and input data, respectively (1 and 7 in this study). The optimum configuration of the multi-layer perceptron (MLP) network was obtained using a trial and error method through selection of the number of neurons in the hidden layer (HL). The number of neurons in the HL is determined during an optimization method that minimizes error indexes. The number of suitable neurons in the HL generally depends on (1) the complexity of the correlation between output and input data, (2) the number of available training and test data, and (3) the noise severity imposed on the data collections [16]. A large number of neurons in the HL can cause overfitting, whereas a low number can result in a network that cannot obtain the desired error. In this study, a total of 57 experiments were divided randomly into three subsets: 68% for the training set, 16% for the validation set, and 16% for the test set.

		Mass of		Commis floor	Eluent con-	Eluent	Eluent	Experime	Due diete d
Run	pН	adsorb-	[PAN],	Sample flow	centration,	volume,	flow rate,	ntal R, %	
		ent, g	moi/L	rate, mL/min	mol/L	mL	mL/min		<i>K</i> , %
Training									
1	8.5	0.4	4	2	0.5	2	2	64.5 ^a	64.5
2	8.5	0.4	4	8	0.5	2	2	65.9	65.7
3	8.5	0.4	4	2	1.5	2	2	63.9	63.9
4	8.5	0.4	4	8	1.5	2	2	74.5	74.5
5	8.5	0.4	4	2	0.5	3	2	62.8	62.9
6	8.5	0.4	4	2	1.5	3	2	68.8	69
7	8.5	0.4	4	8	1.5	3	2	90	90.1
8	10	0.4	4	5	1	2	1	72.2	72.2
9	7	0.4	4	5	1	3	1	44.2	44.3
10	10	0.4	4	5	1	2	3	45.8	45.9
11	10	0.4	4	5	1	3	3	66.8	66.7
12	8.5	0.2	4	5	0.5	2.5	1	60.8	60.4
13	8.5	0.6	4	5	0.5	2.5	1	86.8	86.7
14	8.5	0.2	4	5	0.5	2.5	3	73.9	73.7
15	8.5	0.6	4	5	0.5	2.5	3	91.2	91.1
16	8.5	0.2	4	5	1.5	2.5	3	82.7	82.6
17	7	0.2	4	2	1	2.5	2	37	36.9
18	10	0.2	4	2	1	2.5	2	53.3	53.4
19	7	0.6	4	2	1	2.5	2	58.7	58.8
20	10	0.6	4	2	1	2.5	2	57.9	58.9
21	7	0.2	4	8	1	2.5	2	49.3	49
22	10	0.6	4	8	1	2.5	2	68.2	68.4
23	8.5	0.4	2	2	1	2.5	1	19.5	19.6
24	8.5	0.4	6	2	1	2.5	1	28.6	28.8
25	8.5	0.4	2	8	1	2.5	1	49.6	49.6
26	8.5	0.4	6	8	1	2.5	1	28.4	28.6
27	8.5	0.4	2	2	1	2.5	3	14.2	14.2
28	8.5	0.4	6	2	1	2.5	3	43.5	43.7
29	8.5	0.4	2	8	1	2.5	3	37.1	37.2
30	7	0.4	2	5	0.5	2.5	2	36.5	36.1
31	10	0.4	2	5	0.5	2.5	2	52.5	52.5
32	7	0.4	6	5	0.5	2.5	2	47.4	47.1
33	7	0.4	2	5	1.5	2.5	2	55.3	55.3
34	10	0.4	6	5	1.5	2.5	2	55.1	55.4
35	8.5	0.2	6	5	1	2	2	81.3	81.4
36	8.5	0.6	6	5	1	2	2	69.8	69.9
37	8.5	0.2	6	5	1	3	2	61.7	61.8
38	8.5	0.6	6	5	l	3	2	80.3	80.3
39	8.5	0.4	4	5		2.5	2	83.5	83.6
	Validation								
	8.5	0.4	4	8	0.5	3	2	64.6	64.6
2	8.5	0.2	4	5	1.5	2.5		84.6	82.8
5	8.5	0.6	4	5	1.5	2.5		92.5	80.0
	10	0.2	4	ð S	1	2.5	2	64./	/1.5
5	/	0.6	4	8	1	2.5	2	09.9 70.4	69./ 70.4
0 7	10	0.4) 5 5	1.5	2.5		/0.4	/0.4
0	0.J	0.2		5 5	1			45.4	45.4 57.0
0	0.J 85	0.0	$\frac{2}{2}$	5	1	2	$\frac{2}{2}$	56.2	57.9 56.4
7	0.0	0.2	2	5	1	5	2	30.3	50.4

TABLE 2. Experimental Data was Used for ANN Modeling

								Contin	ue Table 2
Run	pН	Mass of adsorb- ent. g	[PAN], mol/L	Sample flow rate, mL/min	Eluent con- centration, mol/L	Eluent volume, mL	Eluent flow rate, mL/min	Experime ntal <i>R</i> , %	Predicted <i>R</i> , %
		, 8	1	I	Test	1		1	I
1	7	0.4	4	5	1	2	1	51.4	46.8
2	10	0.4	4	5	1	3	1	77.5	77.2
3	7	0.4	4	5	1	2	3	51.5	52.4
4	7	0.4	4	5	1	3	3	73	72.4
5	8.5	0.6	4	5	1.5	2.5	3	72.6	72.6
6	8.5	0.4	6	8	1	2.5	3	40.8	40.9
7	10	0.4	6	5	0.5	2.5	2	47.4	47.4
8	7	0.4	6	5	1.5	2.5	2	66.9	66.9
9	8.5	0.6	2	5	1	3	2	96.8	99.4

^a Average triplicate measurements.

The number of neurons in the HL was evaluated by minimizing the mean-squared error (MSE) and AARD%, and maximizing the determination coefficient (R^2) values of the test, validation, and training data sets. The MSE, AARD%, and R^2 equations are as follows:

$$MSE = \frac{1}{N} \sum_{i=1}^{N} (y_i^{exp} - y_i^{cal})^2,$$
(6)

$$AARD\% = \left(\frac{1}{N}\sum_{i=1}^{N} (y_i^{exp} - y_i^{cal}) / y_i^{exp}\right) \times 100,$$
(7)

$$R^{2} = \frac{\sum_{i=1}^{N} (y_{i}^{\exp} - \overline{y})^{2} - \sum_{i=1}^{N} (y_{i}^{\exp} - y_{i}^{cal})^{2}}{\sum_{i=1}^{N} (y_{i}^{\exp} - \overline{y})^{2}},$$
(8)

 $\sum_{i=1}^{N} (y_i + y_i)$ where y_i^{exp} is the experimental extraction efficiency, y_i^{cal} is the predicted extraction efficiency, \overline{y} is the average value of the experimental extraction efficiency data, and N is the number of points.

All data were normalized in the interval [0,1] to avoid saturation of its parameters and improve the network convergence rate, according to the following equation:

$$x_{\text{norm}} = (x - x_{\min})/(x_{\max} - x_{\min}), \qquad (9)$$

where x is variable, x_{max} is the maximum value, and x_{min} is the minimum value.

This method identified the ANN model with one HL consisting of 17 neurons as the optimum structure. Figure 2 indicates the optimum ANN model topology for lead. The most generally used criteria, with MSE, AARD%, and R^2 for training, testing, and validation, and all data sets are presented in Table 3. The results show that the ANN model produced excellent agreement between the predicted and experimental data. As shown in Fig. 3, variations in the MSE were observed during the training phase using the Levenberg-Marquardt (LM) algorithm for lead, and the MSE value converged to approximately 5×10^{-6} in four iterations. Training of the MLP network was therefore satisfactorily terminated. The experimental data versus the predicted data for lead are plotted in Fig. 4; this plot also indicates the goodness of fit between the input data and the output data given by the ANN model.

TABLE 3. Statistical Criteria for Evaluation of ANN Model

Criterion	All	Train	Validation	Test
MSE	0.0003	0.000005	0.0014	0.0005
AARD%	0.82	0.29	2.26	1.64
R^2	0.994	0.9999	0.956	0.992



Fig. 3. Training, validation and test mean squared errors for the LM algorithm.

The ACO technique was used to optimize the ANN model input space with the objective of maximizing lead recovery. The ACO-specific parameter values used in simulation of optimization were as follows: number of ants = 50; α = 1; β = 2; ρ = 0.05; and mutation rate = 0.2. An optimum condition was selected after evaluation of the ACO for 20 iterations to achieve good extraction efficiency. The optimized conditions were as follows: solution pH 9.8, CZP amount 0.59 g, amount of PAN 6 mol/L, eluent volume 2.4 mL, eluent concentration 0.5 mol/L, flow rate 8 mL/min, and eluent flow rate 1.5 mL/min. The ANN prediction of the recovery under the optimum conditions was 99.2, and the residual error between the predicted and experimental data was 1.2%. These data confirm the validity of the constructed ANN model.

It is well known that binding of metal ions in a chelated compound either on a solid support or in solution is generally dependent on several factors, including size, charge, and the nature of the metal ions [18]. Moreover, the nature of the donor atoms, which are generally sulfur, oxygen, phosphorus, or nitrogen, determine the binding characteristics and selective extraction of such chelated compounds with particular metal ions based on various selectivity factors. Furthermore, buffering conditions favor extraction of particular metal ions and binding to active groups or donors [18]. These factors have been well documented for the solution chemistry and solid-phase extraction of particular metal ions by chelates immobilized on a solid support surface; the effects of pH were therefore investigated in the present study.



Fig. 4. Predicted extraction by ANN versus experimental values.

PAN exists in various monomeric species depending on the pH of the aqueous phase. The acid dissociation constants pK_{NH} and pK_{OH} of PAN are 1.99 and 12.2, respectively. The yellow cation (H₂PAN⁺) exists at lower pH (>3), whereas the neutral form (HPAN), which is insoluble in aqueous solution and responsible for the formation of complexes with metal ions, exists in the pH range 4–10. The anionic species (PAN⁻), which is red and soluble in aqueous solution, exists at pH greater than 12 [19]. A 1:1 complex between PAN and lead ions was formed [20]. Moreover, when the solution pH was above the isoelectric point of the nanoparticles (about 8.75) [10], the nanoparticle surfaces became negatively charged, leading to strong electrostatic attraction between the nanoparticles and cationic complex (Pb–PAN). We therefore selected pH 9.8 for the next investigation.

The results show that the extraction efficiency for lead ions increased with increasing amount of adsorbent. When the amount of adsorbent increased, the available number of sorption sites on the CZP surfaces increased, enlarging the concentration gradient between the Pb^{2+} ions in the sample solution and on the surfaces of the CZPs [21]. The enlarged concentration gradient increased the interactions between the Pb–PAN complex and the CZP adsorbent, improving the extraction efficiency for Pb²⁺ ions [21].

Effects of coexisting ions. In this study, the effects of common coexisting ions on the extraction of lead ions were investigated. Solutions containing 50 μ g/L of Pb²⁺ and added coexisting ions were analyzed as described above. The tolerance limit was identified as the amount of coexisting ions that caused the extraction efficiency for Pb²⁺ ions to be less than 95%. The results indicate that 500-fold increases in Na(I), K(I), Mg(II), Ca(II), and Ba(II), and 50-fold increases in Ni(II), Mn(II), Cd(II), Zn(II), and Co(III) ions had no significant impact on the determination of Pb²⁺ ions.

Evaluation of the methods performance. In this study, the linear range under the optimum conditions occurred between 5 and 400 μ g/L, with a correlation coefficient of 0.998. In accordance with the IUPAC definition, the limit of detection of this procedure was calculated based on three times the standard deviation of 10 runs of the blank and was found to be 0.078 μ g/L. In addition, the relative standard deviation (RSD%) of 10 replicate measurements was 1.8% ($n = 10, C = 50 \mu$ g/L).

To obtain a high enrichment factor, a larger sample solution volume is needed. To study the effects of sample volume, 25, 50, 100, 250, and 500 mL of solutions containing 50 μ g of lead were evaluated using the above method. A quantitative Pb²⁺ ion extraction efficiency greater than 97% was obtained when the sample solution volume was less than 250 mL. The enrichment factor was therefore 104 for a sample solution volume of 250 mL, because the elution volume was 2.4 mL.

Analysis of real samples. The proposed procedure was used for the preconcentration and determination of trace amounts of Pb(II) in environmental water samples; the results are shown in Table 4. The recoveries of lead ions ranged from 97.5 to 99.5%, indicating that the proposed procedure is reliable.

Sampla	Lead cont	Recovery,	
Sample	Added Found		%
Top water	0.0	7.5 ± 0.4	_
Tap water	20.0	27.4 ± 0.3	99.5
Disconstant	0.0	8.5 ± 0.6	_
Kivel water	20.0	28.3 ± 0.9	99.0
Ground water	0.0	10.7 ± 1.1	_
Ground water	20.0	30.2 ± 0.9	97.5

TABLE 4. Determination of Lead in Water Samples (N = 3)

Conclusion. A selective procedure was established for the determination of trace amounts of Pb(II) in water samples, using CZPs modified with PAN as a chelating agent. Quantitative extraction of lead ions from the aqueous samples at trace levels was achieved at pH 9.8. The enrichment factor was 104 for a maximum sample solution volume of 250 mL. ANN-ACO was used for simulation and optimization of the method. The results showed that ACO is a good tool for calculating the optimum factors. This method is simple, fast, and gives a high enrichment factor with a low limit of detection.

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