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Simultaneous extraction of Cu^{2+} and Cd^{2+} ions in water, wastewater, and food samples using solvent-terminated dispersive liquid–liquid microextraction: optimization by multiobjective evolutionary algorithm based on decomposition

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Abstract Solvent-terminated dispersive liquid-liquid microextraction (ST-DLLME) as a simple, fast, and low-cost technique was developed for simultaneous extraction of Cd^{2+} and Cu^{2+} ions in aqueous solutions. Multiobjective evolutionary algorithm based on decomposition with the aid of artificial neural networks (ANN–MOEA/D) was used for the first time in chemistry, environment, and food sciences to optimize several independent variables affecting the extraction efficiency, including disperser volume and extraction solvent volume, pH, and salt addition. To perform the ST-DLLME operations, xylene, methanol, and dithizone were utilized as an extraction solvent, disperser solvent, and chelating agent, respectively. Non-dominated sorting genetic algorithm versions II and III (NSGA II and NSGA III) as multiobjective metaheuristic algorithms and in addition central composite design (CCD) were studied as comparable optimization methods. A comparison of results from these techniques revealed that ANN-MOEA/D model was the best optimization technique owing to its highest efficiency (97.6% for Cd^{2+} and 98.3% for Cu^{2+}). Under optimal conditions obtained by ANN-MOEAD, the detection limit (S/N = 3), the quantitation limit(S/N = 10), and the linear range for Cu^{2+} were 0.05, 0.15, and 0.15–1000 μg L^{-1}, respectively, and for Cd^{2+} were 0.07, 0.21, and 0.21–750 μg L^{-1}, respectively. The real sample recoveries at a spiking level of 0.05, 0.1, and 0.3 mg L^{-1} of Cu^{2+} and Cd^{2+} ions under the optimal conditions obtained by ANN–MOEA/D ranged from 94.8 to 105%.

Keywords Solvent-terminated dispersive liquid–liquid microextraction · Cadmium ions · Copper ions · Multiobjective evolutionary algorithm based on decomposition · Artificial neural networks

Introduction

There are numerous sources of heavy metal contaminations such as metal processing factories, mines, and sewage sludge. They enter into the human body via air, water, and food. Some of these metals such as copper ions are essential micronutrient at low concentrations but can be toxic at higher concentrations and others; for instance, cadmium ions are toxic even at very low concentrations (Furini 2012). In water and food samples, the concentration of heavy metals in trace levels can cause serious health problems to humans, and therefore, preconcentration of analyte was carried out before final assay. Preconcentration of heavy metal ions was carried out by using liquid–liquid extraction (Karadaş and Kara 2014) and solid-phase extraction (Mohammadi et al. 2016). The employments of these methods were limited due to high consumption of organic solvent and high-cost procedure (Shirkhanloo et al. 2010). To eliminate these

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problems, dispersive liquid–liquid microextraction (DLLME) as an efficient miniaturized approach was introduced in 2006 (Rezaee et al. 2006). The extraction in this technique was restricted to the solvents with higher density and also poisonous property which should be isolated in solution using a centrifuge apparatus. Chen and coworkers developed a solvent-terminated dispersive liquid–liquid microextraction (ST-DLLME) with a lower density solvent (H. Chen et al. 2010). The ST-DLLME process can be completed by the injection of demulsifier solvent like acetonitrile into the final turbid solution of the aqueous sample, and as the extraction solvent eliminates the emulsion and consequently, the centrifugation step is not necessary (Mansour and Danielson 2018). One of the issues that has always been of interest to scientists is to optimize the experimental conditions and obtaining the most appropriate response. Recently, scientists have focused on the development of high efficiency multiobjective metaheuristic optimization algorithms such as non-dominated sorting genetic algorithm versions II and III (NSGA-II and NSGA-III) (Deb et al. 2002; Deb and Jain 2014) and multiobjective evolutionary algorithm based on decomposition (MOEA/D) (Zhang and Li 2007). In comparison to NSGA versions II and III, the MOEA/D method uses a different approach for optimization and lower computational complications. MOEA/D decomposes a multiobjective problem (MOP) into a number of single objective subproblems and solving them simultaneously with respect to pareto optimal solutions (Neri and Tirronen 2010). This technique has been applied in limited fields, and so, few reports have been given in the literature in this regard (C.M. Chen et al. 2010; Zhou et al. 2011).

In our previous works, DLLME technique was employed for extraction of several analytes in various samples (Moradi et al. 2017; Maham et al. 2014; Maham et al. 2013c; Maham et al. 2013a; Maham et al. 2013b; Kiarostami et al. 2014; Farajvand et al. 2018). So as far as we are aware, practically no research has been carried out on the simultaneous microextraction of Cd^{2+} and Cu^{2+} ions using ST-DLLME, and furthermore, a MOEA/D approach has not been used in the field of chemistry, environment, and food sciences. Therefore, this study describes the employment of multiobjective evolutionary algorithm based on decomposition with the aid of artificial neural networks(ANN–MOEA/D) to optimize the ST-DLLME of Cu^{2+} and Cd^{2+} ions with dithizone as a complexing agent in water, wastewater, milk, tea, and apple juice samples. In addition, the central composite design (CCD), NSGA-II, and NSGA-III have also been employed as comparable techniques for microextraction optimization.

Materials and methods

Chemical and reagents

All laboratory reagents were analytical grade and purchased from Merck and Sigma-Aldrich. Cadmium and copper ion stock solutions with concentration of 1000 mg L^{-1} were made by dissolution of $CdCl_2$ and $CuCl_2$ (Titrasol, Merck) in deionized water. Dilutions of heavy metal stock solutions in deionized water were carried out to prepare calibration solutions. Adjustment of pH solution was controlled by adding HCl (0.1 M) and NaOH (0.1 M). The natural water (river and well water) and wastewater were collected from agricultural areas and a factory wastewater, respectively (Islamshahr, Iran). The river samples were obtained directly from three separate three sites separated from each other by 1 km. They were then mixed to prepare a bulk sample. The bulk well water samples were prepared by collecting samples of well water at an interval of 3 days from only one site. The bulk wastewater samples were collected from a factory wastewater over a 3-day period. One liter of the laboratory sample was collected directly from the homogenized bulk sample. Additionally, all the other samples such as apple juice (Sunich Co, Iran), low-fat bottled milk (Damdaran Co, Iran), black tea (Ahmad Co, England), and bottled mineral water (Vata Co, Iran) were purchased from a local market and applied to study the proposed ST-DLLME percentage recoveries.

Instruments

Atomic absorption spectrometer equipped with a deuterium background correction and an air-acetylene burner (Varian spectra 240 fs (USA)) was employed for determination of copper and cadmium ions. pH meter Jenway 3510 (United States of America) was used to determine the solution pH.

Real sample preparation

A sample of tea drink was conventionally made by putting 5 g of the tea leaves in 250 mL of boiling water. The samples of wastewater, water, milk, and apple juice were stored individually in a sterile food container and kept at 4 °C. Water and wastewater samples were acidified with nitric acid to a pH 2. The aqueous samples were centrifuged for 20 min at 4000 rpm, and after, the supernatants were passed through a 0.45-μm membrane filter (Millipore Co, MA, USA). After filtration step, the cleaned apple juice and milk were mixed with deionized water for dilution in the ratio of 1:4. Lastly, the prepared aqueous samples were used for ST-DLLME process.

ST-DLLME procedure

To perform ST-DLLME procedure, a 10 mL of deionized water spiked with 0.5 mg L^{-1} Cd^{2+} and Cu^{2+} ions with adjusted pH of 6 was transferred into a 10-mL glass volumetric flask. Triple mix containing 250 μL xylene as an extraction solvent, 100 μL dithizone (1×10^{-4} mol L^{-1}) as a complexing agent, and 550 μL methanol as a disperser solvent was injected by a Hamilton syringe (1 mL) into the above solution, in which a turbid solution was formed. Then, with injection of a 500 μL acetonitrile as a demulsifier, the phase separation was resulted. A Hamilton syringe (100 μL) was used to collect the upper phase which was evaporated using a N_2 gas gentle stream. After evaporation, 1 mL of nitric acid (0.1 M) was added to the obtained residual and finally nebulized into the flame atomic absorption spectrometer for ion determination.

Optimization methods

For optimization of three independent factors such as extraction, disperser solvent types, and extraction time, one variable at a time (OVAT) technique was applied. Other four variables were optimized by multiobjective evolutionary algorithm based on decomposition with the aid of artificial neural networks (ANN–MOEA/D), non-dominated sorting genetic algorithm versions II and III, and response surface methodology (RSM) with regard to the microextraction efficiency.

Central composite design

In this project, a CCD technique with four variables and three levels as a response surface methodology with $\alpha = 2$ including 30 treatment combinations with 16 factorial points, eight axial points, and six replicates at center point was tested using Design Expert (version 7.00, Stat-Ease Inc., Minnea polis, MN). The low and high levels of four independent variables in CCD such as the volumes of extraction (V_1) and disperser (V_2) solvents, pH (V_3), and salt addition (V_4) were 50 and 450 μL, 300 and 800 μL, 2 and 10, and 0 and 7.5%, respectively.

Artificial neural networks-multiobjective evolutionary algorithm

The nonlinear relation between the independent factors (input data) and the dependent factors (output data) was obtained by multilayer preceptrons (MLP) artificial neural network using MATLAB R2010a software. Training of the network was performed by the levenberg marquardt back propagation method. Tansig and pureline were employed as activation functions in the hidden and output layers, respectively.

A problem with multiobjective state (MOP) is introduced as Eq. 1 (Ying et al. 2017).

$$\begin{cases} \min F(v) = (f1(v), \ldots, fm(v))^T \\ Subject \quad to\ v \in \pi \end{cases} \tag{1}$$

where $\mathbf{v} \in \pi$ is the feasible search region and $\boldsymbol{v} = (v_1, v_2, \ldots, v_n)^T$ is the vector of decision factors.

F: $\Omega \rightarrow R^m$, m is the objective function number and R^m is the multi-dimensional space for objective.

By developing the multiobjective genetic algorithm (MOGA), Srinvas and coworkers proposed the non-dominated sorting genetic algorithm (NSGA) (Ying et al. 2017). The basis of this algorithm is based on the genetic algorithm, but the process way of the selection operator is different. The operators of mutation and cross-over remain unchanged. Later, Deb and coworkers developed the NSGA-II (Deb et al. 2002) as a fast non-dominated sorting method for ranking results in selection procedure. The NSGA-II was not very efficient for problems with many objectives, and consequently, a new version of NSGA called NSGA-III was developed (Deb and Jain 2014). Zhang and Li introduced multiobjective evolutionary algorithm based on decomposition (MOEA/D) in 2007 (Zhang and Li 2007). This technique degrades the multiobjective problem into several sub-problems which are optimized simultaneously through neighborhood scalar methods. In all the generations, the population for individual subproblem is composed of the best solution obtained relative to the starting point of the algorithm. The neighborhood relationships between the subproblems are established upon the basis of the intervals among the vectors of their collection coefficients. For two subproblems that are neighbors, the optimal solutions are similar. In MOEA/D method, the information obtained from all neighbor subproblems is used to optimize them. The process begins with a population comprising N generated random solutions and each particular solution is assigned to an individual. v^i is the solution of subproblem i. A weight vector range λ_i is stated as the T nearest weight vectors with λ_1, λ_2…, λ_N. B^i (T) is used to define the collection for the T indices of neighboring subproblems of item i. In the operation of recreation, two solutions are selected from the range of the subproblem i for reproducing an offspring using the operators of genetic algorithm. Next, the range of the subproblem i is renovated using the previous generated offspring. Finally, the optimal solutions for all subproblems are equal to the solutions in the population. The framework of MOEA/D is shown directly below (Ying et al. 2017).

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InPut:  N: size of population, T: range size.
        $N_r$: Maximal number of renovated subproblems.
        $B^i$ (T): The T indices collection of neighbor subproblems of item i
        $\delta$: Control parameter ·
        Termination condition.
Output: All solutions in population
Begin
    Initialization
        population P ←$\{v^i\}$. $wight\ vectors\ \Lambda \leftarrow \{\boldsymbol{\lambda_i}\}$.
        the ideal point $Z^* \leftarrow \{Z_i^*\}$ neighbor index collection $B^i\ (T)$.
        set $F^i = F\ \{v^i\}$ for i= 1, … , N.
    Update
    while the termination condition is not met do
        for each subproblem i= 1, …, N do
            determine the mating or update pool
            Set E ← $B^i\ (T)$. if rand ( ) ≤ $\delta$. Otherwise
             E ← $\{1.2.\cdots.N\}$
            recombination
            select two random index K, L from E
            Generate a new solution
             R ← recombination operators $\{v^k.v^t\}$
            Replacement of population
            Set C = 0.
            While C < $n_r$ and P $\neq \emptyset$ do
                pick Random index j from P
                P: = P \ $\{j\}$
                If y has a better collection function value than $v^j$
                for subproblem j
                Then
                c = c + 1
            end
        end
    end
    return population P= $\{v^1.\cdots.v^N\}$
End
```

Results and discussions

Optimization methods

The extraction solvent type

For studying the effect of extraction solvent type, several low density solvents such as cyclohexane, toluene, n-hexane, cyclohexanone, and xylene were investigated. Triplicate experiments of 10-mL sample were carried out under conditions of 300 μL ethanol, 100 μL extraction solvent, no salt addition, and pH 5.45. Figure 1a reveals that the maximum efficiency was acquired with xylene along with significant difference ($p < 0.05$, single factor ANOVA). Thus, xylene was chosen as the extraction solvent for further experiments.

The disperser solvent type

The disperser solvent type influences the viscosity of the solvent, generation of the droplet, and efficiency of the extraction. Methanol, ethanol, and acetone were studied as disperser solvents. As indicated in Fig. 1b, methanol gave the maximum efficiency with significant difference ($p < 0.05$, single factor ANOVA). Moreover, methanol had the minimum toxicity and price compared to others and consequently, was selected as the disperser solvent for the next experiments.

The time of extraction

The influence of time of extraction was investigated at the time intervals between 2 and 10 min. Figure 1c illustrates the percentage relative recovery of the extraction for Cu^{2+} and Cd^{2+} ions against the time of extraction. As can be seen in Fig. 1c, the extraction time of 6 min was chosen as the maximum extraction efficiency with significant difference ($p < 0.05$, one-way ANOVA).

Central composite design optimization

The CCD was utilized to optimize the extraction and disperser solvent volumes, solution pH, and salt addition of ST-DLLME for Cu^{2+} and Cd^{2+} ions from aqueous solutions. The quadratic response surface models were confirmed for parameters of regression by the analysis of variance (ANOVA) as shown in Table 1. Table 1 indicates the high *F* value and a low probability

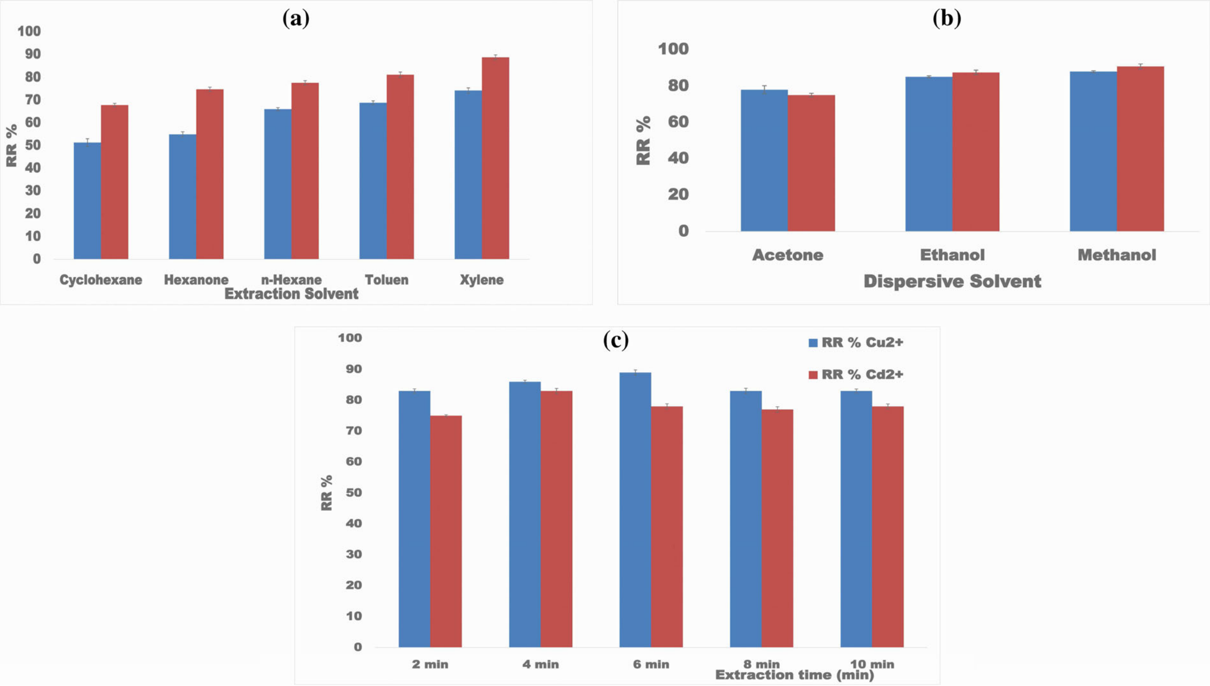

Fig. 1 Effect of **a** type of the extraction solvent, **b** type of the dispersive solvent, **c** the extraction time on the ST-DLLME efficiency

Table 1 The ANOVA of RSM quadratic model for Cu^{2+} and Cd^{2+} ions by ST-DLLME

Source	Sum of squares (Cu^{2+} and Cd^{2+})		*df*	Mean squares (Cu^{2+} and Cd^{2+})		*F* value (Cu^{2+} and Cd^{2+})		*P* value (Cu^{2+} and Cd^{2+})		Prob > *F*
Model	1518.00	1247.66	1	108.43	89.12	11.18	9.64	< 0.0001	< 0.0001	Significant
V_1-solvent extraction volume	325.09	315.67	1	325.09	315.67	33	34.14	< 0.0001	< 0.0001	
V_2-dispersive solvent volume	43.89	8.26	1	43.88	8.26	4.5	0.89	0.0504	0.3596	
V_3-pH	7.56	5.06	1	7.5	5.06	0.7	0.55	0.3912	0.4709	
V_4-salt addition	0.43	7.53	1	0.43	7.5	0.044	0.81	0.8362	0.3812	
V_1V_2	3.64	5.93	1	3.64	5.93	0.038	0.64	0.5494	0.5383	
V_1V_3	0.03	3.6	1	0.032	3.67	3.2×10^{-3}	0.4	09553	0.9553	
V_1V_4	0.052	0.35	1	0.052	0.35	5.3×10^{-3}	0.038	0.9427	0.6669	
V_2V_3	3.25	1.78	1	3.25	1.78	0.33	0.19	0.5713	0.9304	
V_2V_4	0.039	0.078	1	0.039	0.078	4.0×10^{-33}	7.8×10^{-3}	0.9503	0.6798	
V_3V_4	0.47	1.64	1	1.64	0.47	0.049	0.18	0.8283	0.3674	
V_1^2	929.90	887.97	1	929.90	887.98	95.88	96.03	< 0.0001	< 0.0001	
V_2^2	11.64	50.53	1	50.53	11.64	1.20	5.64	0.2906	0.0337	
V_3^2	46.81	29.58	1	46.81	29.58	4.84	3.20	0.0442	0.0939	
V_4^2	330.52	30.73	1	330.52	30.73	34.08	3.32	< 0.0001	0.0883	
Residual	145.48	138.70	15	9.70	9.25					
Lack of fit	123.58	113.98	10	12.31	11.40	2.75	2.31	0.1381	0.1845	Not significant
Pure error	22.40	24.72	5	4.48	4.94					
Cor total	1663.48	1386.36	29							

($p < 0.001$) for models, and consequently, the models were significant. According to the values of *p*, the V_1, V_1^2, V_3^2, and V_4^2 for Cu^{2+} and V_1, V_1^2, V_2^2, and V_4^2 for Cd^{2+} were significant. The rest of the variables and interactions were insignificant. The lack of fit for both metal ions was insignificant ($p > 0.05$). The coded quadratic equations based on the CCD analysis for Cu^{2+} and Cd^{2+} ions are given by Eqs. 2 and 3, respectively.

$$\begin{aligned} \mathrm{R} = {} & 94.56 + 3.67\mathrm{V}_1 + 0.97\mathrm{V}_2 + 0.55\mathrm{V}_3 - 0.31\mathrm{V}_4 \\ & + 0.6\mathrm{V}_1\mathrm{V}_2 + 0.37\mathrm{V1V3} - 0.28\mathrm{V}_2\mathrm{V}_3 - 0.33\mathrm{V}_3\mathrm{V}_4 \\ & + 6.93\mathrm{V}_1^2 - 1.75\mathrm{V}_2^2 - 1.75\mathrm{V}_3^2 - 1.32\mathrm{V}_4^2 \end{aligned} \tag{2}$$

$$\begin{aligned} \mathrm{R} = {} & 91.06 + 3.63\mathrm{V}_1 + 0.59\mathrm{V}_2 + 0.46\mathrm{V}_3 - 0.56\mathrm{V}_4 \\ & + 0.61\mathrm{V}_1\mathrm{V}_2 + 0.48\mathrm{V1V3} - 0.33\mathrm{V}_2\mathrm{V}_3 - 0.32\mathrm{V}_3\mathrm{V}_4 \\ & + -5.69\mathrm{V}_1^2 - 1.36\mathrm{V}_2^2 - 1.04\mathrm{V}_3^2 - 1.06\mathrm{V}_4^2 \end{aligned} \tag{3}$$

Based on the optimal conditions acquired from the CCD for multivariate optimization along with desirability of 0.96 (550 μL methanol, 250 μL xylene, 3.75% salt addition, and pH 6), the predicted response, experimental response, and absolute error were 96.31%, 95.11%, and 1.2 for Cu^{2+} and 94%, 93.5%, and 0.5 for Cd^{2+}, respectively.

ANN–MOEA/D optimization

MOEAD with the aid of artificial neural networks (ANN–MOEA/D) was utilized for optimizing the ST-DLLME of Cu^{2+} and Cd^{2+} ions according to the non-linear equations which were acquired from artificial neural networks. Figure 2 shows the structure of multilayer artificial neural networks with a population of four variables such as the volumes of disperser and extraction solvents, salt addition, and pH that outlined by the CCD. The values of bias and weight for each layer of ANN model were computed, and corresponding equations for Cu^{2+} and Cd^{2+} ions are obtained individually as Eq. 4.

$$\begin{aligned} & \mathit{Response} \\ & = \mathit{Pureline}(K_2 \times \tan\mathit{sig}(K_1 \times [V(1); V(2); V(3); V(4)] + \beta_1) + \beta_2) \end{aligned} \tag{4}$$

where β1 and K_1 are the bias and weight of middle layer with 10 neurons, respectively, and β2 and K_2 are the bias and weight of outer layer with one neuron, respectively. The initial factors like the volumes of disperser and extraction solvents, salt addition, and pH were indicated by *V* (1), *V* (2), *V* (3), and *V* (4), respectively.

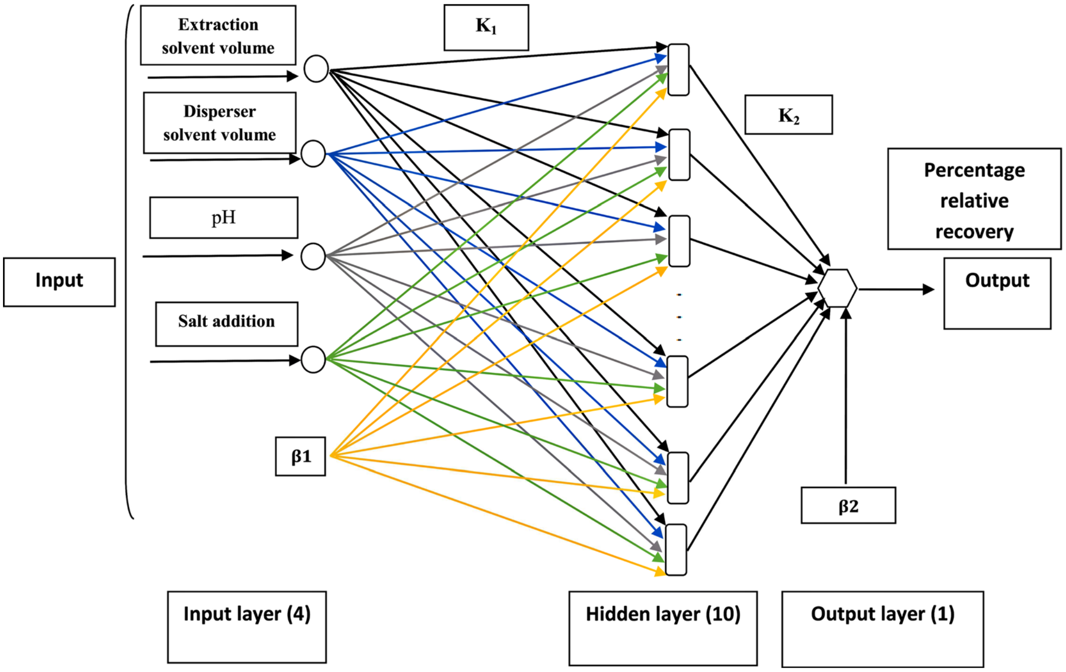

Fig. 2 The structure of three layer artificial neural networks

The weights and biases for Cu^{2+} and Cd^{2+} ions are presented in Table 2. These data were used to obtain an objective function for ANN–MOEA/D optimization technique with 100 maximum iteration number of iteration, subproblem number of 50, and neighbor number of 8. The pareto fronts of two objectives for NSGA (II), NSGA (III), and MOEA/D optimization methods of ST-DLLME for Cu^{2+} and Cd^{2+} ions are illustrated in Fig. 3. MOEA/D showed the best homogeneity and the highest extraction efficiency as stated in Fig. 3 and Table 3, respectively, and consequently, it was proved to be the best technique for optimization. Under the optimal conditions obtained by ANN-MOEA/D (extraction solvent volume 260 μL, disperser solvent volume 500 μL, pH 6, and salt addition 3%), the percentage relative recoveries of ST-DLLME method for Cu^{2+} and Cd^{2+} ions were 98.30 and 97.6%, respectively.

Table 2 The weight and bias of each artificial neural networks layer for Cu^{2+} and Cd^{2+} ions

K_1 (Cu^{2+} and Cd^{2+})								K_2^T (Cu_{2+} and Cd_{2+})		β_1 (Cu^{2+} and Cd^{2+})		β_2 (Cu^{2+} and Cd^{2+})	
− 1.038	0.082	1.627	− 1.550	− 0.571	− 2.008	− 0.652	1.166	− 0.430	− 0.622	2.474	2.552	− 1.060	− 0.484
− 1.489	0.648	0.762	− 1.742	1.603	− 0.960	0.833	1.241	1.695	− 1.627	1.627	− 0.367		
0.582	−0.095	− 0.045	− 2.472	− 0.633	− 1.836	− 1.991	− 2.472	− .0.387	0.235	1.658	− 1.721		
− 0.239	1.711	0.801	− 1.819	− 1.939	0.682	− 0.572	1.059	0.041	0.597	− 0.890	1.122		
− 1.326	0.467	1.212	− 1.749	0.460	− 1.355	1.636	– 1.838	0.193	0.395	0.105	− 0.771		
2.552	0.018	1.018	− 1.402	0.090	− 0.006	− 2.340	0.503	− 0.308	0.057	0.130	0.377		
1.031	1.795	− 1.153	− 0.257	− 1.304	1.158	1.008	– 0.762	0.098	− 0.470	0.546	1.401		
− 1.657	−0.422	0.647	2.262	0.850	1.043	2.958	− 0.380	− 0.224	0.229	− 1.229	0.595		
3.466	−0.119	0.261	0.339	3.428	3.428	0.620	− 0.103	0.991	0.698	1.745	1.906		
− 0.656	−2.031	1.082	0.6568	1.064	− 0.730	− 1.128	0.714	0.316	− 0.100	− 2.513	3.103		

k_1, the weight matrix of hidden layer (10 × 5); k_2, the weight vector of output layer (1 × 10); k_2^T, the matrix transpose of w_2, β_1, the bias vector of hidden layer (10 × 1); β_2, the scalar bias of output layer

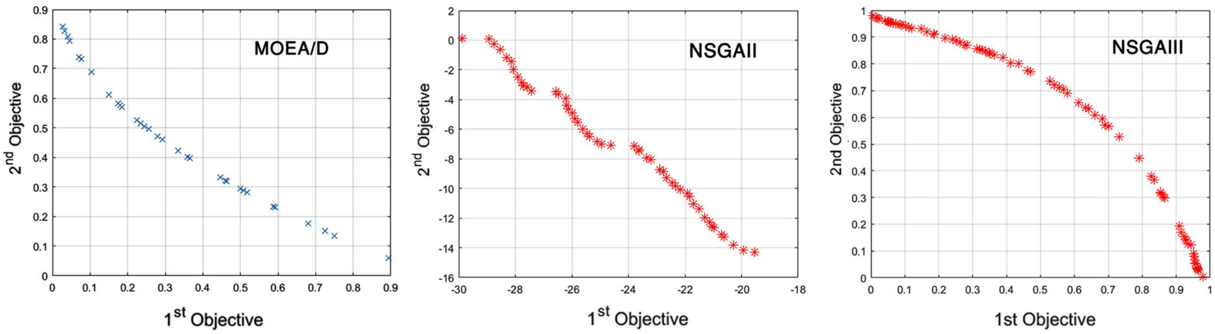

Fig. 3 The variation of pareto fronts of two objectives for MOEA/D, NSGA(II) and NSGA(III)

Figures of merit

In accordance with ANN-MOEAD optimal conditions, some important figures of merit in the ST-DLLME method such as determination (S/N = 10) and detection (S/N = 3) limits, regression line, linear range, and coefficient of determination (R^2) in spiked water samples were acquired and the results are indicated in Table 4.

Study of real samples

Several real samples such as apple juice, milk, tea drink, mineral water, river water, well water, and wastewater were studied to get microextraction efficiency and accuracy. To accomplish this purpose, the percentage relative recovery (R%) was calculated by the following equation:

$$R\% = \frac{C_{founded} - C_{real}}{C_{added}} \times 100 \qquad (5)$$

where C_{founded}, C_{real}, and C_{added} are the concentrations of analyte after addition of a known amount of standard in the real sample, the concentration of analyte in the real sample, and the concentration of known amount of standard which was spiked to the real sample, respectively (Rezaee et al. 2006). Real samples were tested individually with spiking levels of 50, 100, and 200 μg L^{-1} of Cu^{2+} and Cd^{2+} ions. As presented in Table 5, the mean percentage relative recoveries with three replicate experiments for each sample ranged from 94.6 to 105.1% for Cu^{2+} and 94.8 to 106.1% for Cd^{2+} which were in the acceptable range with standard deviations of 0.12 to 0.43 for Cu^{2+} and 0.10 to 0.61 for Cd^{2+} ions. Therefore, the suggested ST-DLLME method can be applied successfully for determination of the above heavy metal ions in real samples.

Comparison with other methods

As presented in Table 6, several pretreatment methods for Cd^{2+} and Cu^{2+} ions that included in the literatures were compared to the proposed ST-DLLME based on the figures of merit and type of optimization techniques. Among the data that are shown in Table 6, the proposed ST-DLLME method, in relation to other methods such as solid-phase extraction, flow injection analysis, and cloud point extraction (rows 1–5 of the Table 6), presents lower solvent and sample consumption, shorter extraction time, more suitable determination, and detection limits and linear range. Unlike DLLME method such as in situ DLLME using ionic liquid and

Table 3 Comparison of the ANN-MOEAD and other optimization methods for ST-DLLME of Cu^{2+} and Cd^{2+} ions

Method	Extraction solvent volume%	Disperser solvent volume %	pH	Salt addition	Percentage recovery (%)	
					Cu^{2+}	Cd^{2+}
ANN-MOEA/D	260	500	6	3	98.3	97.6
CCD	250	550	6	3.75	94.2	92.5
NSCA (II)	350	550	6	3.75	92.3	91.8
NSCA (III)	323.6	490	5.4	3	85.2	97.28

Table 4 Figures of merit of the ST-DLLME method for Cu^{2+} and Cd^{2+} ions under ANN-MOEA/D optimal conditions

Analyte	Regression line	R^2	LOD (S/N = 3, μg L^{-1})	LOQ (S/N = 10, μg L (	LDR (μg L^{-1})
Cu^{2+}	y = 0.0003x + 0.0030	0.9995	0.05	0.15	0.15–1000
Cd^{2+}	y = 0.0029x + 0.0032	0.9992	0.07	0.21	0.21–750

Extraction conditions: extraction solvent and its volume, xylene 250 μL, dispersive solvent and its volume, 550 μL methanol, pH, 6, extraction time, 6 min and 3.75% salt addition–R^2 determination coefficient, *LOD* limit of determination, *LOQ* limit of quantitation, *LDR* linear dynamic range

conventional DLLME (rows 6 and 7 of the Table 6), in the ST-DLLME method, there is no need for centrifugation step for phase separation, and consequently, the extraction time is much shorter. In addition, there are other advantages using ST-DLLME method; namely rapidity, simple processing, and lower cost of operation. One factor at a time (OFAT) method was employed in the most comparable methods presented in Table 6 (rows 1–5 and 7). In the case of interaction between some variables, OFAT method cannot provide the correct optimal conditions. Chemometric optimization methods such as metaheuristic algorithm and experimental design can be used successfully for solving these difficulties. As compared to other methods except the method in row 6 of Table 6, the proposed method showed the suitable potential of ANN–MOEA/D and CCD as multivariate methods to find the optimal conditions.

Table 5 Percentage relative recoveries for Cu^{2+} and Cd^{2+} ions in the spiked real samples

Sample	Initial concentration (μg L^{-1})	Spiking (μg L^{-1}) (Cu^{2+} and Cd^{2+})	Found (μg L^{-1}), means ± 3 s (*N* = 3) (Cu^{2+} and Cd^{2+})		Relative recovery (%)(Cu^{2+} and Cd^{2+})	
Mineral water	N.D	50	48.8 ± 0.14	48.9 ± 0.14	97.60	98.70
Mineral water	N.D	100	99.8 ± 0.12	99.9 ± 0.18	98.80	99.90
Mineral water	N.D	200	202.4 ± 0.43	202.8 ± 0.13	101.20	101.40
River water	N.D	50	48.3 ± 0.15	49.6 ± 0.14	96.60	99.20
River water	N.D	100	97.4 ± 0.12	98.4 ± 0.17	97.40	98.40
River water	N.D	200	198.3 ± 0.16	197.3 ± 0.19	99.10	98.65
Well water	4	50	51.9 ± 0.14	51.7 ± 0.11	95.80	95.40
Well water	4	100	103.3 ± 0.16	102.2 ± 0.11	99.30	98.20
Well water	4	200	213.7 ± 0.23	211.7 ± 0.24	104.85	103.55
Wastewater	7	50	54.3 ± 0.56	54.4 ± 0.12	94.60	94.80
Wastewater	7	100	102.3 ± 0.21	102.5 ± 0.41	95.30	95.50
Wastewater	7	200	215.1 ± 0.15	217.1 ± 0.33	104.05	105.05
Milk	N.D	50	48.7 ± 0.13	47.9 ± 0.10	97.40	95.80
Milk	N.D	100	97.7 ± 0.15	97.2 ± 0.19	97.70	97.20
Milk	N.D	200	212.2 ± 0.26	209.1 ± 0.21	106.10	104.55
Tea	N.D	50	47.6 ± 0.26	47.6 ± 0.19	95.20	95.20
Tea	N.D	100	97.1 ± 0.28	96.3 ± 0.17	97.10	96.30
Tea	N.D	200	197.8 ± 0.21	197.9 ± 0.32	98.80	98.95
Apple juice	N.D	50	48.6 ± 0.11	47.7 ± 0.12	97.20	95.40
Apple juice	N.D	100	99.1 ± 0.21	97.6 ± 0.61	99.10	97.60
Apple juice	N.D	200	196.3 ± 0.39	196.1 ± 0.12	98.15	98.05

Extraction conditions: extraction solvent and its volume, xylene, 260 μL, dispersive solvent and its volume, methanol, 500 μL, pH, 6, extraction time, 6 min and 3.75% salt addition

S standard deviation (*n* = 3), *N.D* not detected

Table 6 Comparison of characteristic data for ST-DLLME of Cu^{2+} and Cd^{2+} ions and other methods

Method	Sample type	Optimization method	LOD (Cu^{2+} and Cd^{2+} μg L^{-1})	LOQ (Cu^{2+} and Cd^{2+} μg L^{-1})	RSD (Cu^{2+} and Cd^{2+}%)	Sample volume (mL) - organic solvent volume (μL)	Extraction time (min)	LDR (Cu^{2+} and Cd^{2+} μg L^{-1})	Reference
[a]SPE using [b]Tw and FAAS	Tobacco and water sample	[l]OVAT	(0.4 and 0.2)	(2 and 1)	(1.9 and 2.1)	(50 mL and 5000 μL)	4	(2–900 and 1–400)	(Mohammadi et al. 2016)
[c]FI using [d]Am XAD-4 and FAAS	Food and water samples	OVAT	(0.35 and 0.14)	(2 and 1)	–	(10 mL and 6700 μL)	–	(2–8 and 1–4)	(Karadaş and Kara 2013)
[e]CPE using [f]PAR and [g]ICP-OES	Water samples	OVAT	(1.2 and 1.0)	(10 and 20)	(1.3 and 1.9)	(15 mL and 1500 μL)	50	(10–500 and 20–2000)	(Silva et al. 2009)
[h]Nano-TiO2-MBT and FAAS	Water and ore samples	OVAT	(0.12 and 0.15)	(0.2 and 0.2)	(4.63 and 3.54)	(250 mL and 3000 μL)	10	(0.2–20 and 0.2–25)	(Pourreza et al. 2014)
[i]CAF-SPE using ZrO_2/B_2O_3 and FAAS	Tea and tap water	OVAT	(3.3.1)	(11 and 10.3)	(1.9 and 4.3)	(50 mL and 10,000 μL)	5	(11–5000 and 11.3–3000)	(Yalçınkaya et al. 2011)
In-situ DLLME using [j]CC10164Im-Br and FAAS	Water samples	[m]DED	(0.3 and 0.5)	(0.9 and 3.5)	(4.5 and 7)	(10 mL and 25 mg)	–	(1–150 and 2–100)	(Khiat et al. 2018)
DLLME using [k]HBDAP and FAAS	Water and tea	OVAT	(1.98 and 0.69)	–	–	(10 mL and 50 μL)	10	–	(Arslan et al. 2016)
ST-DLLME and FAAS (This work)	Water and food sample	[n]ANN–MOEA/D and [o]CCD	(0.05 and 0.07)	(0.15 and 0.21)	(2.2 and 2.6)	(10 mL-260 μL)	6	(0.05–1000 and 0.07–750)	This work

[a] Solid-phase extraction

[b] Tween 80

[c] Flow injection

[d] Amberlite XAD-4

[e] Cloud point extraction

[f] 4-(2-pyridylazo)-resorcinol

[g] Inductively coupled plasma optic emission spectrometry

[h] Nano-TiO_2 modified with 2-mercaptobenzothiazole

[i] Chelating agent free-solid phase extraction

[j] Decyl-guanidinium chloride

[k] N,N′-bis(2-hydroxy-5-bromo-benzyl)1,2 diaminopropane

[l] One variable at a time

[m] Dohlert experimental

[n] Multiobjective evolutionary algorithm based on decomposition with the aid of artificial neural networks

[o] Central composite design

Conclusions

The presented ST-DLLME method for simultaneous extraction of Cu^{2+} and Cd^{2+} ions can be regarded as a safe method due to a very low consumption of hazardous solvents (260 μL) and low volume of sample (10 mL) with suitable figures of merit and acceptable percentage relative recoveries. In addition, the proposed method was performed with uncomplicated equipment and lower solvent volume in a shorter time along with a powerful multiobjective optimization algorithm. Thus, the introduced ST-DLLME method can be recommended as an inexpensive, highly accurate, and fast method for simultaneous analysis of Cu^{2+} and Cd^{2+} ions in various laboratories.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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