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ORIGINAL ARTICLE

Modeling of solid-phase tea waste extraction for the removal of manganese and cobalt from water samples by using PSO-artificial neural network and response surface methodology

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Manganese;
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Response surface methodology

Abstract The aim of this research was to develop a low price adsorbent with the abundant of source to remove manganese and cobalt from water samples. Tea waste solid-phase extraction coupled with flame atomic absorption spectrometry (FAAS) was used for the extraction and determination of manganese and cobalt ions. Response surface methodology (RSM) and hybrid of artificial neural network-particle swarm optimization (ANN-PSO) have been used to develop predictive models for simulation and optimization of tea waste extraction process. The pH, amount of tea waste, concentration of PAN (complexing agent), eluent volume, concentration of eluent, and sample and eluent flow rates were the input variables, while the extraction percent of Mn and Co were the output. Two approaches for their modeling and optimization capabilities were compared. The generalization and predictive capabilities of both RSM and ANN were compared by unseen data. The results have shown the superiority of ANN compared to RSM. Under the optimum conditions, the detection limits of Mn and Co were 0.5 and 0.67 μg L^{-1}, respectively. This method was applied to the preconcentration and determination of manganese and cobalt from water samples.

1. Introduction

Many elements are important to life, but in excess, these same substances can be toxic. The contamination of environmental waters by heavy metals is a major concern today because of their potential influences on living organisms. Heavy traffic, industrial development and urbanization lead to pollution of waters by heavy metals (Lemos et al., 2010; Beiraghi et al., 2012). For the formation of vitamin B12 cobalt is necessary,

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while manganese is an important element to all forms of life, which has both structural and enzymatic functions (Lemos et al., 2010). Cobalt is one of common poisonous elements that affect the environment and is present in waste water industries such as electroplating, pigments, paints and electronic. The low amounts of this element could lead to poisonous influences such as flushing and vasodilatation in animals and humans (Beiraghi et al., 2012). If humans for long period exposed to excessive levels of manganese, this element can develop emotional and mental disturbances and clumsy and slow body movements (Lemos et al., 2008). It is evident that the determination of these metals, at trace levels in natural water samples is necessary.

In this study, tea wastes have been utilized as adsorbent for the extraction of cobalt and manganese from water samples. Tea waste is a household waste available in large amount in Iran. Tea waste is an oxygen pollutant demanding and also requires a long period for biodegradation (Uddin et al., 2009). Insoluble cell walls of tea leaf are largely made up of hemicelluloses and cellulose, structural proteins, condensed tannins and lignin. One-third of the total dry matter in the tea leaf due to contain functional groups must be good potential as metal sorbent from aqueous solution (Tee and Khan, 1988).

Response surface methodology (RSM), in statistical-based methods has been usually used in extraction process optimization (Khajeh and Musavi Zadeh, 2012). In this technique, the experimental responses to experimental design are fitted to quadratic function. The effective application number of this technique proposes that second-order relation can reasonably approximate many extraction systems.

Artificial neural network (ANN), in last two decades as an attractive tool for non-linear multivariate modeling has been developed (Desai et al., 2004, 2008). ANN's power is that it is generic in structure and has the capability to learn from historical data. The major advantages of ANN compared to RSM are (i) it does not need a prior specification of appropriate fitting function and (ii) ANN is capable of universal estimation, i.e. ANN can estimate nearly all types of non-linear functions such as quadratic functions, where RSM is suitable only for quadratic estimations (Desai et al., 2008).

Particle swarm optimization (PSO) is a stochastic optimization procedure motivated by the behavior of a bird flock or the sociological behavior of a people group (Lazzus, 2010).

The present work describes the efficiency of tea waste for the extraction of manganese and cobalt from water samples. The effects of various parameters including pH, amount of tea waste, eluent volume and concentration, concentration of PAN and sample and eluent flow rates were investigated. The aims of this study are: (i) to obtain a predictive model based on ANN and RSM techniques for prediction of the extraction percent of manganese and cobalt, (ii) to maximize the extraction percent of manganese and cobalt using RSM and ANN models, and (iii) to develop a cheap, simple and fast method for the extraction of analytes.

2. Experimental

2.1. Materials

1-(2-pyridylazo)-2-naphthol (PAN) was obtained from Merck (Darmstadt, Germany). All acids used were of the highest purity available from Merck. Reagent grade $Co(NO_3)_2$ and $MnSO_4$ (from Merck) were of the highest purity available. A stock solution of cobalt and manganese (1000 mg L^{-1}) was prepared by dissolving the proper amount of these elements in double distilled water in a 10 mL flask. Dilute solutions were prepared by an appropriate dilution of the stock solution in double distilled water.

2.2. Instrumentation

The measurements were performed with a Konik Won M300 (Barcelona, Spain) flame atomic absorption spectrometer (FAAS), equipped with a conventional pneumatic nebulizer. Hollow cathode lamp for the determination of manganese and cobalt were used. The most sensitive wavelengths for manganese at 279.5 nm and cobalt at 240.7 nm were used. The pH was determined with a model 630 Metrohm pH meter with a combined glass-calomel electrode.

2.3. Preparation of the adsorbent

Tea waste was taken from the tea waste leaves after the process of tea making. Colored and soluble components have been removed from tea waste with washing by boiling water. This washing was repeated until the water was virtually colorless. Then, it was immersed in 0.5 mol L^{-1} nitric acid about 5 h to eliminate traces of alkalinity and other impurities. The acid treated tea waste was washed with distilled water to remove excess of nitric acid and other coloring materials until wash water is colorless. Finally, the tea leaves were then washed by deionized water and were oven dried for 5 h at 105 °C. The dried tea was sieved between 400 and 500 μm and stored in sealed polythene bags.

2.4. Procedure

A plastic syringe with two filters was applied as a cartridge and then, was filled with different amounts of dried tea waste (according to experimental design). One filter was placed at the bottom of adsorbent and other to avoid disturbance during solution passage was placed on the top of adsorbent. First, the cartridge was treated with 5 mL nitric acid and then, was washed with deionized water. A portion of solution containing manganese and cobalt was prepared. After that, the solutions were adjusted to the desired pH values with dropwise addition of 0.1 mol L^{-1} NaOH and HCl and passed through the cartridge with various flow rates. Subsequently, manganese and cobalt retained on the tea waste adsorbent were eluted with the desired volume of nitric acid as eluent. The eluent was analyzed for the determination of manganese and cobalt concentration.

Adsorption equilibrium studies were done under optimum condition at pH 9.5 for tea waste adsorbent. Isotherm studies were performed with a constant tea waste (0.5 g) and varying initial concentration of manganese and cobalt in the range of 1–100 mg L^{-1}. The amount of adsorption was calculated based on the difference between manganese and cobalt concentrations in sample solution before and after adsorption. According to this formula:

$$\text{Adsorption capacity}(q_e) = \frac{(C_0 - C_e)V}{m} \quad (1)$$

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Table 1 Box–Behnken design matrix of independent variables and their corresponding experimental and predicted extraction percent of manganese and cobalt.

Run	pH	Mass of adsorbent (g)	[PAN] ($molL^{-1}$)	Eluent volume (mL)	Eluent concentration ($molL^{-1}$)	Sample flow rate ($mLmin^{-1}$)	Eluent flow rate ($mLmin^{-1}$)	Experimental		Predicted (Mn)		Predicted (Co)	
								R % (Mn)	*R* (%) (Co)	*R* (%) (RSM)	*R* (%) (ANN)	*R* (%) (RSM)	*R* (%) (ANN)
1	9.5	0.3	2	2	0.1	2	2	95	92	95.4	95	93.0	91.3
2	9.5	0.3	2	5	0.1	2	2	96	91	97.1	95.6	88.0	91.4
3	9.5	0.3	2	2	1.5	2	2	95	87	96.8	95	89.9	86.5
4	9.5	0.3	2	5	1.5	2	2	96	83	96.9	96	83.4	83.9
5	9.5	0.3	2	2	0.1	6	2	98	84	97.1	98	83.6	83.6
6	9.5	0.3	2	5	0.1	6	2	97	89	95.3	96.9	86.1	89.1
7	9.5	0.3	2	2	1.5	6	2	99	87	97.9	99	90.0	85.5
8	9.5	0.3	2	5	1.5	6	2	95	92	94.6	95.1	91.0	91.3
9	7	0.3	2	3.5	0.8	2	1	93	91	91.1	93.4	97.3	90
10	12	0.3	2	3.5	0.8	2	1	89	77	88.8	89	76.3	77.3
11	7	0.3	2	3.5	0.8	6	1	93	87	94.3	93	85.5	86.7
12	12	0.3	2	3.5	0.8	6	1	88	61	88.4	88	63.0	61.1
13	7	0.3	2	3.5	0.8	2	3	86	86	85.6	86.2	84.0	86.7
14	12	0.3	2	3.5	0.8	2	3	98	67	96.8	97.8	68.5	65.8
15	7	0.3	2	3.5	0.8	6	3	85	95	85.3	85	95.7	95.7
16	12	0.3	2	3.5	0.8	6	3	91	85	92.9	91	78.7	85
17	9.5	0.1	2	3.5	0.1	4	1	98	79	97.8	97	80.9	79.6
18	9.5	0.5	2	3.5	0.1	4	1	98	93	97.4	98	89.5	90.5
19	9.5	0.1	2	3.5	1.5	4	1	99	80	99.6	99	79.8	80
20	9.5	0.5	2	3.5	1.5	4	1	98	89	98.8	98	85.9	89.4
21	9.5	0.1	2	3.5	0.1	4	3	99	74	98.3	99	77.1	74.9
22	9.5	0.5	2	3.5	0.1	4	3	99	89	98.4	99	89.2	89.2
23	9.5	0.1	2	3.5	1.5	4	3	97	79	97.6	96.8	82.5	78.9
24	9.5	0.5	2	3.5	1.5	4	3	97	94	97.3	97.1	92.1	93.3
25	7	0.1	2	2	0.8	4	2	92	84	91.3	92	81.5	84.8
26	12	0.1	2	2	0.8	4	2	94	63	93.4	95.3	61.0	64.8
27	7	0.5	2	2	0.8	4	2	92	93	92.4	92	94.0	92.7
28	12	0.5	2	2	0.8	4	2	92	71	91.1	92	73.5	71
29	7	0.1	2	5	0.8	4	2	87	84	87.9	87	81.5	84.1
30	12	0.1	2	5	0.8	4	2	95	65	94.6	95	64.0	65.2
31	7	0.5	2	5	0.8	4	2	89	85	89.6	88.8	87.0	87
32	12	0.5	2	5	0.8	4	2	92	67	92.8	92	69.5	67.1
33	9.5	0.3	1	2	0.8	4	1	97	93	97.6	97.1	91.2	93.1
34	9.5	0.3	3	2	0.8	4	1	99	92	99.3	99	90.5	91.2
35	9.5	0.3	1	5	0.8	4	1	96	91	95.8	96	91.2	91.3
36	9.5	0.3	3	5	0.8	4	1	97	89	96.4	96.7	91.0	89.3
37	9.5	0.3	1	2	0.8	4	3	94	93	94.6	94.2	91.0	92.8
38	9.5	0.3	3	2	0.8	4	3	98	98	98.3	98	97.8	97.6
39	9.5	0.3	1	5	0.8	4	3	96	85	95.8	96	86.5	85.6
40	9.5	0.3	3	5	0.8	4	3	99	92	98.4	99	93.8	92

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Table 1 *(continued)*

Run	pH	Mass of adsorbent (g)	[PAN] ($molL^{-1}$)	Eluent volume (mL)	Eluent concentration ($molL^{-1}$)	Sample flow rate ($mLmin^{-1}$)	Eluent flow rate ($mLmin^{-1}$)	Experimental		Predicted (Mn)		Predicted (Co)	
								R % (Mn)	*R* (%) (Co)	*R* (%) (RSM)	*R* (%) (ANN)	*R* (%) (RSM)	*R* (%) (ANN)
41	7	0.3	1	3.5	0.1	4	2	87	86	86.9	87.5	86.4	86.7
42	12	0.3	1	3.5	0.1	4	2	96	63	97.6	96	64.9	60.6
43	7	0.3	3	3.5	0.1	4	2	87	89	88.6	87.3	89.7	89.6
44	12	0.3	3	3.5	0.1	4	2	94	69	94.3	94	69.7	69
45	7	0.3	1	3.5	1.5	4	2	90	87	89.8	90	86.3	86.6
46	12	0.3	1	3.5	1.5	4	2	91	69	89.4	91	68.3	68.7
47	7	0.3	3	3.5	1.5	4	2	99	90	97.4	98.8	88.1	90.2
48	12	0.3	3	3.5	1.5	4	2	92	72	92.1	92.2	71.6	72.2
49	9.5	0.1	1	3.5	0.8	2	2	96	88	95.8	96	87.2	88.4
50	9.5	0.5	1	3.5	0.8	2	2	97	97	96.9	96.2	95.3	96.8
51	9.5	0.1	3	3.5	0.8	2	2	98	95	98.4	98	92.5	95
52	9.5	0.5	3	3.5	0.8	2	2	98	99	97.6	96.8	97.6	98.3
53	9.5	0.1	1	3.5	0.8	6	2	95	83	95.4	95.1	84.4	83
54	9.5	0.5	1	3.5	0.8	6	2	96	95	95.6	96.7	97.5	94.1
55	9.5	0.1	3	3.5	0.8	6	2	99	87	99.1	99	88.7	86.8
56	9.5	0.5	3	3.5	0.8	6	2	97	98	97.3	97.1	98.8	97.8
57	9.5	0.3	2	3.5	0.8	4	2	99	94	97.2	97.2	92.5	92.4
58	9.5	0.3	2	3.5	0.8	4	2	95	89	97.2	97.2	92.5	92.4
59	9.5	0.3	2	3.5	0.8	4	2	98	97	97.2	97.2	92.5	92.4
60	9.5	0.3	2	3.5	0.8	4	2	96	95	97.2	97.2	92.5	92.4
61	9.5	0.3	2	3.5	0.8	4	2	97	88	97.2	97.2	92.5	92.4
62	9.5	0.3	2	3.5	0.8	4	2	98	92	97.2	97.2	92.5	92.4
RMSE										0.106	0.10	0.063	0.051
SEP%										0.11	0.10	0.074	0.059
B_f										1.0	1.0	1.0	0.999
A_f										1.01	1.01	1.02	1.0
MPE%										1.5	1.3	2.2	0.89

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where C_0 is the initial manganese and cobalt concentration, C_e is equilibrium concentration of manganese and cobalt in the solution, m is the mass of the adsorbent (g) and V is the volume of the solution in L.

2.5. Response surface methodology

The relationships between the screened parameters are represented mathematically in the form of quadratic equation under RSM (Khajeh and Sanchooli, 2010; Khajeh, 2011; Khajeh et al., 2010). In this research, the experiments were conducted in the Box–Behnken experimental design and fitted with an empirical, full second order polynomial model expressing in the form of response surface over a relatively wide range of parameters. Eq. (2) is used to fit the experimental data (Table 1) of manganese and cobalt recovery to construct the RSM model.

$$Y = \beta_o + \sum \beta_i \chi_i + \sum \beta_{ii} \chi_{ii}^2 + \sum \sum \beta_{ij} \chi_i \chi_j + \varepsilon \quad (2)$$

where Y is the output (dependent parameter), β_0 is the constant, $x_1, x_2, \ldots, x_k$ are the coded independent parameters, β_i is the linear effect, β_{ii} is the quadratic effect, β_{ij} is the interaction effect, and ε is the random error or allows for description or uncertainties between predicted and measured values.

2.6. Definition of the ANN model

In this work, Neural Network Toolbox V7.12 of MATLAB mathematical software was used to predict the extraction percent of manganese and cobalt from water samples.

An artificial neural network (ANN) generally consists of three layers including input, hidden and output layers. The inputs are used in the input layer and output is achieved at the output layer and the learning acquired when the associations among a specific set of input–output pairs formed. In this study, ANN was used to model the influence of seven input parameters including pH, amount of tea waste, concentration and volume of eluent, concentration of PAN and sample and eluent flow rates on extraction percent of manganese and cobalt as output. A feed-forward artificial neural network (FFANN) *topology* (*architecture*) also famous as multilayer perceptron (MLP), has been used with back propagation (BP) algorithm to build the predictive models. The neuron output signal O is known by the following Eq.

$$O = f(net) = f\left(\sum_{j=1}^{n} w_j x_j\right) \quad (3)$$

where w_j is the weight vector and $f(net)$ is the transfer function.

The most used transfer functions to solve non-linear and linear regression problems are log-sigmoid transfer function (*logsig*), hyperbolic tangent sigmoid transfer function (*tansig*) and linear transfer function (*purelin*) Khayet and Cojocaru, 2012. In this work, *tansig* was used as transfer function between input and hidden layers, while *purelin* was used as transfer function between hidden and output layers, shown by the following equations:

$$Purelin(O) = O \quad (4)$$

$$\text{tansig}(O) = \frac{1 - \exp(-O)}{1 + \exp(-O)} \quad (5)$$

There are many variations of BP algorithm for training neural networks (NNs). During training step the *weight* (w) and biases (b) are iterative updated by Levenberg–Marquardt (LM) method until the convergence to the certain value is achieved. In order to assess the fitting and prediction accuracy of models made, the root mean-squared-error (RMSE), model predictive error (MPE) and standard error of prediction (SEP) are used along with the bias (B_f) and accuracy (A_f) Zafar et al., 2012.

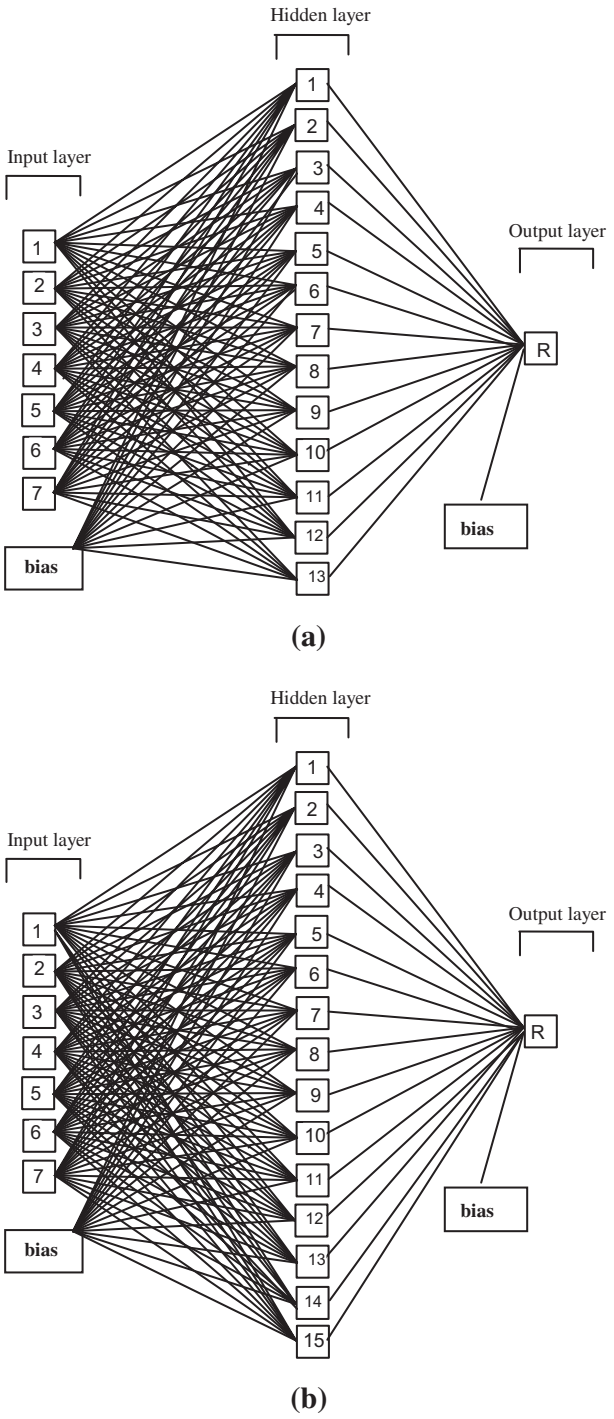

Figure 1 Optimal ANN structure (a) manganese and (b) cobalt.

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$$\mathrm{RMSE} = \sqrt{\sum_{i=1}^{N} \frac{(Y_{i,e} - Y_{i,p})^2}{N}} \quad (6)$$

$$\mathrm{SEP}(\%) = \frac{RMSE}{Y_e} \times 100. \quad (7)$$

$$\mathrm{MPE}(\%) = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{Y_{i,e} - Y_{i,p}}{Y_{i,p}} \right| \quad (8)$$

$$\mathrm{B_f} = 10\left(\sum_{i=1}^{N} \log\left(\frac{Y_{i,p}}{Y_{i,e}}\right) / N \right) \quad (9)$$

$$\mathrm{A_f} = 10\left(\sum_{i=1}^{N} \left| \log\left(\frac{Y_{i,p}}{Y_{i,e}}\right) \right| / N \right) \quad (10)$$

where $Y_{i,e}$ is the target output, $Y_{i,p}$ is the predicted output, N is the number of points and Y_e is the average value of experimentally determined extraction percent of manganese and cobalt in N number of experiments.

Different variables may have various magnitudes, and some of them could have unmerited, but favorable, and effective on the monitored quantity. In this research, all inputs and outputs are normalized within a uniform range of [0–1] according to the below equation:

$$x_{\mathrm{norm}} = \frac{(x - x_{\min})}{(x_{\max} - x_{\min})} \quad (11)$$

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

The corresponding experimental values are plotted versus to the values predicted by the ANN and RSM models visualize the modeling abilities of the ANN and RSM models.

Table 2 Analysis of variance (ANOVA) for the experimental results of the Box–Behnken design.

Source	Coefficients		Sum of squares		Degree of freedom	Mean of square		*F*-value		*p*-Value	
	Mn	Co	Mn	Co		Mn	Co	Mn	Co	Mn	Co
Intercept or model	4.35	−2.8	828.876	5572.647	35	23.682	159.2185	11.99	12.52	< 0.0001	< 0.0001
A	17.91	29.78	288.798	798.2490	1	288.798	798.2490	146.27	62.76	< 0.0001	< 0.0001
B	12.76	73.57	1.340	44.5755	1	1.340	44.5755	0.68	3.50	0.4175	0.0725
C	3.17	−8.16	1.954	12.9217	1	1.954	12.9217	0.99	1.02	0.3290	0.3228
D	−1.52	3.03	0.957	3.8320	1	0.957	3.8320	0.48	0.30	0.4924	0.5878
E	13.09	1.88	17.882	0.3682	1	17.882	0.3682	9.06	0.03	0.0058	0.8662
F	5.35	−12.31	22.160	117.5650	1	22.160	117.5650	11.22	9.24	0.0025	0.0053
G	−13.33	−16.81	34.436	54.8040	1	34.436	54.8040	17.44	4.31	0.0003	0.0479
AB	−1.75	0	6.125	0.0000	1	6.125	0.0000	3.10	0.00	0.0899	1.0000
AC	−0.50	0.15	12.500	1.1250	1	12.500	1.1250	6.33	0.09	0.0184	0.7685
AD	0.30	0.2	10.125	4.5000	1	10.125	4.5000	5.13	0.35	0.0321	0.5571
AE	−1.57	0.5	60.500	6.1250	1	60.500	6.1250	30.64	0.48	< 0.0001	0.4939
AF	−0.18	−0.075	6.125	1.1250	1	6.125	1.1250	3.10	0.09	0.0899	0.7685
AG	1.35	0.55	91.125	15.1250	1	91.125	15.1250	46.15	1.19	< 0.0001	0.2855
BC	−2.50	−3.75	2.000	4.5000	1	2.000	4.5000	1.01	0.35	0.3235	0.5571
BD	0.42	−5.83	0.125	24.5000	1	0.125	24.5000	0.06	1.93	0.8033	0.1770
BE	−0.89	−4.46	0.125	3.1250	1	0.125	3.1250	0.06	0.25	0.8033	0.6243
BF	−0.63	3.12	0.500	12.5000	1	0.500	12.5000	0.25	0.98	0.6190	0.3307
BG	0.63	4.37	0.125	6.1250	1	0.125	6.1250	0.06	0.48	0.8033	0.4939
CD	−0.17	0.083	0.500	0.1250	1	0.500	0.1250	0.25	0.01	0.6190	0.9218
CE	2.14	−0.54	18.000	1.1250	1	18.000	1.1250	9.12	0.09	0.0056	0.7685
CF	0.13	−0.13	0.500	0.5000	1	0.500	0.5000	0.25	0.04	0.6190	0.8444
CG	0.50	1.87	2.000	28.1250	1	2.000	28.1250	1.01	2.21	0.3235	0.1490
DE	−0.36	−0.36	1.125	1.1250	1	1.125	1.1250	0.57	0.09	0.4571	0.7685
DF	−0.29	0.63	6.125	28.1250	1	6.125	28.1250	3.10	2.21	0.0899	0.1490
DG	0.50	−0.75	4.500	10.1250	1	4.500	10.1250	2.28	0.80	0.1432	0.3805
EF	−0.09	1.7	0.125	45.1250	1	0.125	45.1250	0.06	3.55	0.8033	0.0709
EG	−0.89	2.32	3.125	21.1250	1	3.125	21.1250	1.58	1.66	0.2195	0.2088
FG	−0.44	2.94	6.125	276.1250	1	6.125	276.1250	3.10	21.71	0.0899	< 0.0001
A^2	−0.93	−1.88	455.010	1870.4590	1	455.010	1870.4590	230.46	147.05	< 0.0001	< 0.0001
B^2	14.24	−67.71	4.378	99.0234	1	4.378	99.0234	2.22	7.79	0.1485	0.0097
C^2	0.19	1.6	0.510	34.7402	1	0.510	34.7402	0.26	2.73	0.6154	0.1104
D^2	−0.14	−0.68	1.260	31.2246	1	1.260	31.2246	0.64	2.45	0.4315	0.1293
E^2	0.91	−8.59	2.667	239.0859	1	2.667	239.0859	1.35	18.80	0.2557	0.0002
F^2	−0.23	0.34	11.690	24.7559	1	11.690	24.7559	5.92	1.95	0.0221	0.1748
G^2	−0.06	−0.96	0.042	12.3984	1	0.042	12.3984	0.02	0.97	0.8856	0.3326
Residual			51.333	330.7083	26	1.974	12.7196				
Lack of Fit			40.500	269.2083	21	1.929	12.8194	0.89	1.04	0.6216	0.5355
Pure Error			10.833	61.5000	5	2.167	12.3000				
R^2	0.942	0.944									
Adj-R^2	0.863	0.869									

(A) pH; (B) mass of adsorbent; (C) concentration of PAN; (D) volume of eluent; (E) concentration of eluent (nitric acid); (F) sample flow rate and (G) eluent flow rate

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2.7. The concept of particle swarm optimization (PSO)

When the generalized ANN model is developed, its input space can be optimized by PSO method. The input vector containing input parameters of model converts the decision parameter for the PSO. Kennedy and Eberhart in 1995 (Kennedy et al., 2001; Che, 2010) proposed the PSO method. It is an evolutionary computational algorithm. PSO has been developed based on the simulation of the behavior of foraging birds and searches for optimization by updating generations (Che, 2010). Namely, the position (x_i^j) and velocity v_i^j of each particle will be changed by the particle best value (x_i^{j*}) and global best value ($x_i^{j\#}$). Kennedy and Spears (Kennedy and Spears, 1998) offered the inertia weighing technique, and presented inertia weight, w, into the basic update rule to decrease the particle speed when particle swarms are searching a large area using the inertia weight [163]. Then, the particles are forced into a better search area to find better practical solution by a more effective technique. The particles' new position and velocity are updated by the below Eq.:

$$v_i^{j+1} = wv_i^j + \emptyset_1 r_1(x_i^{j*} - x_i^j) + \emptyset_2 r_2(x^{j\#} - x_i^j) \quad (12)$$

$$x_i^{j+1} = x_i^j + v_i^{j+1} \quad (13)$$

v_i^j, v_i^{j+1}, velocities of particle i at iterations j and $j + 1$; x_i^j, x_i^{j+1}, positions of particle i at iterations j and $j + 1$; $\varnothing_1$, $\varnothing_2$, cognition and social learning factors; x_i^{j*}, the best solution that particle i has obtained until iteration j, called the particle best value. $x_i^{j\#}$, the best solution obtained from x_i^{j*} in the population at iteration j, called the global best value. w, inertia weight; r_1, r_2, random numbers uniformly distributed in [0,1].

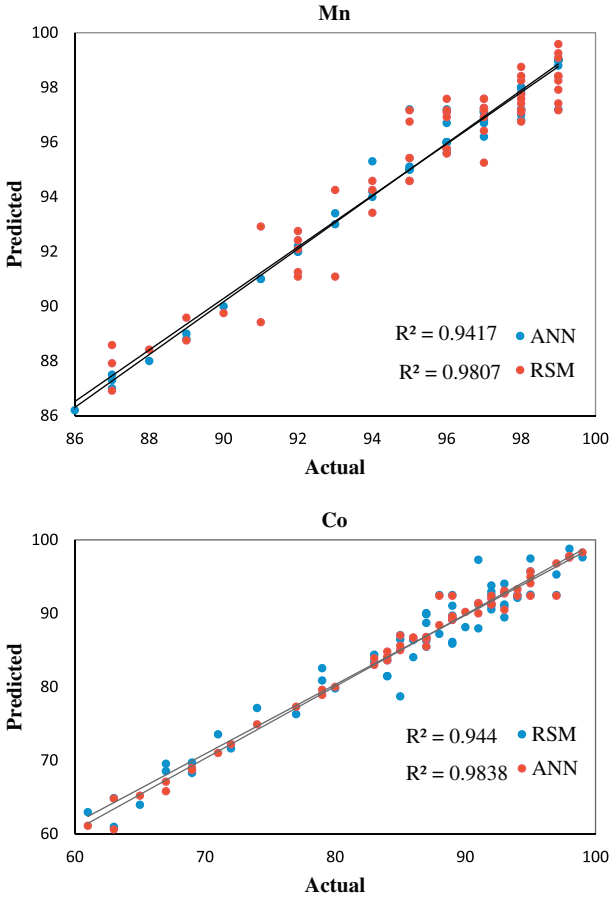

Figure 2 RSM and ANN predicted vs. experimental data for manganese and cobalt.

2.8. Adsorption isotherms

In this study, the equilibrium data were analyzed by the Langmuir and Freundlich isotherm expression given by the following Eq.:

$$\text{Langmuir}: q_e = \frac{q_e K_L C_e}{1 + K_L C_e} \quad (14)$$

$$\text{Freundlich}: q_e = K_f C_e^{1/n} \quad (15)$$

where q_e is the adsorption capacity at equilibrium of manganese and cobalt, C_e is the equilibrium concentration of the manganese and cobalt in solution, q_0 is the monolayer adsorption capacity and K_L is the Langmuir constant associated to the free energy of adsorption. K_F and n are Freundlich constants associated to sorption capacity and sorption intensity of adsorbents, respectively. The value of n falling in the range of 1–10 shows good sorption (Uddin et al., 2009). The linearized forms of Langmuir and Freundlich equations can be written as follows:

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{q_{0K_L}} \frac{1}{C_e} \quad (16)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (17)$$

3. Results and discussion

3.1. Hybrid ANN-PSO optimization

3.1.1. Predictive modeling with ANN

Table 1 shows the main factors and extraction percent of manganese and cobalt. The ANN contains three processes that were training, validation and testing. The aim of training was to decide the w and b of the network; testing verifies whether the network was over-trained and validation determined whether the output values estimated using the ANN was accurate (Che, 2010). In this study, ANN with *tansig* transfer function at hidden layer and a *purelin* transfer function at output layer was used. The experimental data were randomly divided into three subsets: 76% for the training set, 12% for the validation set and 12% for the test set. The split of data into training, test and validation subsets was performed to estimate the performance of the NN for prediction of "unseen" data, which were not used for training. Network architecture has important influences on the predicted values. The number of input and output nodes is equal to the number of input and output data, respectively (7 and 1 in this work). However, the number of neurons in the hidden layer was recognized by training several FFANNs of different architectures and selecting the optimal one based on the minimization of MSE and improving generalization ability of the topology. In this study, the optimal topology of the ANN model developed involves seven inputs, one hidden layer with 13 neurons for manganese and 15 neurons for cobalt and one output layer (7:13:1 for manganese and 7:15:1 for cobalt). Fig. 1 shows the

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Table 3 RSM and ANN predictions for totally unseen data.

No	pH	Mass of adsorbent	[PAN]	Eluent volume	Eluent concentration	Sample flow rate	Eluent flow rate	*R* (%)					
								Experimental		Predicted			
								Mn	Co	Mn		Co	
										RSM	ANN	RSM	ANN
1	8	0.2	2.5	3	1	5	1.5	98.9	89.2	97.7	100.5	89.7	89.6
2	8	0.2	2.5	4	1	3	1.5	85.6	91.6	86	85	92.8	89.6
3	8	0.4	2.5	3	0.5	3	1.5	92.5	95	94.9	91.3	98.3	97.6
4	10.5	0.2	1.5	3	0.5	5	2.5	97.9	82.5	97.3	98.2	81.5	83
5	10.5	0.2	1.5	3	1	5	1.5	96.5	82.4	96	96.3	80.8	83.4
6	10.5	0.2	2.5	3	0.5	3	1.5	94	85.1	96.5	93.4	86.3	86.2
7	10.5	0.2	2.5	4	0.5	5	1.5	97	79.2	96.6	97.1	81.6	78.1
8	10.5	0.4	1.5	3	0.5	3	1.5	90.2	88.4	90.5	90.8	89.5	87.6
9	10.5	0.4	1.5	4	0.5	5	1.5	95.2	86.7	96.2	92.7	85.1	86.1
10	10.5	0.4	1.5	4	1	5	2.5	96.1	91.1	95.6	96.6	89.9	92.3

Table 4 Optimized medium composition for manganese and cobalt extraction by tea waste using different methods.

Approach	Variables							*R* (%)		
	pH	Mass of adsorbent	[PAN]	Eluent volume	Eluent concentration	Sample flow rate	Eluent flow rate	Predicted	Experimental[a]	
Mn	Before optimization	7	0.1	1	2	0.1	2	1		91.0
	At center point of experimental design	9.5	0.3	2	3.5	0.8	4	2		98.2
	RSM	9.5	0.1	1	3.5	0.8	6	2	95.5	98.9
	Hybrid ANN-PSO	9.8	0.5	3	3.8	0.1	3.1	1	100.2	99.5
Co	Before optimization	7	0.1	1	2	0.1	2	1		88.3
	At center point of experimental design	9.5	0.3	2	3.5	0.8	4	2		94.5
	RSM	9.5	0.5	3	3.5	0.8	6	2	98.8	99.4
	Hybrid ANN-PSO	9.1	0.35	3	2	1	6	3	100.1	99.5

[a] Average of three analyses.

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optimal topology of the developed ANN model. The RMSE, SEP (%), MPE (%), B_f and A_f are shown in Table 1.

3.1.2. PSO-based optimization of input variables in ANN

The PSO technique was utilized to optimize the input space of the ANN model with an objective of maximizing extraction percent of manganese and cobalt. The values of PSO-specific parameters used in the optimization simulation for manganese and cobalt, respectively, were number of particle in swarm = 15 and 10; cognitive component = 2; social component = 2; maximum velocity = 7; minimum inertia weight = 0.6 and 0.05; and maximum inertia weight = 0.8 and 0.1. Optimum conditions have been selected after the evaluation of PSO for 10 iterations for manganese and cobalt to achieved good extraction percent of them. The optimized process conditions are as follows: for manganese; the pH of solution is 9.8, amount of tea waste is 0.5 g, concentration of PAN is 3.0 mol L^{-1}, eluent volume is 3.8 mL, eluent concentration is 0.1 mol L^{-1}, sample flow rate is 3.1 ml min^{-1} and eluent flow rate is 1.0 mL min^{-1} and for cobalt; the pH of solution is 9.1, amount of tea waste is 0.35 g, concentration of PAN is 3.0 mol L^{-1}, eluent volume is 2.0 mL, eluent concentration is 1.0 mol L^{-1}, sample flow rate is 6.0 ml min^{-1} and eluent flow rate is 3.0 mL min^{-1}. The ANN prediction of the extraction percent under the optimized process conditions is 100.2% and 100.1% for manganese and cobalt, respectively.

3.2. Response surface methodology

The below equation explains the relationship of the seven variables, that is, pH (A), amount of tea waste (B), concentration of PAN (C), eluent volume (D), eluent concentration (E), sample flow rate (F) and eluent flow rate (G) and response (Y).

For manganese

$$Y = 4 + 5.35F - 13.33G - 0.5AC - 1.57AE + 1.35AG + 2.14CE - 0.93A^2 - 0.23F^2 \quad (18)$$

For cobalt

$$Y = -2.8 + 29.78A - 16.81G + 2.94FG - 1.88A^2 - 67.71B^2 - 8.59E^2 \quad (19)$$

In Eqs. (18) and (19) only the significant terms are given. The coefficients of EQ. 18 and 19 for each data set are determined by using software Design-Expert 8. The optimal points determined with this software are as follows: for manganese; the pH of solution is 9.5, amount of tea waste is 0.1 g, concentration of PAN is 1.0 mol L^{-1}, eluent volume is 3.5 mL, eluent concentration is 0.8 mol L^{-1}, sample flow rate is 6.0 ml min^{-1} and eluent flow rate is 2.0 mL min^{-1} and for cobalt; the pH of solution is 9.5, amount of tea waste is 0.5 g, concentration of PAN is 3.0 mol L^{-1}, eluent volume is 3.5 mL, eluent concentration is 0.8 mol L^{-1}, sample flow rate is 6.0 ml min^{-1} and eluent flow rate is 2.0 mL min^{-1}. The maximum extraction percent of manganese and cobalt obtained experimentally by the optimized medium were 98.9 and 99.4, respectively, while the predicted values were 95.5 and 98.8 for manganese and cobalt, respectively. The results were analyzed by using analysis of variance (ANOVA), which are shown in Table 2. The model F-values of 11.99 and 12.52 for manganese and cobalt, respectively suggest that the models are significant. Model p-values are very low (< 0.0001) for both analytes. These re-signify the significance of the models. The p-values are used as a tool to verify the significance of each of the model coefficients. When the magnitude of the p-value is smaller, the corresponding coefficient is more significant. P-values less than 0.05 show model terms are significant. The fit of the model was expressed by the determination coefficients (R^2), which were found to be 0.942 and 0.944 for manganese and cobalt, respectively.

3.3. Comparison of RSM and hybrid ANN-PSO

The ANN and RSM models were compared for the design of experiments. The comparison was made on the basis of different parameters including RMSE, SEP%, B_f, A_f and MPE, which are shown in Table 1. For cobalt extraction, as shown in Table 1, the RMSE (0.063) and SEP (0.074%) for the RSM model are almost bigger than those 0.051% and 0.059%, respectively for the ANN model, showing that the ANN model has better modeling ability than the RSM model for the extraction of cobalt. For manganese extraction, as shown in Table 1, the RMSE and SEP are 0.106% and 0.11%, respectively for the RSM model as compared to 0.1% and 0.1%, respectively for the ANN model. These values show a good fit of the experimental data by ANN in comparison to the RSM model. Moreover, as shown in Table 1, the B_f and A_f are closed to unity for both ANN and RSM models for manganese and cobalt, showing a good concordance between the predicted and experimental values. Better accuracy of predictions (MPE%) is observed by the ANN model with 0.89% and 1.3% prediction error for cobalt and manganese, respectively as compared to 2.2% and 1.5% prediction error for cobalt and manganese, respectively by RSM. Fig. 2 indicates the comparative parity plot for RSM and ANN prediction for design experiments of manganese and cobalt. The generalization

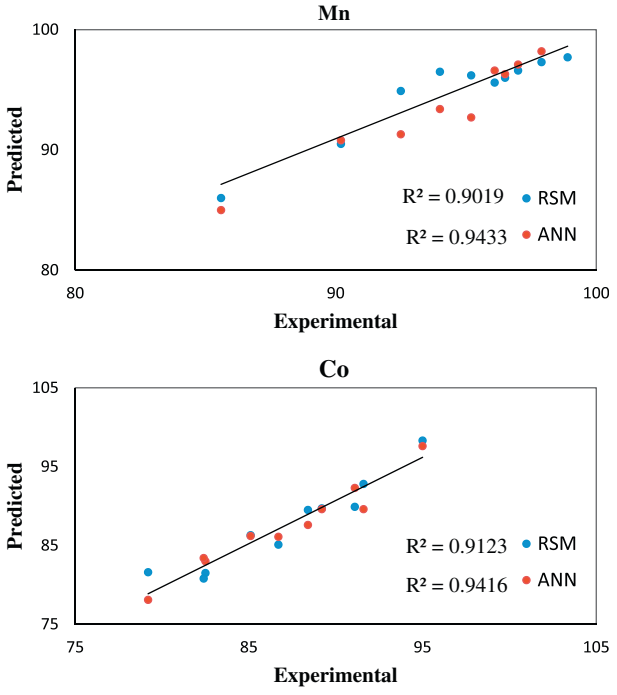

Figure 3 Comparison of generalization ability of RSM and ANN models for unseen data.

Table 5 Determination of cobalt and manganese in water samples ($N = 3$).

Analytes	Samples	Manganese and cobalt content (μg g^{-1} ± RSD%)		R (%)
		Added	Found	
Mn	Tap water	0	41.25 ± 1.2	–
		50	90.9 ± 1.3	99.3
	Well water	0	18.43 ± 1.3	–
		50	68.83 ± 1.0	100.8
	Mineral water	0	5.1 ± 1.2	–
		50	53.35 ± 1.4	96.5
Co	Tap water	0	12.65 ± 1.1	–
		50	62.5 ± 0.7	99.7
	Well water	0	10.06 ± 1.1	–
		50	60.16 ± 0.9	100.2
	Mineral water	0	–	–
		50	48.95 ± 1.8	97.9

capability only with completely unseen dataset can be best judged. Therefore, both the models were tested using unseen data. The experimental and predicted extraction percent are summarized in Table 3. Fig. 3 indicates the comparative parity plot for RSM and ANN prediction for unseen data. The correlation coefficients for unseen data by ANN and RSM are 0.944 and 0.902 for manganese and 0.942 and 0.912 for cobalt, respectively. Therefore, ANN has shown a higher generalization ability compared to RSM. ANN model's upper predictive accuracy can be attributed to its universal capability of it for approximate non-linearity of the system, while the RSM model is only limited to second-order polynomial.

3.4. Adsorption isotherms

The results of adsorption isotherms of Langmuir and Freundlich for manganese and cobalt exhibited that the equilibrium data represented by the Langmuir isotherm equation were superior from the Freundlich equation. The calculated Freundlich constants, for cobalt K_F and n are 29.7 and 1.75, respectively and for manganese K_F and n are 8.0 and 1.4, respectively. The best fit of equilibrium data in the Langmuir isotherm equation predicts the monolayer coverage of manganese and cobalt onto tea waste. From the slope of the straight line and intercept, the q_o of adsorbent and the K_L for cobalt and manganese were determined to be 135.1 and 128.2 mg g^{-1} and 0.25 and 0.05, respectively. The correlation coefficients for Langmuir and Freundlich were 0.999 and 0.995 for cobalt and 0.982 and 0.978 for manganese, respectively.

3.5. Optimization

The comparison of the extraction of manganese and cobalt for optimized media using various methods is given in Table 4. This table clearly demonstrates that the extraction percent of manganese and cobalt predicted by hybrid ANN-PSO are much more close to the experimentally validated results than those predicted by the RSM.

3.6. Study of coexisting ions

In order to evaluate the analytical application of the present study, some foreign ions' effects, which often accompany manganese and cobalt ions in different real samples and may interfere with the above method, under the optimized conditions were tested. For this purpose, a solution of 10 μg of cobalt and manganese in 25 mL water containing the corresponding interfere ions was prepared. The tolerance limit was defined as the foreign ions' concentration needed to cause a ±5% error. The tolerable ratio of each foreign ions' concentration was as below: 500-fold for Li^+, Na^+, K^+, Cl^-, NO_3^-, Mg^{2+}, Ca^{2+}, Ba^{2+}, and CO_3^{2-}, 50-fold for Cu^{2+}, Fe^{3+}, Pb^{2+} and Ni^{2+}. The results show that the tested ions do not interference on the pre-concentration and determination of manganese and cobalt.

3.7. Evaluation of method performance

In this study, under the optimum condition, the linear range was obtained between 0.05 and 0.90 mg L^{-1} for manganese and cobalt with a correlation coefficient of 0.995 and 0.997, respectively. The limit of detection (LOD) for the determination of manganese and cobalt was studied under the optimum condition. The LOD is evaluated using $3(S_d)_{blank}/m$ and was 0.5 and 0.67 μgL^{-1} for manganese and cobalt, respectively where S_d is the standard deviation of the blank signals and m is the slope of the calibration curve. The relative standard deviation (RSD%) of the ten replicate determination was $<1.9\%$ for both analytes.

In order to obtain a high pre-concentration factor, the sample volume effect on the extraction of manganese and cobalt on tea waste was investigated in the range of 25–500 mL. The results showed that the extraction percent of manganese and cobalt was quantitative ($>97\%$) in the sample volume range of 25–250 mL. After that, the extraction percent of manganese and cobalt were decreased. In this work, the pre-concentration factor was 71 for 250 mL sample volume due to the elution volume of 3.5 mL.

3.8. Analysis of real samples

The procedure was used for separation and determines the concentration of manganese and cobalt in water samples. The results are shown in Table 5.

4. Conclusions

In this study, hybrid ANN-PSO and RSM have been successfully used to study the modeling of the variables for maximum

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extraction of manganese and cobalt based experimental data using the Box–Behnken design. The modeling capability of ANN has shown its superiority over RSM with comparative less values of RMSE and SEP%. Hybrid ANN-PSO approach has predicted maximum extraction for manganese and cobalt of 100.2% and 100.1%, respectively, while, maximum extraction of 95.5% and 98.8% is reported by RSM for manganese and cobalt, respectively. The predictive and generalization capabilities of both RSM and ANN were compared using separate dataset. The correlation coefficients for ANN and RSM were 0.944 and 0.902 for manganese and 0.942 and 0.912 for cobalt, respectively, representing the superiority of ANN in capturing the non-linear behavior of the system.

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