**Membrane Water Treatment**, *Vol. 9, No. 5 (2018) 363-371*
DOI: https://doi.org/10.12989/mwt.2018.9.5.363


# Modeling of Co(II) adsorption by artificial bee colony and genetic algorithm

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*(Received January 23, 2018, Revised April 13, 2018, Accepted April 17, 2018)*

**Abstract.** In this work, it was investigated the usability of artificial bee colony (ABC) and genetic algorithm (GA) in modeling adsorption of Co(II) onto drinking water treatment sludge (DWTS). DWTS, obtained as inevitable byproduct at the end of drinking water treatment stages, was used as an adsorbent without any physical or chemical pre-treatment in the adsorption experiments. Firstly, DWTS was characterized employing various analytical procedures such as elemental, FT-IR, SEM-EDS, XRD, XRF and TGA/DTA analysis. Then, adsorption experiments were carried out in a batch system and DWTS's Co(II) removal potential was modelled via ABC and GA methods considering the effects of certain experimental parameters (initial pH, contact time, initial Co(II) concentration, DWTS dosage) called as the input parameters. The accuracy of ABC and GA method was determined and these methods were applied to four different functions: quadratic, exponential, linear and power. Some statistical indices (sum square error, root mean square error, mean absolute error, average relative error, and determination coefficient) were used to evaluate the performance of these models. The ABC and GA method with quadratic forms obtained better prediction. As a result, it was shown ABC and GA can be used optimization of the regression function coefficients in modeling adsorption experiments.

**Keywords:** adsorption; artificial bee colony algorithm; modeling; genetic algorithm

## 1. Introduction

Drinking Water Treatment Sludge (DWTS) is an inevitable end product at the end of treatment stages, and one of the most promising adsorbent due to its zero price and easy availability. The utilization of the waste materials is a significant application because of serious disposal problems of them. It has been investigated usability of DWTS, as an adsorbent for removal of the organic and inorganic pollutants (Cu(II), Ni(II), Pb(II), Cd(II), Hg(II) and Methylene blue) present in wastewaters, and Artificial Neural Network (ANN) models have been developed considering the effects of certain experimental parameters for adsorption of these contaminants on DWTS (Öztürk 2014). Also, DWTS has been successfully applied as an adsorbent for Pb(II), Cd(II) and Ni(II) removal from wastewater (Abo-El-Enein *et al.* 2017).

When metals are classified in terms of environmental impact, cobalt is class of metals with environmental concern due to its high concentration. Cobalt is mainly used as a component of very hard, strong and heat resistant alloys and in permanent magnets. It is also used as drying agent in paintings, as color pigment in porcelain, as a catalyzer in the rubber manufacturing and as an additive in fertilizers and fodders. Elevated cobalt concentrations found in the terrestrial environment can be caused, by deposition from the burning of fossil fuels, wear of cobalt containing alloys and spreading of sewage sludge and manure (Lock *et al.* 2004). In industries producing or using cobalt metal and cobalt compounds if workers are exposed to inhalation or skin contact with higher cobalt levels, harmful health effects can thus occur including asthma, pneumonia and wheezing as well as allergy (Gault *et al.* 2010). Therefore, cobalt must be removed from waste waters to protect the environment and human health. Adsorption, a mass transfer process, occurs between a liquid phase and solid phase to eliminate undesirable substances (Sunil and Saifiya 2015). Even though there are several treatment techniques carried out for removing the heavy metals from aqueous solutions, adsorption is amongst the most commonly preferred methods as its technology has environmentally reliability, high capacity, relative simplicity and low cost (Khan *et al*. 2016, Varma and Misra 2016, Lee *et al*. 2017, Jafari and Bandarchian 2017). Today, a range of solid materials such as biochar (Vilvanathan and Shanthakumar 2018), biomass (Peres *et al*. 2017, Vafajoo *et al*. 2017, Hymavathi and Prabhakar 2017), carbonaceous material (Ozbay and Yargıc 2017), modified activated carbon (Dobrowolski and Otto 2012), ion-imprinted activated carbon (Turan *et al.* 2018), ion-imprinted polymer (Li *et al.* 2011, Khoddami and Shemirani 2016), nanomaterial (Amer *et al.* 2017) and nanocomposite (Zhang *et al.* 2017) have been used as adsorbent for efficient removing of Co(II). In this study, it was investigated that DWTS was utilized as an adsorbent to remove Co(II) from aqueous solutions by using adsorption

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ISSN: 2005-8624 (Print), 2092-7037 (Online)

method and adsorption of Co(II) was modelled via Artificial Bee Colony (ABC) and Genetic Algorithm (GA) methods. ABC and GA, meta-heuristic algorithms, were used to find out the optimum coefficient in the regression functions.

The ABC algorithm was developed by Karaboğa (2007) inspired from nectar-seeking behavior of bees (Karaboğa 2007). The GA is known as a frequently used optimization algorithm in technical literature developed by John Holland (Goldberg 1989).

The aim of the present study is to develop equations being quadratic, exponential, linear and power functions for prediction of Co(II) adsorption using ABC and GA methods.

## 2. Materials and methods

### 2.1 Equipments

Autosorp-6B model specific surface area analyzer was used to determine DWTS's specific surface area. The FT-IR spectrum of the DWTS was recorded between 500 and 4000 $cm^{-1}$ in a Perkin Elmer Frontier ATR – FTIR spektrometer. SEM-EDS analyses were applied using Zeiss Evo LS-10-Quanta 400F Field Emission apparatus. Elemental analysis of DWTS was performed on a LECO, CHNS-932 apparatus. Rigaku D/MAX-3C, Thermo ARL and Seteram Labsys analyzer was used for XRD, XRF and TGA/DTA analysis of DWTS, respectively. A Perkin Elmer model AAnalyst-400 Flame Atomic Absorption Spectrometer (FAAS) with deuterium background corrector was used for the Co(II) determination in solutions. Edmund Bühler GmbH model mechanical shaker was used for batch adsorption experiments. The pH measurements were made on Hanna pH-211 (HANNA instruments/Romania) digital pH meter. A centrifuge Sigma 3-16P was employed for the centrifugation of solutions. Distilled/deionized water was obtained from Sartorius Milli-Q system (arium® 611UV).

### 2.2 Chemicals

Used reagents were analytical grade of Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland). The working solutions of Co(II) for batch adsorption were prepared by diluting from 1000 mg $L^{-1}$ Co(II) with Milli Q water.

### 2.3 Preparation of DWTS

DWTS was dried at 105°C in a hot air oven for 24 h and then ground and sieved to the particle size of 74 μm.

### 2.4 Batch adsorption procedure

Batch adsorption experiments were carried out by optimizing the operation conditions for Co(II) adsorption onto DWTS. In a typical experiment, 10 mL of Co(II) solution in the concentration range of 100-1000 mg $L^{-1}$ was transferred into a 15 mL polyethylene centrifuge tube. Then, 50 mg of DWTS (5 g $L^{-1}$) was added to the solution and content was agitated on a mechanical shaker at 400 rpm for 4.0 h. After equilibrium, the phases were separated by filtration and the Co(II) concentration in the filtrate was determined by FAAS. Adsorption parameters such as initial pH of Co(II) solution, initial concentration of Co(II), contact time and adsorbent dosage were optimized by continuous variation method. For pH optimization, the initial pH of each Co(II) solution was adjusted to the required pH by addition of 0.1 M HCl or NaOH solutions. Throughout the study, the pH was varied from 2 to 7, the initial Co(II) concentration from 100 to 1000 mg $L^{-1}$, the contact time from 1 to 480 min, and the adsorbent dosage from 1 to 20 g $L^{-1}$.

Table 1 Basic statistic for the experimental data of Co(II) adsorption on DWTS

| Experimental Parameters | Unit | Min | Mean | Max | Standard Deviation | Coefficient of variation | Correlation |
|---|---|---|---|---|---|---|---|
| Initial Co(II) concentration | $mgL^{-1}$ | 80.8 | 255.125 | 946 | 228.575 | 89.593 | 0.808 |
| Initial pH | - | 2 | 4.104 | 7 | 0.755 | 18.409 | -0.074 |
| DWTS dosage | g | 0.01 | 0.052 | 0.2 | 0.03 | 57.315 | -0.083 |
| Contact time | min | 1 | 168.226 | 480 | 109.678 | 65.197 | -0.09 |
| Co(II) adsorption | $mgg^{-1}$ | 1.57 | 12.587 | 26.5 | 6.233 | 49.52 | 1 |

The adsorption capacity was calculated using the following formula

$$Q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where $Q_e$ is the amount of metal ion adsorbed on the adsorbent (mg $g^{-1}$), $C_o$ and $C_e$ are the initial and the equilibrium Co(II) concentrations (mg $L^{-1}$),V is the volume of metal ion solution used (L), and W is the mass of dry adsorbent used (g).

### 2.5 Experimental data preprocessing

Selected input parameters (initial pH, contact time, initial Co(II) concentration, DWTS dosage) affect adsorption of metal ion and play an important role in modelling. The experiments were conducted in triplicate at room temperature and the final experiment result was presented as the arithmetic mean of the triplicate experiments. The main statistics of the experimental parameters are given in Table 1. Input data were normalized between 0.1 and 0.9 to avoid numerical overflows because of parameters in different orders. The utilized normalization function is defined as follows:

$$E_i = 0.8\frac{E - E_{\min}}{E_{\max} - E_{\min}} + 0.1 \quad (2)$$

where E is input and output data, $E_i$ is the normalized value of E, the $E_{max}$ and $E_{min}$ are the maximum and minimum value of E, respectively.

Regression models such as quadratic, exponential, linear, and power functions are used in modelling of Co(II) adsorption on DWTS. Coefficients of regression functions are optimized for effective model using ABC and GA.

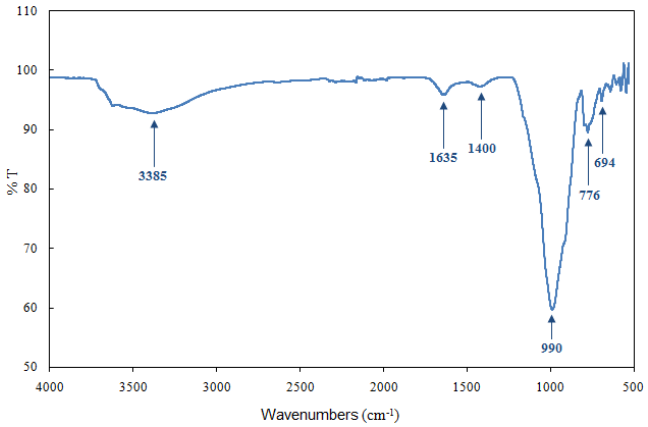


Fig. 1 FT-IR spectrum of DWTS

These algorithms pseudo-codes are given below (Öztürk *et al.* 2016).

### 2.6 Artificial Bee Colony (ABC) algorithm

The algorithm simulated the intelligent foraging behavior of honey bee is composed from three main components namely nectar sources, employed bees and unemployed bees. Unemployed bees are onlooker and scout bees. In the optimization problem, possible solutions correspond to nectar sources (Karaboğa *et al.* 2014, Aderhold *et al.* 2010). In this study, ABC algorithm was applied to find out optimum coefficient of the regression functions. Pseudocode of ABC algorithm is given below:

1: Initialize the population
2: Evaluate the population
3: cycle=1
4: **repeat**
5: Produce new solution and evaluate them
6: Apply selection process according to greedy selection applied to the current and new solution
7: Calculate the probability values for the solutions
8: Produce the new solutions for onlooker bees from the solution selected depending on probability values and evaluate them
9: Apply selection process according to greedy selection applied to the current and new solution
10: Determine the abandoned solution for the scout, if exists and replace it with a new randomly produced solution
11: Memorize the best solution
12: cycle =cycle + 1
13: **until** cycle =MCN

### 2.7 Genetic algorithm (GA)

GA, search algorithm, is based on concepts of natural selection and natural genetics (Holland 1992). GA was developed to simulate some of the processes observed in natural evolution, a process that operates on chromosomes (organic devices for encoding the structure of living being). The GA method differs from other search methods in that it searches among a population of points and works with a coding of parameters set, rather than the parameter values themselves (Goldberg 1989, Ding *et al.* 2018, Sivanandam and Deepa 2008, Donelli 2017). GA was used to obtain optimum coefficient of the regression functions. The working principle of GA is illustrated in the form of a pseudocode as follows:

1: Initialize the population
2: Evaluate the population
3: cycle=1
4: **While** cycle=MCN do
5: Calculate objective functions
6: Calculate fitness
7: Select parents for crossover
8: Set the crossover and mutation probability
9: Perform crossover and mutation
10: Evaluate population
11: Memorize the best solution
12: cycle =cycle + 1
13: **EndWhile**

### 2.8 Performance of the developed models

Since the pollutant removal efficiency and performance of developed ABC and GA models are measured, different types of statistical parameters can be used to determine the generalization error. In the present work, the objective function of the models is sum square error (SSE) calculated as follows:

$$\min f(x) = \sum_{i=1}^{N} (P_i - E_i) \tag{3}$$

where N is the number of experiments, $E_i$ is the ith experimental adsorption value, and $P_i$ is the ith predicted adsorption value for the regression functions.

The regression equations were evaluated using data in training set for each experimental parameter and the best ones having minimum SSE are determined. Root mean square error (RMSE), mean absolute error (MAE), average relative error (ARE), and coefficient of determination ($R^2$) for training and testing sets were selected to measure the performance of models ABC and GA.

$$RMSE = \left[ \frac{1}{N} \sum_{i=1}^{N} (P_i - E_i)^2 \right]^{\frac{1}{2}} \tag{4}$$

$$MAE = \frac{1}{N} \sum_{i=1}^{N} |P_i - E_i| \tag{5}$$

$$ARE = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{P_i - E_i}{P_i} \right) x100 \tag{6}$$

$$R^2 = 1 - \left( \frac{\sum_{i=1}^{N} (P_i - E_i)^2}{\sum_{i=1}^{N} P_i^2} \right) \tag{7}$$

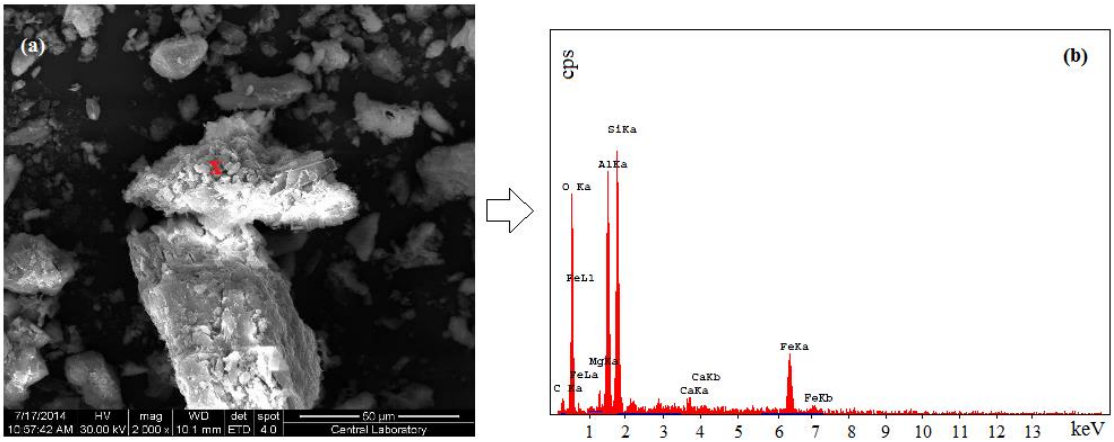


Fig. 2 (a) SEM micrograph of DWTS (magnification: 2000 folds) and (b) EDS spectrum

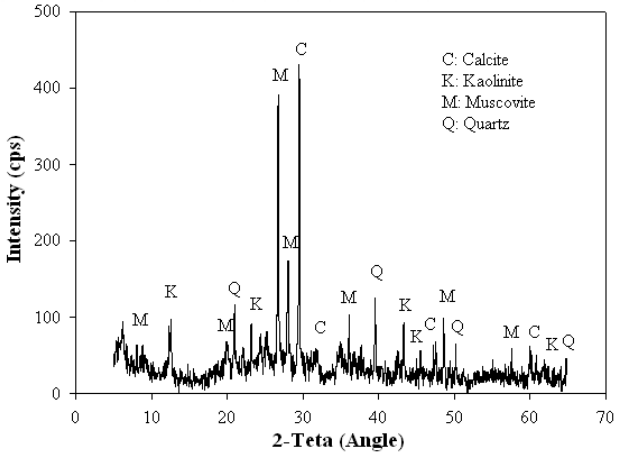


Fig. 3 XRD pattern for DWTS

Table 2 XRF analysis of DWTS

| Components % by mass | | | | | | |
|---|---|---|---|---|---|---|
| $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $Na_2O$ | $K_2O$ |
| 52.50 | 17.70 | 7.30 | 4.60 | 2.70 | 1.90 | 1.80 |
| $TiO_2$ | $SO_3$ | MnO | $P_2O_5$ | BaO | SrO | $V_2O_5$ |
| 0.6 | 0.25 | 0.2 | 0.2 | 0.06 | 0.02 | 0.02 |
| ZnO | $ZrO_2$ | CuO | Loss on ignition | | | Total |
| 0.02 | 0.02 | 0.01 | 9.70 | | | 99.6 |

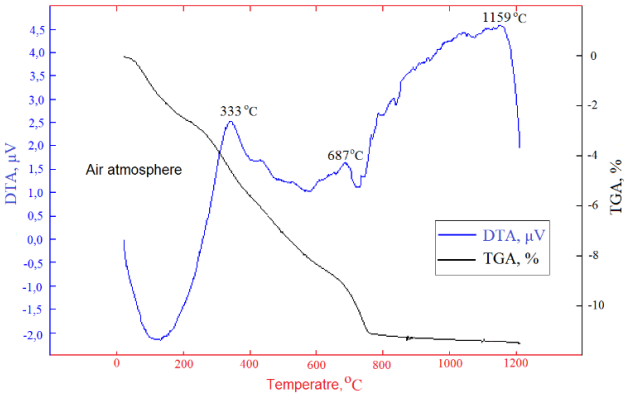


Fig. 4 DTA/TGA plot of DWTS

## 3. Results and discussion

### *3.1 Characterization of DWTS*

The chemical structure and functional groups of adsorbents can define its adsorption capacity. For this purpose, the infrared spectrum (500-4000 $cm^{-1}$) of DWTS was depicted in Fig. 1. The broad peak observed at 3385$cm^{-1}$ is due to stretching vibrations of the bonded hydroxyl (–OH) groups present in the sample. The peak at 1635 $cm^{-1}$ can indicate C=C group and/or hydroxyl deformation of water. The peak appearing at 1400 $cm^{-1}$ can be stretching vibrations peak of C–H group. Two peaks at 990 and 694 $cm^{-1}$ point to existence Si–O group and the peak at 776 $cm^{-1}$ is Al–O–H peak (Öztürk 2014).

The Scanning electron microscopy (SEM) analysis method was used to determine the grain size and surface morphology of the mineral phases in DWTS. As a result of micro structure analysis of DWTS, it was observed that it contained flocked square and leafy particles at the changing sizes (Fig. 2). EDS analysis was also performed to determine the presence of elemental information on DWTS. The prominent peaks in the EDS spectrum (Fig. 2) correspond to CKα, OKα, FeKα, AlKα, SiKα, MgKα, CaKβ, etc. in DWTS.

The crystallinity of the DWTS was determined by X-ray diffraction (XRD) and the result indicates that DWTS consists mainly of calcite, kaolinite, muscovite and quartz (Fig. 3).

The chemical composition of DWTS was determined by XRF. As seen from Table 2, $SiO_2$, $Al_2O_3$, $Fe_2O_3$ and CaO are found mainly in DWTS. It is known, adsorbents with inorganic oxides (such as $SiO_2$, $Al_2O_3$ and $Fe_2O_3$) can show an extremely high adsorption ability.

Thermal behavior of DWTS was observed by employing TGA/DTA analysis. In air atmosphere, changes occurring in the DWTS structure were investigated by drawing temperature versus DTA/TGA plot. As can be seen from Fig. 4, the rate of mass change decreased by increasing the temperature. The results of the BET (Brunauer-Emmett-Teller) surface area ($S_{BET}$), t-plot micropore area ($S_{micro}$), mesopore area ($S_{meso}$), total pore volume ($V_t$), micropore

Table 3 Characteristics of DWTS

| Pore structure of DWTS | |
|---|---|
| SBET ($m^2$ $g^{-1}$) | 15.53 |
| Smicro ($m^2$ $g^{-1}$) | 16.15 |
| Smeso ($m^2$ $g^{-1}$) | 6.93 |
| Vt ($cm^3$ $g^{-1}$) | 0.041 |
| Vmicro ($cm^3$ $g^{-1}$) | 0.006 |
| Dp (nm) | 2.80 |
| Elemental analysis (wt%) | |
| C | 2.37 |
| H | 0.91 |
| N | 0.60 |
| S | 0.25 |
| Surface functional groups (mmol $g^{-1}$) | |
| Carboxylic | 1.93 |
| Phenolic | 0.11 |
| Lactonic | 0.05 |
| Total acidic value | 2.09 |
| Proximate analyses (wt%) | |
| Moisture | 1.78 |
| Volatile matter | 10.46 |
| Fixed carbon | 4.76 |
| Ash | 84.77 |
| Iodine number (mg $g^{-1}$) | 235.8 |
| Methylene Blue number (mg $g^{-1}$) | 256.9 |
| pH | 6.65 |
| $pH_{PZC}$ | 6.95 |

volume ($V_{micro}$) and average pore diameter ($D_p$) calculated from $4V_t/S_{BET}$ formula for DWTS were listed in Table 3. The BET surface area of the DWTS shows that it does not have a porous structure, and SEM images support this. However, surface area and porosity of an adsorbent may not explain its the adsorption properties. When we look at the pore size distributions of DWTS (Table 3), it is seen that the adsorbent is composed of micro and meso pores. Macro pores are less effective in the adsorption process, but they play an important role in separating very large molecules. Therefore, meso and micro pores are highly active in the adsorption process. Percentage amount of moisture, volatile matter, fixed carbon, ash and C, H, N, S and O contents obtained from the elemental analysis of DWTS was given in Table 3. According to proximate analysis results, low amounts of fixed carbon and volatile matter and high ash content indicate that the structure of the adsorbent has an inorganic content, also elemental analysis results support this. The quantity of acidic functional groups affecting adsorption capacity on DWTS surface were determined and listed in Table 3. The quantitative values of the carboxylic, phenolic and lactone groups present on the DWTS have been determined by Boehm titration. When the values in Table 3 are examined, it is seen that there are more

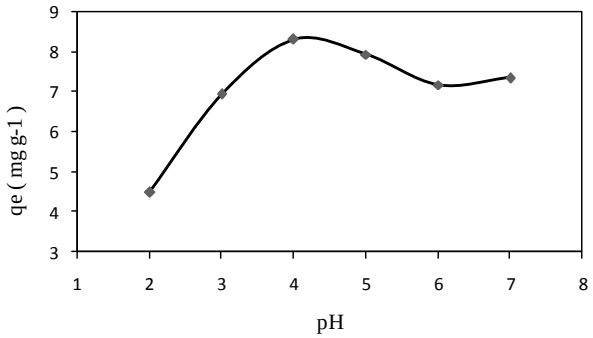


Fig. 5 Effect of pH on the adsorption of Co(II) by DWTS (Initial Co(II) conc.: 100 mg $L^{-1}$, DWTS conc.: 5.0 g $L^{-1}$, contact time: 45 min; agitation speed: 400 rpm)

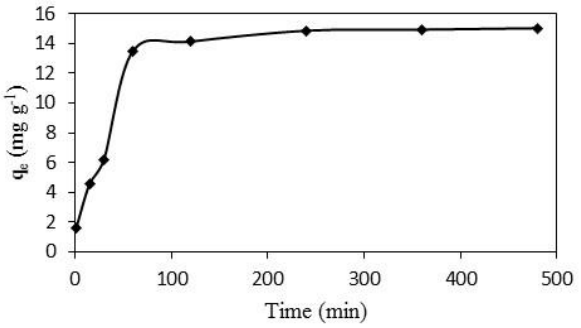


Fig. 6 Effect of contact time (initial Co(II) conc.: 100 $mgL^{-1}$; DWTS conc.: 5.0 g $L^{-1}$; pH: 4.0; agitation speed: 400 rpm)

carboxylic groups among the acidic groups on the surface of the adsorbent. Methylene blue and iodine numbers, can give an idea about the mesopore and micropore (pore diameter lower than 1nm) structure respectively, were defined (ASTM D4607-94 2006). Iodine and Methylene Blue numbers have given a preliminary idea of the development of pore structures of DWTS. It has an average pore diameter (2.80 nm) in excess. DWTS's pH value and value of $pH_{PZC}$ were determined. The $pH_{PZC}$ is the pH value at which net surface charge of the adsorbent is neutral (Mestre *et al*. 2007). The surface charge of DWTS was negative at $pH>pH_{PZC}$, while it was positive at $pH<pH_{PZC}$ (Öztürk 2014). The pH value of the adsorbent is 6.65. The pH value of the adsorbent is found to be slightly acidic and the $pH_{PZC}$ values lower than 7 (6.95) indicate that the acidic groups are more dominant than the basic groups. Although the net surface charge of the adsorbent is still positive at this pH value (4.0) because of $pH< pH_{PZC}$, the adsorption of this metal on the DWTS is highly efficient in the aqueous solution. At this pH value (4.0), although the surface functional groups of the adsorbent are slightly protonated, the proton and metal cations can be displaced, and so the adsorbent is more likely to prefer metal ions. The protonated surface functional groups of DWTS can play a crucial role in Co(II) removal.

### *3.2 Effect of solution pH*

The pH of the solution is an important parameter affecting the activity of the functional groups on the

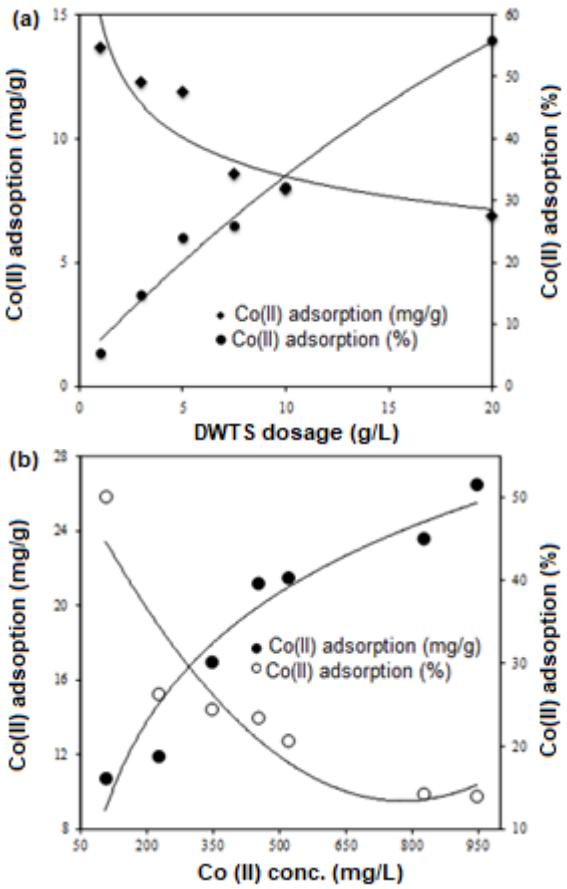


Fig. 7 (a) Effect of adsorbent dosage on the adsorption of Co(II), (b) effect of initial Co(II) concentration on the adsorption of Co(II)

adsorbent surface and the competition of metal ions to get adsorbed to the active sites. The effect of pH on the adsorption of Co(II) onto DWTS was investigated in the pH range of 2-7 using 10 mL of model solutions containing 5.0 g $L^{-1}$ of DWTS suspension for 2.0 h as shown in Fig. 5. The experimental results revealed that the maximum adsorption (8.3 mg $g^{-1}$) of Co(II) took place at pH 4.0.

### *3.3 Effect of contact time*

The effect of contact time on the adsorption Co(II) ions onto DWTS was investigated in the time ranges of 1-480 min by contacting 100 mg $L^{-1}$ of Co(II) solutions at initial pH 4.0 with 5.0 g $L^{-1}$ of DWTS suspensions to decide whether the equilibrium was reached. It was observed that Co(II) adsorption rate is high at the beginning of the adsorption because of more available adsorption sites easily adsorbing Co(II) ions and then Co(II)-DWTS interactions reached equilibrium at 4.0 h (Fig. 6). Thus, the contact time of 4.0 h was used in the following adsorption experiments.

### *3.4 Effect of DWTS and initial Co(II) concentrations*

The adsorption process was conducted with initial Co(II) concentrations between 100 and 1000 mg $L^{-1}$ and DWTS concentrations between 1.0 and 20.0 g $L^{-1}$ at constant values of pH (4.0) and contact time (4.0 h) to investigate the effect of Co(II) and DWTS concentration on

Table 4 The coefficient obtained from the analysis

| Coefficients | Quadratic Function (QF) | | Exponential Function (EF) | | Linear Function (LF) | | Power Function (PF) | |
|---|---|---|---|---|---|---|---|---|
| | ABC | GA | ABC | GA | ABC | GA | ABC | GA |
| $w_0$ | 0.9672 | 0.0978 | -0.7341 | 0.0372 | 0.2289 | 0.2606 | 1.1094 | 1.1958 |
| $w_1$ | 2.6597 | 3.4763 | 0.0950 | -1.3018 | 0.8269 | 0.8133 | 0.5258 | 0.5355 |
| $w_2$ | -0.7446 | 0.7175 | 0.5942 | 1.4377 | -0.0218 | -0.0489 | 0.1169 | 0.0946 |
| $w_3$ | -0.0019 | -1.0759 | -0.0585 | -0.0487 | -0.1771 | -0.2061 | -0.1390 | -0.1177 |
| $w_4$ | -2.9202 | -0.7929 | -0.2482 | -0.3736 | 0.1739 | 0.1544 | 0.1932 | 0.2417 |
| $w_5$ | -5.0000 | -4.3327 | 0.0282 | 0.3317 | | | | |
| $w_6$ | -4.1034 | -5.0000 | | | | | | |
| $w_7$ | 5.0000 | 1.6754 | | | | | | |
| $w_8$ | -1.8020 | 1.1365 | $x_1$ : | Initial Co(II) concentration | | | | |
| $w_9$ | 4.6889 | 0.8150 | $x_2$ : | Initial pH | | | | |
| $w_{10}$ | 5.0000 | 5.0000 | $x_3$ : | DWTS dosage | | | | |
| $w_{11}$ | -0.3695 | -0.1333 | $x_4$ : | Contact time | | | | |
| $w_{12}$ | -1.0887 | -0.8514 | y : | Co(II) adsorption | | | | |
| $w_{13}$ | -0.1429 | -0.0113 | | | | | | |
| $w_{14}$ | -0.8011 | -0.7654 | | | | | | |

$$y_{Quadratic} = w_0 + w_1x_1 + w_2x_2 + w_3x_3 + w_4x_4 + w_5x_1x_2 + w_6x_1x_3 + w_7x_1x_4 + w_8x_2x_3 + w_9x_2x_4 + w_{10}x_3x_4 + w_{11}x_1^2 + w_{12}x_2^2 + w_{13}x_3^2 + w_{14}x_4^2$$

$$y_{Exponential} = w_0 + exp(w_1 + w_2x_1 + w_3x_2 + w_4x_3 + w_5x_4)$$

$$y_{Linear} = w_0 + w_1x_1 + w_2x_2 + w_3x_3 + w_4x_4$$

$$y_{Power} = w_0x_1^{w_1}x_2^{w_2}x_3^{w_3}x_4^{w_4}$$

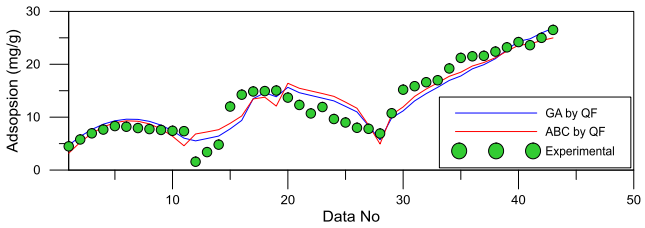


Fig. 8 The comparison of the experimental adsorption with the predicted ones by ABC and GA models for training set

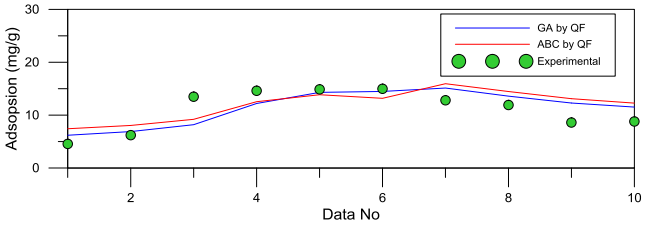


Fig. 9 The comparison of the experimental adsorption with the predicted ones by ABC and GA models for testing set

the removal of this metal. The experimental results showed that percentage of Co(II) adsorption increased by increasing DWTS concentration even though the amount of Co(II) adsorbed by per gram of DWTS decreased (Fig. 7(a)) because the available adsorption sites or functional groups increased with more adsorbent present, and the interactions may also take place between adsorbent and metal ions as

Table 5 Modelling results for training set

| | Algorithm | SSE (mg/g) | RMSE (mg/g) | MAE (mg/g) | ARE (%) | $R^2$ |
|---|---|---|---|---|---|---|
| QF | ABC | 322.65 | 2.467 | 2.066 | 19.98 | 0.968 |
| | GA | 275.64 | 2.281 | 1.882 | 18.07 | 0.973 |
| LF | ABC | 619.91 | 3.42 | 3.039 | 29.10 | 0.937 |
| | GA | 618.06 | 3.415 | 3.022 | 28.70 | 0.937 |
| EF | ABC | 666.50 | 3.546 | 3.104 | 28.17 | 0.933 |
| | GA | 708.68 | 3.657 | 3.307 | 29.56 | 0.927 |
| PF | ABC | 610.92 | 3.395 | 3.013 | 30.21 | 0.938 |
| | GA | 608.82 | 3.389 | 2.992 | 30.08 | 0.938 |

Table 6 Modelling results for testing set

| | Algorithm | RMSE (mg/g) | MAE (mg/g) | ARE (%) | $R^2$ |
|---|---|---|---|---|---|
| QF | ABC | 2.95 | 2.75 | 24.55 | 0.942 |
| | GA | 2.58 | 2.15 | 20.92 | 0.953 |
| LF | ABC | 3.44 | 2.91 | 31.10 | 0.889 |
| | GA | 3.45 | 2.96 | 31.28 | 0.890 |
| EF | ABC | 3.69 | 3.28 | 33.16 | 0.880 |
| | GA | 3.33 | 2.97 | 29.76 | 0.900 |
| PF | ABC | 3.82 | 3.38 | 35.69 | 0.868 |
| | GA | 3.75 | 3.22 | 34.26 | 0.872 |

the amount of adsorbent decreases at certain metal ion concentration. This is related to limiting factor and limiting factor in Fig 7(a) could be a limited amount of Co(II) while the DWTS amount could be a limiting factor in Fig 7(b). Therefore, the Co(II) adsorption (%) continuously decrease as both factors increased. Besides, the amount of Co(II) uptake increased by increasing the initial Co(II) concentration although adsorption percentages decreased with increase in the Co(II) concentration (Fig. 7(b)).

### *3.5 Modelling Results*

In this study the parameters of ABC algorithm such as colony size, limit and max. number of cycles were taken 100, 100 and 10000 respectively. The parameters of GA such as population size, mutation rate, mutation percentage, crossover percentage, max. number of cycles were taken 100, 0.1, 0.3, 0.7 and 10000 respectively. Roulette wheel selection method and two point crossover were used in GA. ABC and GA were programmed in MATLAB (2014).

Four regression functions were used in modeling to predict Co(II) adsorption considering with the experimental results. ABC and GA were utilized to optimize unknown coefficients ($w_i$) of the independent variables ($x_i$). Obtained coefficients from the algorithms are shown in Table 4. The data set is divided into two parts as training and testing set. The training set is chosen larger to train the generated regression equation in a good way and this set is used to optimize the coefficients whereas the testing set does not participate in the optimization process. The testing set is randomly selected from the data and used to measure the performance of the generated equation.

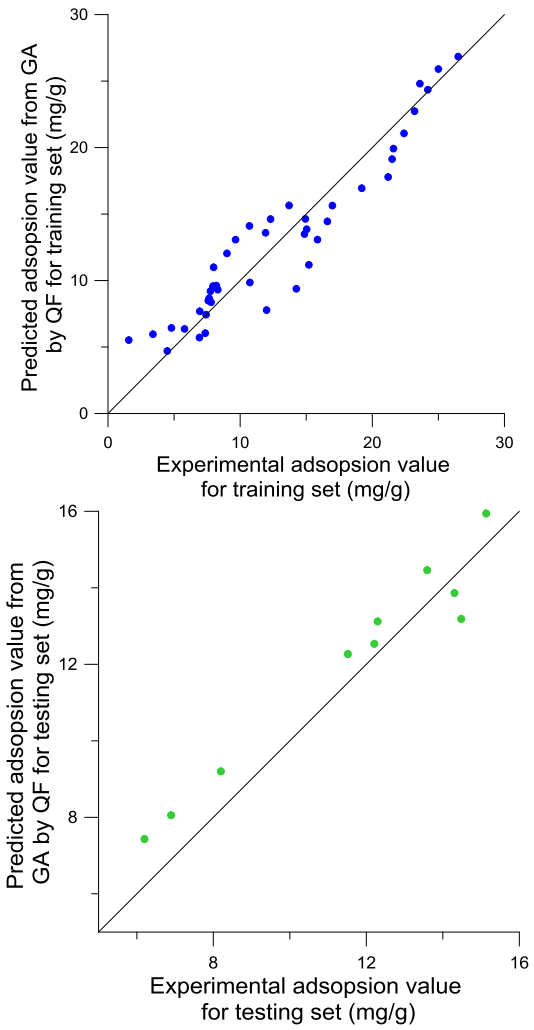


Fig. 10 The comparison of the experimental adsorption with the predicted ones by GA models for training and testing sets

The results obtained from the determined equations were compared with considering SSE, RMSE, MAE, ARE and $R^2$ indices. The error indices for testing and training sets are presented in Table 5-6. It is seen from Table 5 that the best equation is obtained from the quadratic function employing GA for training set. Also, quadratic function employing GA for testing set has the best error and $R^2$ values.

Fig. 8 and 9 illustrate a comparison of the experimental results with the predicted ones from the determined QF for the training and testing sets. Fig. 10 also supplies a different presentation of the performance for the best fitting model for the training and testing sets. If the points gather around the diagonal, smaller error and greater $R^2$ values are obtained.

## 4. Conclusions

The utilization of waste materials such as DWTS, occurred as a by-product of the use of coagulation-

flocculation processes in drinking water treatment, in wastewater treatment has an important role in terms of the environment. Based on the idea that waste materials should be recycled, it has been investigated the usage of DWTS as an adsorbent to remove Co(II) from aqueous solution in this work. Furthermore, the application of ABC and GA to model Co(II) adsorption prediction on the experimental parameters (initial pH, contact time, initial Co(II) concentration, DWTS dosage) is examined and verified by conducted experiments. This study shows the best fit equation for each parameter is obtained from the quadratic function. Performance of GA is better than ABC in the prediction of Co(II) adsorption.

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