Mostafa Khajeh*, Shahnaz Afzali Moghaddam, Mousa Bohlooli and Mansour Ghaffari-Moghaddam

Application of the artificial neural network and imperialist competitive algorithm for optimization of molecularly imprinted solid phase extraction of methylene blue

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Abstract: In this study, a hybrid of the artificial neural network-imperialist competitive algorithm (ANN-ICA) has been applied for prediction and optimization of the molecularly imprinted solid phase extraction method. This method has been used for the pre-concentration of methylene blue (MB) from environmental water samples prior to UV-Vis spectrophotometry. Molecular imprinted polymer sorbents were synthesized using radical polymerization by MB, 4-vinylpyridine, ethylene-glycol-dimethacrylate, 2,2′-azobisisobutyronitrile and methanol as a template, functional monomer, cross-linker, initiator, and porogen, respectively. The imprinted polymer was characterized by Fourier transform infrared spectroscopy and scanning electron microscopy. The pH, adsorbent mass, adsorption time, eluent volume, and extraction time were been selected as input parameters and the recovery of MB was considered as an output variable of the ANN model. The results were then compared according to the performance function and determination coefficient. The Freundlich and Langmuir adsorption models were used to explain the isotherm constant. The maximum adsorption capacity was 417 mg g^{-1}. At the optimized conditions, the limit of detection and relative standard deviation was found to be 0.31 μg l^{-1} and <1.7%, respectively. This method was applied to analysis the MB in various water samples.

Keywords: artificial neural network; imperialist competitive algorithm; methylene blue; molecularly imprinted polymer; water samples.

***Corresponding author: Mostafa Khajeh,** Department of Chemistry, University of Zabol, Zabol, Iran, Fax: +98-543-2226765, e-mail: m_khajeh@uoz.ac.ir
Shahnaz Afzali Moghaddam and Mansour Ghaffari-Moghaddam: Department of Chemistry, University of Zabol, Zabol, Iran
Mousa Bohlooli: Department of Biology, University of Zabol, Zabol, Iran

1 Introduction

The large amount of emission of dyes in natural water along with bleaches or organics affects the physicochemical characteristics of water samples. The frequent change in the dyes significantly changes their properties in wastewater, particularly COD, pH and color. Methylene blue (MB) is a cationic dye which is applied for dying wood, silk and cotton. Dyes such as MB can cause serious damage to humans including in the brain, liver, central nervous system, and dysfunction of kidneys and are also characterized as carcinogenic. Thereby, it is important to remove dyes (i.e. MB) from water samples before disposal to the environment (1–4).

The molecular imprinted polymer (MIP) is a suitable technique for the selective separation, preconcentration and clean-up of different types of organic and inorganic analytes in complex matrices such as biological and environmental samples (5). MIP is synthesized using the functional monomer and cross-linker agent copolymerization with a template analytes, resulting in extremely cross-linked three dimensional networks (5–7). After desorption of the template analyte by solvent, three-dimensional cavities whose functionality, size, shape, and spatial arrangement of functional groups are complimentary to the template analyte are generated (8). Because of more selective affinity for target compounds, MIP-solid phase extraction has been used increasingly for the selective adsorption and cleaning of various types of analytes from environmental and biological complex samples, compared to traditional solid phase extraction sorbents (9).

The artificial neural network (ANN) model is a soft-computing procedure for data fitting, classification, recognizing of the model and output prediction through a complex matrix. The essential element of ANN is producing new structures for data analyses process. ANN consists of different analyses components, called neurons, to solve problems (10–12). ANN has been applied in several works.

For example, Adabi et al. (13) prepared electrospun carbon nanofibers (CNF) and investigated the effective parameters for predicting the cathodic current in CNF electrodes via ANN (14). The prediction of nanofibers diameters was also evaluated by ANN in several studies (15, 16). The size and toxicity of chitosan/streptokinase nanoparticles was predicted using ANN (17).

Atashpaz-Gargari and Lucas suggested an algorithm according to a sociopolitical phenomenon famous as the imperialist competitive algorithm (ICA). It can be found for global optimization, even when faced with problem nonlinear optimization, in addition to its rapid convergence (11).

The aims of this study are as follows: (i) MIP is used as an adsorbent for the extraction of MB in a simple and fast method, (ii) the ANN model is applied for predicting the extraction recovery of MB, (iii) the optimization of the extraction recovery of MB is done by ICA, and finally (iv), UV-Vis spectrophotometry is applied for determination of MB from water samples. To the best of our knowledge, this is the first report to use the hybrid of ANN-ICA in this field.

2 Materials and methods

2.1 Reagents and samples

Methylene blue and all HPLC grade solvents such as acetic acid, methanol were obtained from Merck (Darmstadt, Germany). 4-Vinylpyridine (VP), ethyleneglycoldimethacrylate (EGDMA) and 2,2′-azobisisobutyronitrile (AIBN) were purchased from Aldrich (Milwaukee, WI, USA). A stock standard solution of MB was prepared by dissolving suitable amount of MB in double distilled water. Daily solutions were obtained from the stock standard solution by diluting with double distilled water.

2.2 Apparatus

All experiments were carried out using a UV-Vis (UV-2100 RAY Leigh, Beijing, China) by measuring the change of absorbance at λ_{max} of 470 nm. All tests were done three times and average values were applied for the optimization. For determination of pH a model 630 Metrohm pH meter was used. The scanning electron microscopy (SEM) was performed by gently distributing the powder sample on the stainless steel stubs using SEM (Hitachi S4160, Japan) instrument.

2.3 Synthesis of MB imprinted polymers

MIP was synthesized with the functional monomer VP, EGDMA as the cross-linker, methanol as the perogen and MB (template), and in its absence template for the non-imprinted polymer (NIP) (Figure 1) as follows: 1 mmol of MB, 4 mmol of VP, and 20 mmol of EGDMA were dissolved in 12 ml of methanol. Then, 50 mg of AIBN as the

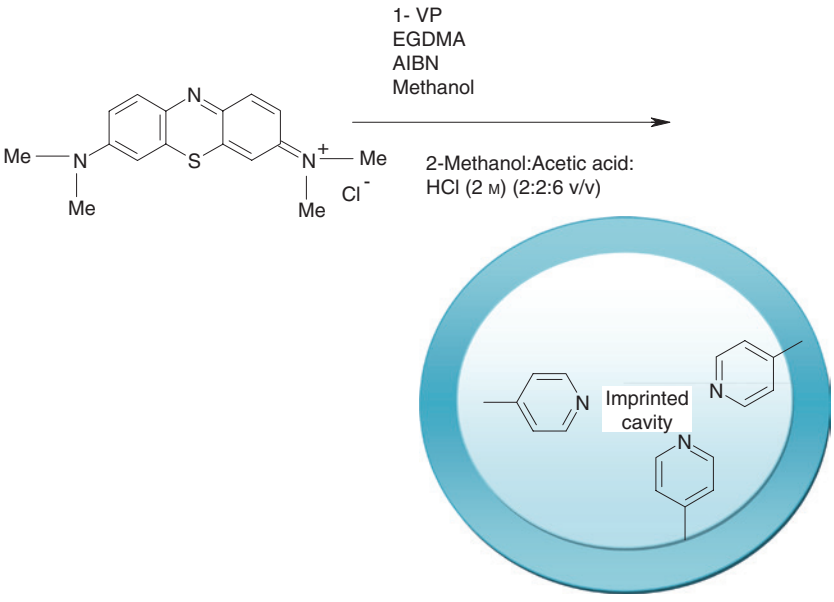

Figure 1: Representative scheme for the MIP.

initiator was added to the reaction mixture. Afterward, the mixture was stirred under a nitrogen atmosphere for 7 min for deoxygenated of mixture. The tube was sealed in a vacuum. The polymerization was done in the water bath at 60°C for a 7 h. The polymer was then suspended in methanol to remove the residual and then crushed and ground. The polymer particles were washed in a soxhlet extractor with methanol/acetic acid/HCl solution (2:2:6 v/v), until no MB template was detected by UV-Vis spectrophotometer analysis of the washing solvent. Finally, MIP was washed with methanol to remove the residual of acetic acid and HCl and then dried under vacuum at 60°C. The NIP was also synthesized by the same method but without a template.

The MB binding of the MIP and NIP were evaluated and the formulation was optimized to the ideal molar ratio of the cross-linker, functional monomer, and template. Table 1 represents the functional monomer, cross-linker agent, template and initiator with the amounts used for each step. Imprinting factor (IF) represents amounts of MB adsorbed by MIP/amount of MB adsorbed by NIP. The results showed that in MIP 8, high IF was obtained. Also, the adsorbing strength of MIP was higher from NIP.

2.4 Procedure

The batch solid-phase extraction (SPE) method was applied to assess the MIP binding affinity. The technique for extraction of MB was as follows: the suitable amount of MIP particles was poured into water solution containing 0.5 mg l^{-1} of MB and the pH of solution was adjusted by drop-wise addition of 1 mol l^{-1} NaOH and HCl. Then, the aqueous phase was shaken for an appropriate time. Finally, the adsorbed MB with MIP particles was desorbed by treatment with acetonitrile, and the extraction recovery was calculated. When the MB was added to the sample solution containing polymer adsorbent, the interaction between MB and VP as functional monomer (Figure 1) can occur. After that, the eluent can cause the binding between MB and polymer to break.

Adsorption equilibrium was studied at optimum conditions using a constant MIP adsorbent weight (0.1 g) and contact time of 10 min at pH 8.0. The initial concentration was in the range of 1–100 mg l^{-1}.

The adsorption capacity (q_e) of the MIP adsorbent was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad [1]$$

where C_0, and C_e (mg l^{-1}) are the concentration of the MB in the initial solution and in the equilibrium, respectively. m is the MIP adsorbent mass (g) and V is the sample volume (L).

Table 1: Optimization of polymer composition with respect imprinting factor.

Sorbent	MB (mmol)	VP (mmol)	EGDMA (mmol)	AIBN (mg)	Imprinting factor (IF)[a]
MIP 1	1	1	10	50	2.1
MIP 2	1	1	20	50	2.9
MIP 3	1	2	10	50	3.7
MIP 4	1	2	20	50	4.5
MIP 5	1	3	10	50	6.2
MIP 6	1	3	20	50	7.5
MIP 7	1	4	10	50	10.6
MIP 8	1	4	20	50	14.9

[a]IF represents "amounts of MB adsorbed by MIP/amount of MB adsorbed by NIP".

2.5 Artificial neural network

The neurons and hidden layer number in the ANN depends on the problem complexity. Each neuron in the hidden layer is linked to the output and input layers with a corresponding weight. The net inputs for each neuron are multiplied by its connection weights and then summed up together with the bias. Then, the sum is processed by a transfer function like the hyperbolic tangent sigmoid (*tansig*). This matrix is subjected to the layer weight and bias between hidden and output layers. The result is used for the linear transfer function (*purelin*) to produce an output. The general neural network (NN) architecture used is renowned as the feed forward neural network (FFNN). The FFNN is a network structure in which the signals propagate or information in one direction, only, from input layer to output layer. A three layer FFNN by a back-propagation (BP) algorithm is able of approximate any given continuous non-linear function with an arbitrary precision. In the BP algorithm, neurons are organized in the layers, and send their signals to the "forward", and then the errors are propagated in the backward. The training process of the BP procedure provides a number of inputs and outputs and the network predicts the outputs on the initial random weights. Then, the mean squared error (MSE) between the experimental and obtained data by ANN is obtained. The weights are continuously modified during the training process until the MSE among the experimental and the predicted output is minimized. The MSE is defined as follows:

$$\mathrm{MSE} = \frac{\sum_{i=1}^{N} (Y_t - Y_N)^2}{N} \quad [2]$$

where Y_t, Y_N are the target and predicted output and N is the number of data.

When the MSE come close to zero, the absolute error of the NN is reduced. There are numerous BP algorithm variations for training a NN. Throughout the training process, the weights and biases are frequently updated with the Levenberg-Marquardt (LM) technique until convergence value to the determined is obtained.

Before starting the modeling step all the input and the output experimental data were normalized because of avoid any false effect of parameters with higher magnitude orders. Normalization of data in the range of [0–1] was performed using as the following equation:

$$x_{norm} = \frac{(x - x_{min})}{(x_{max} - x_{min})} \quad [3]$$

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

2.6 Imperialistic competitive algorithm

The imperialistic competitive algorithm (ICA) is a novel meta-heuristic algorithm which is considered as socio-politically motivated. This meta-heuristic algorithm was derived from the colonial phenomenon in history and human society (10–12).

The algorithm starts with a randomly produced initial population which are called countries. Certain of these countries are chosen as the imperialist and others which are colonized by the imperialists collectively make an empire (10–12).

For optimization of a problem with size of N, an individual country is determined by $1 \times N$ array as follows:

$$\text{Country} = [P_1, P_2, P_3, \ldots, P_{N_{variable}}] \quad [4]$$

The cost is considered as the following equation:

$$\text{Cost } t_i = f(\text{country}) = f(P_1, P_2, P_3, \ldots, P_{N_{variable}}) \quad [5]$$

Among these N countries, N_{imp} with the least costs are considered as the imperialists. For colonization of the countries in proportion with imperialists' power, the normalized cost of an imperialist is characterized as follows:

$$C_n = \max_i\{c_i\} - c_n \quad [6]$$

where C_n, $\max_i\{c_i\}$ and c_n are the cost of nth imperialist, the highest cost among imperialists and the normalized cost of imperialists, respectively. Therefore, the imperialist with the highest cost (weakest imperialist) denotes lower normalized cost. The normalized power (P_n) of each imperialist is calculated according to its normalized cost function as follows:

$$P_n = \left| \frac{C_i}{\sum_{i=1}^{N_{imperialist}} C_i} \right| \quad [7]$$

The number of initial colonies for each empire is determined as follows:

$$N \cdot C_{.n} = \text{round}\{P_n \cdot N_{col}\} \quad [8]$$

where $N \cdot C_{.n}$, N_{col} and round are the number of occupied colonies by the Nth empire, the total number of initial colonies and a function to denote round numbers, respectively.

The next step is assimilation which all colonies will move toward the position of the imperialist with x units via the following equation:

$$x \sim U(0, \beta \times d) \quad [9]$$

where x is a random variable with uniform distribution, β is a number >1, and d is the distance between a colony and an imperialist.

The next step is revolution which certain colonies are randomly chosen out and replaced with new generated countries. The sudden change was simulated by this process in the socio-political characteristics of a colony in a realistic society. In the procedure of revolution and assimilation, if a colony becomes better than the imperialist, the colony and the imperialist will exchange their roles.

The core of the ICA is characterized by the competitive behavior between the empires. In this phase, all empires attempt to occupy colonies from others. The total cost of every empire is first determined and normalized based on the following equations:

$$TC_n = \text{Cost}(\text{imperialist}_n) + \xi\, \text{mean}\{\text{Cost}(\text{colonies of impire}_n)\} \quad [10]$$

$$NTC_n = TC_n - \max_i\{TC_i\} \quad [11]$$

where TC_n is the total cost of the nth empire, and ξ is a positive number which is considered to be <1. The NTC_n represents the total normalized cost of nth empire (10–12).

3 Results and discussion

3.1 Characterization studies

The FT-IR spectra of leached and unleached MB MIP were obtained by KBr pellet technique (Figure 2). There were

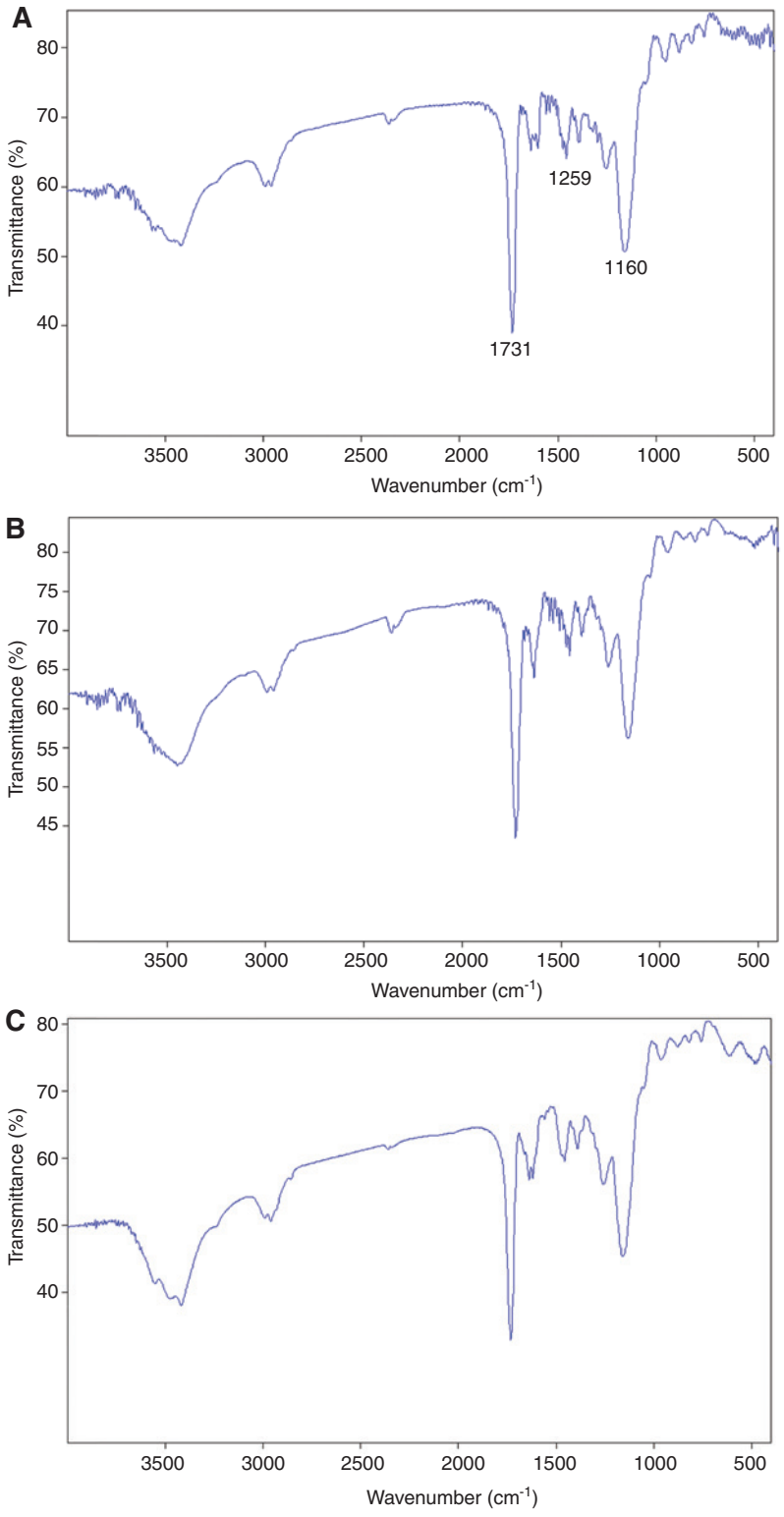

Figure 2: FT-IR spectra of unleached (A), leached (B) and NIP (C).

not any peak in the range of 1648–1638 cm^{-1} which indicates the vinyl groups in MIP does not exist. This phenomenon shows the complete vinyl pyridine polymerization. The morphology of the MIP was characterized by SEM (Figure 3). According to the Figure 3, the particle size of synthesized MIP was ranging between 100 and 180 nm. These results show that the MB-MIP was successfully synthesized. The MB-MIP can be used as a selective solid

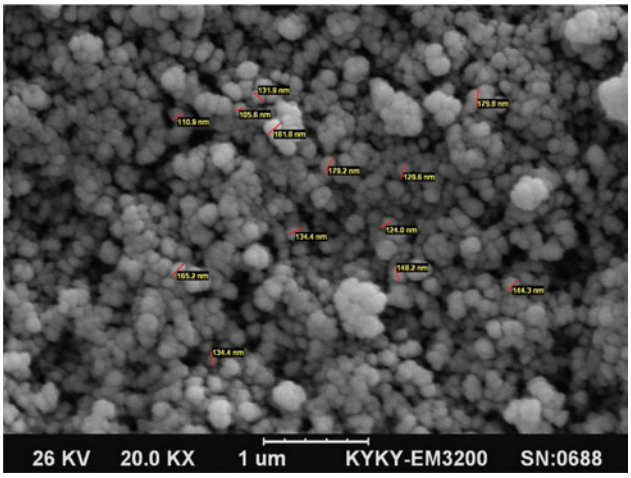

Figure 3: The image of SEM of imprinted polymer.

phase adsorbent for extraction of trace amounts of MB from sample solution.

3.2 Optimization of MIP

3.2.1 Predictive modeling with ANN

In this study, several variables such as pH, adsorbent mass, adsorption time, eluent volume, and extraction time were selected as inputs. Table 2 indicates these variables and extraction recovery as output.

The data in this work were divided into three sets: testing, training, and validation. During the training dataset, the aim is to obtain a weights optimum set. The validation dataset is applied to minimize the over-fitting. The testing data is used only in order to test the final solution to show the real predictive ANN power. Here, the totals of 53 experimental data were divided into three subsets randomly: 70, 15 and 15%, for the training, validation and testing, respectively.

The number of neurons (node) in the input layer and the output is identical to the input and the output number, respectively (5 and 1). The optimal design of the NN is obtained by a trial-and-error process during choice the number of node in hidden layer (HL). The numbers HL neurons are obtained by an optimization process that minimizes some error indexes. The HL node in the large excess may result in over-fitting, while a low HL node number can result in an NN not capable of getting to the desired error. In this study, the neurons number in the HL has been calculated during minimizing MSE, determination coefficient (R^2) and average absolute relative deviation percent (AARD%). The AARD% and R^2 were calculated as follows:

$$\text{AARD\%} = \left(\frac{\sum_{i=1}^{n} \left(\frac{|y_{i,\text{exp}} - y_{i,\text{cal}}|}{y_{i,\text{exp}}} \right)}{N} \times 100 \right) \quad [12]$$

$$R^2 = \frac{\sum_{i=1}^{N} (y_{i,\text{exp}} - \bar{y})^2 - \sum_{i=1}^{N} (y_{i,\text{exp}} - y_{i,\text{cal}})^2}{\sum_{i=1}^{N} (y_{i,\text{exp}} - \bar{y})^2} \quad [13]$$

where $Y_{i,exp}$ is the actual extraction recovery, $Y_{i,cal}$ is the predicted extraction recovery, $\bar{y}$ is the average value of the actual extraction recovery data and N is the number of data.

The optimal topology was obtained as follows: input layer: one hidden layer: output layer (5:10:1). Figure 4 shows the ANN optimal topology. The MSE, AARD%, and R^2 for all, training, testing, and validation data are presented in Table 3. These data indicate a good agreement among actual and predicted data with this model. Figure 5 shows the MSE variation through training by the Levenberg-Marquardt (LM) algorithm. This figure illustrates that the MSE values converged to approximately 1×10^{-4} in six iterations. Therefore, the training process of ANN has been considered as acceptably terminated. Figure 6 indicates the actual data versus predicted data obtained by the ANN model. This figure shows a good fit between the input and output data obtained by the ANN model.

The relative contribution of independent input parameters is calculated using the connection weight method (18), as follows:

$$V = \frac{\sum_{j=1}^{h} \left[\left(\frac{|IW_{ij}|}{\sum_{k=1}^{m} |IW_{kj}|} \right) |LW_j| \right]}{\sum_{i=1}^{m} \left\{ \sum_{j=1}^{h} \left[\left(\frac{|IW_{ij}|}{\sum_{k=1}^{m} |IW_{kj}|} \right) LW_j \right] \right\}} \quad [14]$$

where, m and h were the numbers of neuron in the input and HL, respectively, V is the relative influence of the input parameter I.

The relative contribution of each of the input parameters is shown in Figure 7 based on this equation. This figure indicates the pH had significant influence on the extraction of MB.

3.2.2 ICA

The ICA method has been developed in the optimization of the input space of the ANN technique with goal of maximizing of the extraction recovery of MB. The ICA

Table 2: Experimental data was used for ANN modeling.

No.	pH	Adsorbent mass (g)	Adsorption time (min)	Eluent volume (ml)	Extraction time (min)	Experimental R%	Predicted R%
Training							
1	4	0.05	20	2	20	27.4	27
2	11	0.05	20	2	20	70.8	72.2
3	11	0.1	20	2	20	96.4	96.6
4	7.5	0.075	5	1	20	49.5	49
5	7.5	0.075	35	1	20	54.3	56.2
6	7.5	0.075	5	3	20	49.8	48.3
7	7.5	0.075	35	3	20	57.1	57.7
8	7.5	0.1	20	2	5	47.5	47.9
9	7.5	0.05	20	2	35	40	40.1
10	7.5	0.1	20	2	35	57.8	58.2
11	4	0.075	35	2	20	34.3	34.4
12	11	0.075	35	2	20	91.1	91.4
13	7.5	0.075	20	1	5	42.5	43.6
14	7.5	0.075	20	3	5	43.4	43.7
15	7.5	0.075	20	1	35	51.2	51.3
16	7.5	0.075	20	3	35	53.4	52.8
17	7.5	0.05	5	2	20	34.5	33.3
18	7.5	0.1	35	2	20	57.4	57.8
19	4	0.075	20	1	20	31.5	31.5
20	11	0.075	20	1	20	88.7	89.2
21	11	0.075	20	3	20	85.2	85.6
22	7.5	0.075	5	2	5	47.1	46.9
23	7.5	0.075	35	2	5	36.4	37.6
24	7.5	0.075	35	2	35	62.4	63.2
25	4	0.075	20	2	5	30.4	30.4
26	11	0.075	20	2	5	69.5	70.3
27	4	0.075	20	2	35	26.6	26.6
28	11	0.075	20	2	35	91.9	92.1
29	7.5	0.05	20	1	20	42.2	42.6
30	7.5	0.05	20	3	20	42	42.1
31	6	0.03	15	1.5	15	22	22
32	6	0.125	25	1.5	25	50	50.2
33	6	0.125	25	2.5	15	48	47.9
34	9	0.03	25	1.5	25	55	56.2
35	9	0.03	15	2.5	25	60	59.9
36	9	0.125	15	2.5	15	72	71.9
37	9	0.125	15	1.5	25	76	75
Validation							
1	4	0.075	5	2	20	27.9	27.9
2	11	0.075	5	2	20	80.4	80.5
3	7.5	0.05	35	2	20	47.3	48.7
4	4	0.075	20	3	20	38.1	36.4
5	7.5	0.1	20	3	20	60.6	59.2
6	6	0.03	15	1.5	15	22	22
7	6	0.125	15	2.5	25	44	44.9
8	9	0.125	25	1.5	15	75	75.7
Testing							
1	4	0.1	20	2	20	35.4	35.1
2	7.5	0.05	20	2	5	31.7	31.7
3	7.5	0.1	5	2	20	52	52
4	7.5	0.075	5	2	35	39.7	38
5	7.5	0.1	20	1	20	57.3	60
6	7.5	0.075	20	2	20	53.1	53.2
7	6	0.03	25	2.5	25	36	36
8	9	0.03	25	2.5	15	50.2	50.2

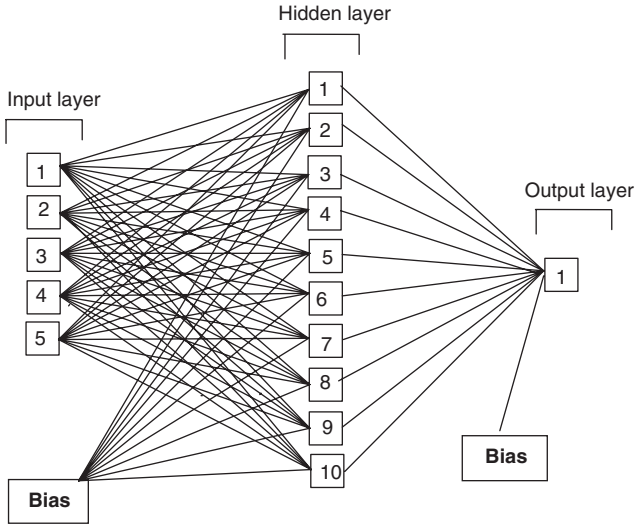

Figure 4: Optimal ANN structure.

Table 3: Statistical criteria for evaluation of ANN model.

Criterion	All	Train	Validation	Test
MSE	0.0001	0.0001	0.0002	0.0003
AARD%	1.11	0.98	1.6	1.25
R^2	0.998	0.999	0.998	0.991

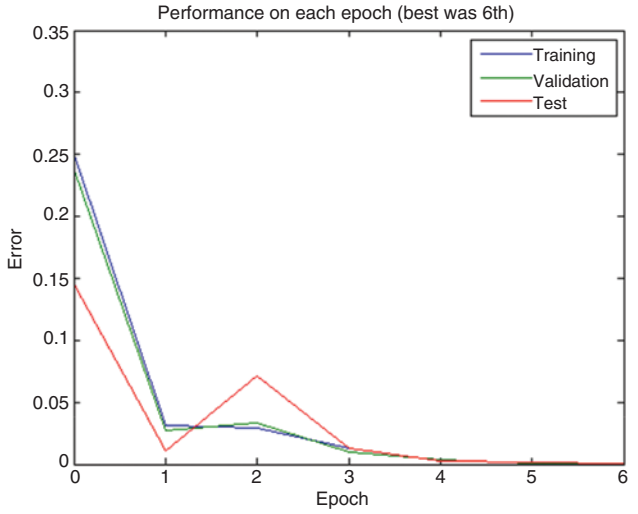

Figure 5: Training, validation and testing mean squared errors for the LM algorithm.

parameters are used in this study as follows: population size=30; number of iterations=10; number of imperialists=8; mutation rate=0.3 and moving coefficient=2. The optimized conditions were: pH 11, mass of adsorbent 0.11 g, adsorption time 29.5 min, eluent volume 2.5 ml and extraction time 35 min. The predictive of extraction recovery was

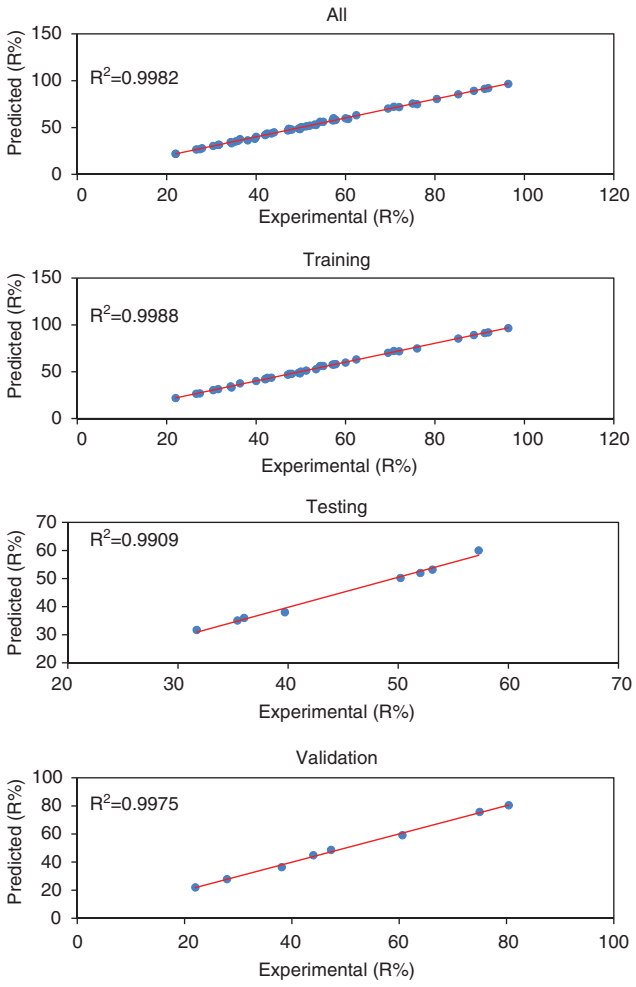

Figure 6: Predicted values by ANN versus experimental values for MB.

101.8, while the error between actual and predicted data was 1.6%. This confirmed the validity of the ANN model.

According to Figure 7, pH is a significant factor. MB is a cationic compound which is in environmental water samples in the form of positively-charged-ions (3). MB as a charged ion, when adsorbed onto the MIP surface is mainly affected using the MIP surface charge, which in turn is affected by the pH of the solution. The pH was investigated in the range between 4 and 11. According to ICA results, at pH 11 the extraction recovery is high. At lower pH, perhaps a protonation of the MIP surface could also happen. Therefore, a repulsion force happens among the MB cations and the MIP. So, at lower pH, the extraction recovery is low. At pH 11 the extraction recovery is high.

Another important parameter is the amount of polymer which determines the extraction efficiency of MB. In this study, different amounts of imprinted polymer (0.03–0.125 g) were added to the sample solution. Based on the obtained results, when the mass of the adsorbent

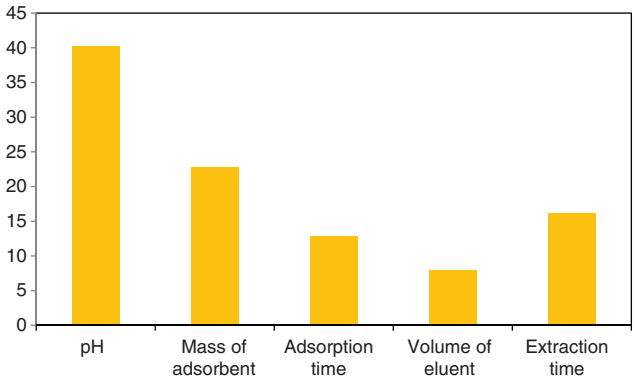

Figure 7: The relative effects of input variables on output factor.

increases the extraction efficiency of MB was increased. This can be explained that the higher adsorption sites with the mass of polymer available. The best extraction recovery was obtained when the mass of adsorbent was higher than 0.11 g.

Also, the adsorption time, eluent volume and extraction time were investigated and optimized. According to Figure 7, these variables have little effect on the extraction recovery.

3.3 Adsorption isotherms

The Freundlich and Langmuir isotherms (19) models were applied to show the adsorption of MB from aqueous samples. The following equation was used for the Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{C_e}{q_m} \quad [15]$$

where q_m (mg g^{-1}) and K (l mg^{-1}) are constants related to the maximum adsorption capacity and the relative adsorption energy, respectively.

The Freundlich model is obtained as follows:

$$\text{Ln } q_e = \ln K_F + \frac{1}{n} \ln C_e \quad [16]$$

where $1/n$ and K_F are Freundlich isotherm constants. If the values of n was falling, 1–10 indicates the good adsorption (20).

The Freundlich constant was calculated from the least square technique (Figure 8) and the amount of K_F and n were 1.4 and 1.1, respectively. The best-fitting equilibrium data in the Langmuir isotherm equation predicts the monolayer coverage of MB onto MIP. From the slope and intercept (Figure 8), the q_m and the K_L were obtained

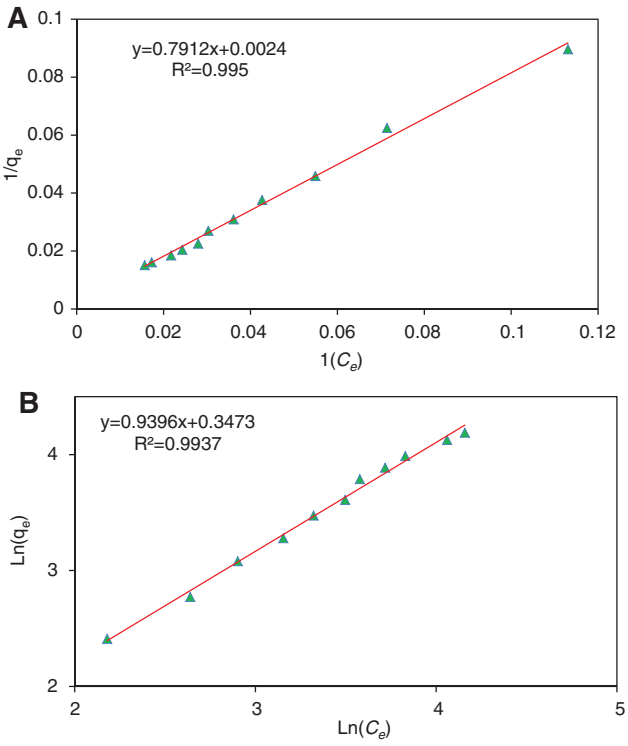

Figure 8: Langmuir (a) and Freundlich (b) plot for MB adsorption onto MIP.

to be 417 mg g^{-1} and 0.003, respectively. The determination coefficient for Langmuir and Freundlich were 0.995 and 0.994, respectively.

3.4 Analytical parameters

In this research, the linear range in the optimum conditions was obtained between 2 and 1200 µg l^{-1} with a determination coefficient (R^2) of 0.9997. At these conditions, the limit of detection (LOD) is evaluated by $3(S_d)_{blank}/m$ was 0.31 µgl^{-1} where m is the slope of the calibration curve and S_d is the standard deviation of the blank signals. The relative standard deviation (RSD%) of the 10 replicates determination was <1.7%, which showed the above procedure has good precision for the trace amount analysis of MB in the environmental water sample solution.

To obtain the enrichment factor, the effect of the sample volume on the extraction recovery of MB onto the MIP was considered in the range of 25–500 ml. The results confirmed which extraction recovery of MB was quantitative (>97%) in the aqueous sample volume range between 25 and 250 ml. After this volume, the extraction recovery of MB was decreased. Therefore, the enrichment factor was 100 for 250 ml sample volume because of the elution volume of 2.5 ml.

Table 4: Comparison of MIP procedure with reported previous methods.

Adsorbent	Sorption capacity (mg g^{-1})	Ref.
Clay	6.3	(21)
Silica	11.21	(22)
Tea waste	85.16	(3)
Parthenium	98.06	(2)
MMIPS	417	This work

Table 5: Determination of MB in water samples (N=3).

Samples	MB content (μg l^{-1})		R (%)
	Added	Found (±RSD%)	
Tap water	0.0	0.0	–
	100.0	99.1±0.8	99.1
Waste water	0.0	0.0	–
	100.0	99.7±1.5	99.7
River water	0.0	0.0	–
	100.0	98.9±1.7	98.9

This method was compared with other procedures (Table 4). According to these results; the maximum sorption capacity of the current method is better than those obtained from most other methods.

3.5 Real sample analysis

To assess the applicability and accuracy of the above method for real environmental water samples, the separation and preconcentration of MB in various environmental water samples were performed. To evaluate the matrix effect, the environmental water samples were spiked with MB at a concentration of 100 μg l^{-1}. Table 5 indicates the results of each environmental water samples obtained by this method.

4 Conclusions

In this study, a MIP adsorbent was synthesized and was then used as an SPE sorbent in combination with a very simple and cheap spectrophotometry procedure for selective separation and determination of MB in environmental water samples. A high imprinting factor (14.9) indicated the success of MIP. The MIP has good advantages including reusability, cost effectiveness, low detection limits and high storage stability. Using an experimental design technique is becoming increasingly more extensive in chemistry (23–26). A hybrid of ANN-ICA could predict the effect of parameters on extraction recovery of MB. In this research, for the first time, ICA was used for optimization study in the field of chemistry and is a worthy technique for estimating of the optimal parameters. By this technique, the optimized conditions were: pH 11, mass of adsorbent 0.11 g, adsorption time 29.5 min, eluent volume 2.5 ml and extraction time 35 min.

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