Prediction of Methyl Orange Removal by Iron Decorated Activated Carbon using an Artificial Neural Network

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Abstract

Date Stones were used as a bio-degradable waste source for preparing iron impregnated activated carbon. The prepared activated carbon-containing oxides of iron were characterized using SEM, XRD, FTIR, and BET. The specific surface area of the iron decorated activated carbon was 738.65 m²/g. The XRD confirmed the presence of magnetite and hematite while the SEM images assured the presence of pores. The prepared activated carbon was used to remove methyl orange from wastewater. Genetic Algorithm was used to develop a model which could predict the removal efficiency of the dye. The ANN model was validated and the effect of different parameters like adsorbent dosage (0.1-1g/L), initial dye concentration (2-20 mg/L), pH (2-11), time (10-55 minutes) and temperature (30-75°C) was estimated both experimentally and predicted using the model. The adsorption process follows the Freundlich isotherm and pseudo-second-order kinetic model. The values of 1/n and K_F obtained from the Freundlich isotherm designate good adsorption capacity. Both experimental and model-predicted data agrees with the kinetic model. The adsorption rate is proportionate to the square of the number of vacant adsorption sites. From the thermodynamic study, the positive worth of ΔH° indicates the energy-absorbing nature of the surface assimilation method and the process is endothermic in nature. The low values of each ΔG° (-200 to 0 kJ/mol) and ΔH° correspond to physical surface assimilation. A positive worth of ΔS° reflects the inflated randomness at the solid-aqueous interface with some structural changes in adsorbate and adsorbent.

Keywords: *activated carbon, artificial neural network, date stones, methyl orange, regression*

1. Introduction

Discharge of wastewater containing chemicals and dyes from industries such as textiles, paper, etc., is considered as a serious global problem due to aquatic and environmental pollution. Synthetic dyes are man-made chemicals that are extremely toxic and have a carcinogenic effect on humans and animals and will cause irreversible damage to the ecosystem, if released untreated in the environment (Tsuboy et al. 2007, Vinitnantharat et al. 2008). Therefore, it is necessary that these effluents are treated to an acceptable industry standard before being discharged into the environment. Methyl Orange (MO) is a common dye used in textile industries. It has been shown that MO is highly toxic and causes severe irritation of eyes and may lead to permanent ocular damage (Mitra and Mukherjee 2018). Treatment technologies such as adsorption, oxidation-ozonation, biological treatment, coagulation-flocculation, and membrane processes were shown to be used for the treatment of dye-containing effluents (Ghaedi et al. 2017). Among the above-mentioned methods, the adsorption process was proved to be the most commonly used method for dye removal due to its high efficiency, availability of different sorbent materials and easy handling.

Activated carbon is the most commonly used absorbent material and is found to be more effective in dye removal compared to other natural or synthetic adsorbents due to its large surface area, micro-porosity and high degrees of surface reactivity and adsorption capacity (Alslaibi et al. 2013). The process is a high-temperature application with wide-ranging pH and high porosity that increases adsorption capacity etc. (Noorimotlagh et al. 2016, Jaafarzadeh et al. 2019). Activated carbon impregnated with metal oxides increases catalytic oxidation and enhances adsorption capacities. However, activated carbon is expensive and therefore, it is necessary to find an alternative cheap and easily available adsorbent (Mirzaei et al. 2017). Agricultural wastes such as coconut shells, peanut shells, rice straw, sugarcane bagasse, rice husk etc. have been of great research interest due to its abundance and ability to biodegrade in nature benignly and can be disposed of without regeneration (Vinitnantharat et al. 2008, Alslaibi et al. 2013). The bio-sorption process is dependent on the availability of the functional groups such as carboxylic, phenolic, ether, cellulose, lignin, alcohols and aldehydes on the biosorbents (Qada et al. 2006).

Date palm (*Phoenix dactylifera* Linn) stones or pits are the leftover waste products obtained from the Date processing industries. These stones or pits contain about 47.14% carbon

and have been used to produce commercially feasible adsorbent for removal of dye in wastewaters (Ghouti et al. 2010, Ozbelge et al. 2002, Pasalari et al. 2017). If a theoretical prediction model is developed it can be used to obtain reasonable estimates of the adsorption of dye at different parameter value which can be obtained by using different statistical and learning procedures, like multiple linear regression (MLR), artificial neural network (ANN), partial least square (PLS), etc. (Ghaedi et al. 2011). Among the modeling tools, ANN has recently become a very efficient and popular modeling tool. It is an information processing tool that can establish a relationship between input and output data by extracting information presented to the network. The major advantage of ANN is its ability to use and solve nonlinear relationships and thereby predict adsorption accurately (Mukherjee et al. 2018, Mukherjee and Rahaman 2018, Roosta et al. 2014, Kalyanmoy 1996).

Thus, a model predicting the removal of MO dye using activated carbon obtained from biodegradable waste (Date stones) has not been reported to that extent. This research focuses on the production of value-added products for the treatment of wastewater and also developing a prediction model using Artificial Neural Network. In this study, the adsorption behavior of Date stone activated carbon impregnated with iron particles for the removal of MO dye from aqueous solution was investigated. The impregnated activated carbon can be separated from the wastewater using an external magnet source (Nia et al. 2014). This prevents the loss of produced activated carbon and its easy separation from the solution. Different parameters such as pH, adsorbent dosage (g/L), the initial concentration of dye (mg/L) and temperature (°C) were studied by using ANN. Freundlich isotherm and Langmuir isotherm models were used to describing the experimental sorption data (Karimi et al. 2014). Finally, the mechanism of bio-sorption was elucidated by using pseudo-first-order and second-order kinetic models.

2. Materials and Methods

2.1. Feedstock

Date stones (DS) were collected from a local dry fruit vendor. The stones were washed and dried at room temperature prior to use.

2.2. Materials and Measurements

For laboratory experiments, analytical grade chemical reagents were sourced from Sigma-Aldrich, Bhupendra Shah & Co., Kolkata, India. Iron Sulphate Heptahydrate ($\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$) was used for iron impregnation. Potassium Hydroxide (KOH), 37% hydrochloric acid (HCl), Sodium Hydroxide (NaOH) were used for the pH adjustment. Methyl Orange (MO) was purchased from Hexon Laboratories, Mumbai, India. All reagents were used without further purification.

For the determination of the removal efficiency of the MO solution, UV–visible spectrophotometer (LMSP UV1000B) was used. The morphological studies were carried out using Scanning electron microscopy (SEM) (ZEISS EVO-MA). The scan settings were fixed at an emission current of 100 mA and an accelerator voltage of 10 kV. The diffraction patterns of the prepared activated carbon were analyzed using an XRD performed with Pananalytical PW 3040/60 X'pert Pro-powder diffractometer. ASAP 2020 MICROMERITICS was used to measure the specific surface area and to characterize the pore structure of the activated carbons. Chemical characterization was carried out by FTIR spectroscopy in order to identify the functional groups at the surface of DSAC using Thermo Nicolet Nexus 870 FTIR instrument in the region of 400–4000 cm^{-1} . The samples were prepared as KBr pellets, comprised of a 1 mg sample of dried DSAC and 100 mg ground KBr.

2.3. Preparation of Date Stone Activated Carbon (DSAC)

Dust particles were removed by thoroughly washing the DS. Later, DS was dried at 85 °C for 24 hours in a hot air oven. The dried DS was then carbonized at 400 °C for 2 hours in a muffle furnace. The carbonized Date stones (CDS) were then passed through a 250 μm mesh (0.250 mm). The fine particles collected thus were then chemically treated with 5% KOH. The ratio of KOH solution and CDS was kept at a 2:1 ratio. Activation was progressed for 12 hours and then it was thoroughly washed to make it neutral. Partially activated carbon was again dried in a hot air oven for 24 hours and then the dried material was put into muffle furnace for further carbonization at 700 °C for 2 hours.

2.4. Preparation of iron impregnated DSAC (DSAC/Fe)

DSAC was precisely weighed in a requisite amount (1:5 (w/w) ratio) and mixed with iron salt ($\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$). The solution was agitated and heated to 100 °C for 2 hours using a

magnetic stirrer. The hydrated iron oxides were precipitated using 10% NaOH solution. Lastly, the Fe impregnated DSAC product (DSAC/Fe) was carefully washed with excess water to neutralize it. Then it was dried for storage. The final product was approximately spherical in shape with a diameter of around 0.090mm.

2.5. Experimental set-up

All experiments were performed in batch mode. For each batch, 100 ml of an aqueous solution of MO dye was transferred to a flask. Temperature controlled magnetic stirrer was used to ensure proper mixing. Reactor contents were mixed at a mixing speed of 350 rpm and were kept constant for all the experiments. Initial concentrations of the dye solution were varied in the experiments. At acidic conditions the removal efficiency is maximum (Refer to section: 3.3.1.) and hence, the preliminary pH of the solution was kept constant at 2 pH by adding 0.1M HCl and 0.1M NaOH solution before DSAC/Fe was added. A pre-determined amount of activated carbon was used here. After a fixed amount of time elapsed (300 minutes), the solution was filtered. UV-Visible Spectrophotometer at a wavelength of 463nm was used to obtain the final MO solution concentration. The amount of adsorption at equilibrium or the adsorption capacity (q_e) was calculated using equation 1 (Karimi et al. 2014):

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

where, C_o and C_e (mg/L) are the concentrations of the MO dye in solution initially and at equilibrium respectively, while V is the solution volume (L) and W is the mass of adsorbent used (g). The percentage removal of dye was determined using equation 2:

$$\text{Removal Efficiency} = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

Where, C_i and C_f are the initial and final concentrations of the MO solution, respectively.

2.6. Isotherm and Kinetics of Adsorption

Designing and choosing the finest operating conditions for a full-scale batch process, the prediction of the adsorption rate offers important information. Adsorption kinetics and isotherms

deliver valuable data about the mechanism of the reactions, the reaction pathways, and the mechanisms governing the adsorption routes, such as mass transfer (Karimi et al. 2014; Zeinali et al. 2014).

2.6.1. Langmuir Isotherm

The Langmuir isotherm assumes simple monolayer adsorption onto an adsorbent surface comprising of a finite number of adsorption sites. There is no lateral interaction between the dye molecules and no migration of adsorbate in the same plane. Moreover, the model assumes only a fixed number of energetically invariant active sites. The Langmuir isotherm in its linear form is shown in equation 3 (Kakavandi et al. 2014):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (3)$$

where q_e is the mass of adsorbate adsorbed per unit mass of adsorbent, C_e is the equilibrium concentration of the adsorbate, b and Q_0 are the Langmuir constants which are dependent on the rate and adsorption capacity respectively. To confirm the acceptance of the process, the dimensionless equilibrium parameter R_L was used (equation 4)(Kakavandi et al. 2014):

$$R_L = \frac{1}{(1 + b \times C_0)} \quad (4)$$

Where, b is the Langmuir constant and C_0 is the highest MO dye concentration (mg/L). R_L values indicate the type of adsorption that is taking place (unfavorable($R_L > 1$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$)).

2.6.2. Freundlich Isotherm

Freundlich isotherm assumes varied scattering of the surface energy of the active sites which also depends on the surface coverage. The linear form of the Freundlich model is shown in equation 5(Kakavandi et al. 2014):

$$\log q_e = \log K_F + \frac{1}{n} \times \log C_e \quad (5)$$

where K_F and n are constants combining the factors affecting the adsorption capacity and the amount of non-linearity between the MO dye concentration in the solution and the amount adsorbed at equilibrium, respectively. The value of $1/n$ summarizes the adsorption characteristics. If the value is between 0 and 1, the adsorption intensity attains a more non-uniform distribution. Moreover, if the value is less than 1, normal Langmuir isotherm can elucidate the adsorption process without loss of generalization while a value greater than 1 is a characteristic of co-operative adsorption (Zeinali et al. 2014, Kakavandi et al. 2014).

2.6.3. Pseudo-First-Order kinetic model

The Lagergren pseudo-first-order model has established on the postulation that the adsorption rate is related to the number of existing adsorption sites, and is expressed in equation 6 (Karimi et al. 2014, Azari et al. 2015):

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad (6)$$

Where, K_1 (1/min) is the rate constant of the pseudo-first-order adsorption, q_t and q_e (mg/g) are the amounts of the adsorbate adsorbed per gram of adsorbent at any time t and at equilibrium, respectively. Applying $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ as the boundary conditions, and integrating, the following equation 7 is obtained (Zeinali et al. 2014):

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (7)$$

The plot of $\ln(q_e - q_t)$ against t permits the kinetic model to be assessed and the values of K_1 and q_e to be determined from the slope and intercept, respectively.

2.6.4. Pseudo-Second-Order kinetic model

The pseudo-second-order kinetic model was founded on the hypothesis that the adsorption rate is proportionate to the square of the number of vacant adsorption sites. It is shown inequation 8 (Zeinali et al. 2014):

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (8)$$

Where K_2 (g/mg min) is the rate constant of the pseudo-second-order adsorption. Applying $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ as the boundary conditions, and integrating, the following equation 9 is obtained (Zeinali et al. 2014):

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + K_2 t \quad (9)$$

Equation 9 is generally expressed as equation 10 (Karimi et al. 2014):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

Where $K_2 q_e^2$ can be considered as the preliminary adsorption rate as $t \rightarrow 0$. The plot of t/q_t against t permits the kinetic model to be assessed and the values of K_2 and q_e to be determined from the intercept and slope, respectively.

2.7. Development of a Genetic Algorithm

2.7.1. Artificial Neural Network (ANN)

ANNs are highly efficient, non-linear analytical tools that can find the relationship between input/output data without previous information of the connection among the variables involved in the scheme (Hoda et al. 2006). The essentials of a neural network are the neurons, which are concealed and output layers of the network (Figure 1).

$$a_i = m \sum_{j=1}^m W_{ij} X_j \quad (11)$$

$$n_i = f(a_i + b_i) \quad (12)$$

in which are the input values, w_{ij} s; are the weights of neuron i , b_i is the bias, $f(-)$ is the initiation function, and n_i is the yield value of the neuron.

Figure 1: Schematic representation of the Artificial Neural Network

The ANN method resolves problems using a multilayer perceptron (MLP). This MLP topology is made of (i) input layer of the neuron (independent variables), (ii) a number of hidden layers, and (iii) output layer (dependent variables) (Kumar et al. 2009). The complexity of the problem decides the number of hidden layer neurons. Most problems can be modeled by ten hidden layers. An algorithm known as “training” is used by the MLP to learn the data pattern and modify weights of the neurons in accordance with the error between the values of real and net output that gives the connection between inputs and outputs variables and are very valuable in identifying forms in intricate statistics (Mitra et al. 2018). An instance of training algorithms is the backpropagation algorithm that is extensively used to train ANN in numerous complications of science and engineering.

2.7.2. Optimal conditions based on genetic algorithm

A successful method for solving linear and nonlinear problems is the genetic algorithm (GA). The algorithm discovers diverse parts of the constricted space and guides the pursuit to the area wherever a high prospect of global optimum occurs (Ahn 2006 and Montgomery 2007). In the planned technique, the ANN is trained and subsequently, the genetic algorithm then can be used to improve the input variables, with a goal to maximize the percentage of dye removal. GA based optimization methods were performed by utilizing trained ANN models as the suitability functions to yield the globally optimized solutions (Zhang et al. 2010, Carlos et al. 2010). A neural network with three layers ($M - 3$); the l th layer has n_l neurons. Given S training samples (U_s, T_s), $s=1, 2, 3 \dots S$, where $U_s = [u_1^s, \dots, u_{n_l}^s]$ and $T_s = [t_1^s, \dots, t_{n_M}^s]$. For certain input $U = [u_1, \dots, u_{n_l}^s]$ of the network, the input x_1^l and output y_1^l of i^{th} neuron of l^{th} layer are as follows (Carlos et al. 2010):

Input Layer (13)

$$y_0^l = x_0^l \equiv 1,$$

$$y_j^l = x_j^l \equiv u_j,$$

Where $j=1, 2 \dots n_l$

Hidden Layer (14)

$$y_0^l = x_0^l \equiv 1,$$

$$x_j^l = \sum_{i=0}^{n_{l-1}} w_{i,j}^{l-1,l} y_{i,j}^{l-1},$$

$$y_j^l = g(x_j^l) = \frac{1}{(1 + \exp(-x_j^l))}$$

Where $j=1, 2 \dots n_l$, $i=1, 2 \dots M-1$. $w_{i,j}^{l-1,l}$ is the weight from the i^{th} neuron of $(l-1)^{\text{th}}$ layer to the j^{th} neuron of l^{th} layer, and $g(\cdot)$ is the transfer function.

Output Layer (15)

$$x_j^M = \sum_{i=0}^{n_{M-1}} w_{i,j}^{M-1,M} y_{i,j}^{M-1},$$

$$y_j^M = g(x_j^M) = \frac{1}{(1 + \exp(-x_j^M))}$$

Where $j=1, 2 \dots n_M$. Training a neural network minimizes the error function by modifying the weights $w_{i,j}^{l-1}$. The widely used training error function is as follows:

$$E = \sum_{s=1}^S E_s = \frac{1}{2} \sum_{s=1}^S \sum_{i=1}^{N_M} (t_i^s - y_i^{s,M}) \quad (16)$$

Where, $y_i^{s,M}$ is the output of i^{th} neuron of M^{th} layer when inputting s^{th} sample.

The GA was trained in stages as follows: (1) The preliminary population was selected arbitrarily. Each individual of the initial generation was categorized by a random set of ANN weights; (2) every individual of the population was assessed: for doing this the ANN was run for all S experimental inputs, to compute the yields, utilizing the weights related to each discrete

individual. Afterward, the computed outputs were related to the experimental ones; (3) the individuals of the population were graded according to the lower “E” (neural network error values Eq. (7)); (4) The lowest “E” value of the population (best individual) was copied to the next generation (elitism); (5) The finest parents were elected to produce the progenies, using the GA operators; (6) Similar method is repeated for the next generation and the algorithm is run for a definite number of cycles (Soleymani et al. 2011). The ultimate set of weights (chromosome of the best individual the previous generation) is kept for backpropagation (BP) training; (7) after concluding the GA training, the BP algorithm begins from the solution given by GA. The BP continues in accordance with the conjugate gradient backpropagation training method, reducing the error “E” until it lies below a particular limit determined by the user (Karimi et al. 2011). As the training is completed, the ANN is used to estimate the density values for a new set of data (Testing and unseen data). The overall BPN–GA training algorithm is represented in Figure 2.

Figure 2: Flow chart representing the BPN-GA training algorithm

2.7.3. Design of Experiments

In this study, ANN was established utilizing five parameters to find out the removal efficiency of the MO solution by using DSAC/Fe. It is imperative to assure that the data set covers a substantial range of the variables to have good ANN training. Else, the model could fail on the generalization test and could be limited to the fine range of the parameters characterized by the experimental data. One of the dangers of ANN training is the over-training when the net fits effortlessly to the data used for training, but it is rendered ineffective to deal with new data. Initially, the ANN training was started with 2 neurons in the hidden layer and progressively the neurons number increased. The performance of the network in the training phase should increase as the number of neurons increases, while the performance of the network in the testing data stage leads to an optimum value at an optimal number of hidden neurons. In all instances, the trained ANN was used to calculate the removal efficiency of MO dye at varied situations not used for training (testing data) and the results were compared to experimental ones. pH, adsorbent dosage, initial dye concentration, time and temperature are the input nodes of the ANN model while removal efficiency of MO dye is the output node. These are the significant parameters that influence the adsorption quality of DSAC/Fe. 50 experiments were performed as test runs to train the ANN model. Table 1 lists the parameter range within which different experiments were carried out.

Table 1: The parameter range within which different experiments were carried out

Parameter	Range
pH	2-12
Adsorbent dosage	0.1-0.5 g/L
Initial dye concentration	1-10mg/L
Time	5-300 min
Temperature	30-70 °C

3. Results and Discussion

3.1. Chemical and morphological characterization of DSAC/Fe

Fig. 3 illustrates the morphological characteristics of DSAC/Fe material acquired from SEM. Figures 3A and 3B illustrate the DSAC/Fe structure at 100 μ m magnification. It can be clearly seen that the deposition of the iron particles had altered the surface characteristics of the activated carbon. The prominence of pores can be considered distinct surrounding which the iron at different states of oxidation can be seen to exist. It can also be observed that the pores attained are micropores (Karimi et al. 2012). The white particles present on the surface of this porous carbon were the complexes of iron (Fig. 3B). Iron particles are not only present on the surface of carbon, but some iron had penetrated the pores of carbon thereby causing a reduction in the porosity by forming Fe_2O_3 , Fe_3O_4 , etc. (Alslaibi et al. 2013).

Figure 3: SEM images of (A) Activated Carbon (DSAC) (B) DSAC/Fe

Fig. 4A shows the XRD profile of the activated carbon produced from Date stones. The prepared activated carbon exhibits a very broad band of diffraction peaks along with the absence of sharp peaks which indicated that it is predominantly an amorphous structure (Sivapathasekaran et al. 2010). There are two broad diffraction peaks around $2\theta = 24.6^\circ$ and 43.1° in the spectrum, corresponding to the diffraction of (0 0 2) and (1 0 0), respectively.

Figure 4: XRD image of (A) Activated Carbon (DSAC) (B) DSAC/Fe showing the peaks of Fe

Fig. 4B shows the XRD patterns as obtained for DSAC/Fe. Two crystalline phases can be distinctly determined from the XRD pattern. The two characteristic crystalline phases are of magnetite and hematite. Magnetite is an oxidized crystal form of iron with an inverse spinel-type cubic structure having two active sites that are not equivalent in symmetry (Ghaedi et al. 2011). The two nonequivalent structures being tetrahedral and octahedral while hematite being a crystalline solid of the hexagonal compact structure. 29.8, 35.5, 43.4, 57.1 and 62.9 are the intensities obtained at 2θ values. Furthermore, a higher degree of crystallinity is observed at the magnetite portion of the material. It may be worth stating here about another member of the iron oxide family namely maghemite, containing the cubic structure of inverse spinel-type having a similar structure to that of magnetite only differing in the fact that exclusively contains Fe(III) oxide (Mesdaghinia et al. 2017, Azari et al. 2019). Similarly, in the structure of maghemite and magnetite makes it very difficult for the distinct identification of one form to the other using XRD alone as a characterization method (Qada et al. 2006).

The FTIR spectra for both DSAC and DSAC/Fe were recorded in the range of 4000–300 cm^{-1} and are depicted in Fig 5. In DSAC, the band 2938 cm^{-1} is attributed to asymmetric and symmetric aliphatic bonding C-H stretching vibrations. The bands centered at 1682 and 1569 cm^{-1} can be assigned to the presence of C=C stretching vibration of the aromatic rings. The band at 1433 cm^{-1} may be a result of the angular deformation of the O-H bonds, or due to C-H aliphatic and aromatic groups in the deformation vibrations of methyl and methylene groups. The bands between 1000 and 1300 cm^{-1} can be assigned to the C-O stretching vibration of carboxylic acids and alcohols, and C-N in aliphatic amines. Finally, the vibration bands below 900 cm^{-1}

may be linked to the aromatic ring, C-H bond with different degrees of substitution, or to N-H bonds according to the literature. The characteristic absorption peak appearing at 3484.8 cm^{-1} DSAC/Fe spectra can be assigned to the moisture contents/chemisorbed water in the sample matrix or due to the O–H stretching and bending vibrations as suggested by Liu et al. However, no such peak was found in the FTIR spectrum of DSAC. A small peak at 1596.89 cm^{-1} in DSAC but comparatively sharper peak at 1634.73 cm^{-1} in DSAC/Fe due to the stretching vibration of C=O was detected.

Figure 5: FTIR spectra of (A) Activated Carbon (DSAC) (B) DSAC/Fe

Both the specific surface area and pore volume values of DSAC/Fe decreases significantly on the incorporation of Fe and the specific surface area reaches 1031.467 to $738.6571\text{ m}^2/\text{g}$, respectively, and the total pore volume decreases from 0.615901 to $0.27277\text{ cm}^3/\text{g}$, respectively, for DSAC and DSAC/Fe. The physical properties of DSAC and DSAC/Fe including BET surface area (S_{BET}), micropore surface area (S_{mic}), total pore volume (V_{T}), micropore volume (V_{mic}) and average pore diameter (D_{p}) are given in Table 2.

Table 2. Texture characteristics of DSAC and DSAC/Fe.

Adsorbent	Surface area of pores (m^2/g)			Pore volume (cm^3/g)		
	S_{BET}	S_{ext}	S_{mic}	V_{T}	V_{mes}	V_{mic}
DSAC	1031.467	686.7637	386.2458	0.615901	0.407139	0.19463

<i>DSAC/Fe</i>	738.6571	293.41026	94.0253	0.27277	0.10965	0.05707
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3.2. Training of ANN

A three-layer MLP with a tangent sigmoid transfer function at the hidden layer and a linear transfer function at the output layer were used in this work. The developed ANN model had three layers as illustrated in Fig. 2. The experimental removal efficiency and the efficiency predicted by the ANN model are illustrated in Fig. 6. In total, 50 different sets of experiments were carried out to train the model. The maximum standard deviation obtained between the experimental value and the predicted value was 6.64 while the least deviation was 0.07. Similar results were reported using activated carbon from pine seeds, waste tire and spent tea leaves (Ghaedi et al. 2017, Ozbelge et al. 2002, Roosta et al. 2014).

Figure 6: Removal efficiency of MO dye for each of the 50 different experiments

From Fig. 6 it can be observed that the removal efficiency varied for each of the 50 experiments as the parameter's values were different for each of the runs. The ANN model formed in this study, containing three layers and ten neurons were analyzed at a learning rate of 0.01 and 700 epochs to obtain a dynamic model for the adsorption of MO solution using DSAC/Fe. The regression coefficient was selected for assessing the performance standard of the

model. To avoid net complexity and overtraining probability, the ten neurons were chosen for the hidden layer. The configuration of the trained neural network was accomplished in terms of weights and bias values of each layer after the training and validation of construct networks (Roosta et al. 2014). At epoch 13 the best validation performance was obtained (Fig. 7).

Figure 7: Validation performance of the ANN

The results of the testing data are calculated and presented in Fig. 8. The regression coefficient of both training and validating was stopped when it was greater than 0.95. This program was performed using MATLAB. From Fig. 7 we can see that the R^2 value for training was 0.98 and validation was 0.99. These results confirm that the ANN model could simulate the adsorption process adequately well, under different conditions, within the experimental range adopted in the model fitting.

Figure 8: R^2 value of training and validation

3.3. Effect of different parameters on the removal efficiency of MO dye

3.3.1. Effect of pH on the removal of MO dye

The pH of an aqueous solution is a very significant parameter in the dye adsorption process as it affects the surface charge of the adsorbent material and the amount of ionization of the dye molecule. The effect of initial pH on MO adsorption onto DSAC/Fe is presented in Figure 8. The adsorbent dosage and initial dye concentration were kept constant at 0.5 g/L and 10 mg/L, respectively. The temperature and time for the process was fixed at 30 °C and 300

minutes while the pH was varied between 2 and 11. As the figure illustrates, pH had a prominent effect on the removal of the dye from the aqueous solution. The removal efficiency was seen to be marginally increased in the pH range of 1-3. It was seen to attain a highest of 76.6% at pH 2, while a conflicting removal efficiency of only 57.7% was noted at pH 11. The ANN predicted model also showed the same trend as the experimental values (Fig 9). The maximum removal efficiency obtained by the model was 76.3% and the least was 58.2%. The maximum standard deviation of 1.06 was obtained at pH 3 while the least deviation of 0.07 was observed at pH 7. At basic pH conditions, the double bond conjugation of MO dye was lost along with a proton, and the molecule rearranges to form a negatively charged species (Sivapathasekaran et al. 2010). The positive charges were neutralized. At high pH, the surplus anions in the solution will repel the dye from the negatively charged surfaces of the adsorbents. Moreover, an increase in pH leads to the alteration of the pi (Π) system delocalization pattern (Li et al. 2011). Additionally, at lower pH, the surface of the DSAC/Fewas activated by the acid in the solution and the MO dye became protonated and thus enhanced the adsorption process.

Figure 9: Effect of pH on the removal efficiency of MO

3.3.2. Effect of initial dye concentration in the removal of MO dye

An initial concentration of MO dye in the range of 2 – 20mg/L was taken where absorption onto DSAC/Fe was carried out. The adsorbent dosage and pH were kept constant at 0.5 g/L and 2, respectively. The temperature and time for the process was fixed at 30 °C and 300 minutes. From Figure 9 it can be seen that the removal efficiency steadily decreased with the increase in the concentration of the MO dye. As expected, the ANN predicted model showed the same trend as that of the experimental values (Fig. 10). The maximum removal efficiency obtained by the model was 105.1% while the lowest removal efficiency was 69.3%. The maximum standard deviation of 4.24 was obtained at 2mg/L concentration. The corresponding value for 10mg/L concentration was a meagre 0.21. This increase in removal efficiency with the initial MO dye concentration onto DSAC/Fe may be due to the fact that the escalation in the driving force to overcome the resistance of the mass transfer of MO dye between the solid phase and the aqueous phase, improving the interaction between MO and DSAC/Fe (Li et al. 2011, Mukherjee et al. 2018). The decrease in the MO removal efficiency can be credited to the saturation of existing active sites on the absorbent above a certain concentration of adsorbate.

Figure 10: Effect of initial concentration on the removal efficiency of MO

3.3.3. Effect of adsorbent dosage in the removal of MO dye

The amount of adsorbent used is a vital feature as it governs the degree of dye removal and can be used to regulate the cost of adsorbent per unit volume of solution to be treated. The adsorbent dosage of DSAC/Fevaried from 0.1 – 1.0g/L. From Figure 11. a steady increase in the removal of MO with an increase in the amount of adsorbent dosage was noticed. The initial dye concentration and pH were kept constant at 10mg/L and 2, respectively. Similarly, temperature and time for the process were also fixed at 30 °C and 300 minutes, respectively whilst the adsorbent dosage was varied from 0.1 to 1.0 g/L. The ANN predicted model showed the same trend as that of the experimental values. The maximum and minimum removal efficiency obtained by the experiment was 105.1% and 69.3%, respectively. The maximum and minimum standard deviations of the model were 10.7 and 0.14 and were obtained at a dosage of 1.0 and 0.20 g/L, respectively. The probable reason for the increase in the number of free pores and surface area with an increase in dosage was greatly due to increasing in the adsorption and thus resulted in increased removal efficiency (Soleimani et al. 2012). The abrupt increase in removal efficiency when DSAC/Fedosage increased from 0.5 to 1.0 g/L was probably due to the fact that the concentration difference or the split in the flux between the dye concentration in the aqueous solution and the dye concentration on the surface of the adsorbent (Gupta et al. 1997, Mitra and Mukherjee 2018).

Figure 11: Effect of adsorbent dosage on the removal efficiency of MO

3.3.4. Effect of temperature in the removal of MO dye

It is a well-established fact that temperature is another important parameter that critically affects any adsorption process. Fig. 12 shows the effects of different temperatures on the MO removal efficiency. The initial dye concentration and pH were kept constant at 10mg/L and 2, respectively. The adsorbent dosage and time for the process were fixed at 0.5g/L and 300 minutes while the temperature range varied from 30 °C to 75 °C. An increase in temperature from 30 °C to 65 °C led to an increase in the removal efficiency of MO dye onto DSAC/Fe. This may be due to the fact that both an escalation in the MO dye motion to infiltrate inside the adsorbent pores, for the reduction in solution viscosity, and an increase in the interactions between the functional groups of the DSAC/Fe and the MO dye (Choy et al. 2004). From the figure, it can also be depicted that the adsorption of MO dye onto DSAC/Fe is an endothermic process. However, from 65°C to 75°C, the removal efficiency decreases. This is probably due to a more increase in the random motion of the pollutants, which leads to the desorption of the MO dye from DSAC/Fe.

Figure 12: Effect of temperature on the removal efficiency of MO

The thermodynamic parameters that are assessed are the changes in standard enthalpy (ΔH°), standard entropy (ΔS°) and standard free energy (ΔG°). The ΔH° and ΔS° are determined from Van't Hoff equation (17, 18):

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (17)$$

$$\Delta G^\circ = -RT \ln K \quad (18)$$

Where R is the universal gas constant (8.314 J/mol K), T is the absolute temperature and K is the equilibrium constant. The calculated values of ΔG° are given in Table 2. A negative worth of ΔG° suggests the viability and spontaneous nature of the surface assimilation method with a high preference of MO onto the DSAC/Fe. A positive worth of ΔH° indicates the energy-absorbing nature of the surface assimilation method and the process is endothermic in nature. The low values of each ΔG° (-200 to 0 kJ/mol) and ΔH° correspond to physical surface assimilation (Kalantary et al. 2016). A positive worth of ΔS° reflects the inflated randomness at the solid-aqueous interface with some structural changes in adsorbate and adsorbent. From Table 2, it can be observed that the ΔG° value increases at higher temperatures.

Table 2: ΔG° obtained by experiments and ANN model predicted

Temp. (K)	Experimental ΔG° (KJ/mol)	Experimental ΔH° (KJ/mol)	Experimental ΔS° (J/molK)	Model Predicted ΔG° (KJ/mol)	Model Predicted ΔH° (KJ/mol)	Model Predicted ΔS° (J/molK)
303	-2987.35	7.557	0.0083	-2945.38	7.548	0.0081
308	-3152.33			-3331.44		
313	-4107.85			-3945.96		
318	-4821.38			-4910.84		
323	-6148.15			-6522.45		
328	-9210.94			-9673.05		

3.3.5. Effect of time in the removal of MO dye

A 55-minute time range was considered to study the removal efficiency of the MO solution onto DSAC/Fe. The initial dye concentration and pH were kept constant at 10mg/L and 2, respectively. The temperature and dosage for the process were fixed at 30 °C and 0.5 g/L, respectively while the time varied from 10 to 55 minutes with a 5-minute interval. From Figure 12, it was evident that there was a continuous increase in the removal efficiency with time. Removal efficiency by experiment was seen to attain a highest of 47.7% at a time of 55 minutes. On the contrary, only 34.2% removal efficiency noticed at a time of 10 minutes. The change in the rate of adsorption might be due to the fact that initially, all the adsorbent sites were vacant, and a solute concentration gradient was very high. Later, the lower adsorption rate was due to a decrease in the number of vacant sites of adsorbent and dye concentrations. The decreased absorption rate, particularly, toward the end of experiments, indicates the possible monolayer formation of MO on the adsorbent surface. This may be attributed to the lack of available active sites required for further uptake after attaining the equilibrium (Bellifa et al. 2017, Bakouri et al. 2009). From Fig. 13 it was observed that the ANN predicted model had a similar trend as that of the experimental values. The maximum removal efficiency obtained by the model was 47.5 % and the least was 34.3%. The maximum standard deviation of 0.77 was obtained at a time of 20 minutes while the least deviation of 0.14 was observed at a time of 55 minutes.

Figure 13: Effect of temperature on the removal efficiency of MO

3.4. Adsorption Isotherm and kinetics

To conclude the best fitting isotherm to any adsorption method, the frequently used equation is the linear regression. The obtained correlation coefficients are used to compare the applicability of isotherm equations. Langmuir, Freundlich, pseudo-first-order, and pseudo-second-order were implemented as described above. The linear representation of Langmuir and Freundlich models for both predicted and experimental model is shown in Fig. 14 (A-D), while the R^2 values and constants are included in Table 3.

Figure 14: Isotherm study on removal efficiency of MO: (A) ANN Predicted Langmuir Model (B) Experimental Langmuir Model (C) ANN Predicted Freundlich Model (D) Experimental Freundlich Model

Table 3: Isotherm Models and Parameter Estimation for MO removal onto DSAC/Fe

Isotherm Model	Type	Model Constants	R^2
Langmuir	Experimental	$Q_0 = 80.64$ mg/g $B = 8.12$ L/mg $R_L = 0.00408$	0.9072
	ANN Model	$Q_0 = 78.74$ mg/g	0.9127

	Predicted	$B = 7.07 \text{ L/mg}$ $R_L = 0.00469$	
Freundlich	Experimental	$K_F = 3.36 \text{ L/g}$ $1/n = 0.4202$	0.9651
	ANN Model Predicted	$K_F = 3.33 \text{ L/g}$ $1/n = 0.4227$	0.9794

From Table 3 it is evident that the Freundlich isotherm model provides the highest R^2 values (Experimental: 0.9651 and ANN Model predicted: 0.9794). Thus the adsorption assumes varied scattering of the surface energy of the active sites which also depends on the surface coverage. The values of $1/n$ and K_F obtained from the Freundlich isotherm designate good adsorption capacity (Table 3). The Freundlich model adequately pronounces the adsorption of MO onto DSAC/Fe. From the isotherm study, it is evident that the adsorption of MO was done in multilayers on heterogeneous surfaces. Both experimental and model-predicted data agree with each other. The value of $1/n$ (Experimental: 0.4202 and ANN Model predicted: 0.4227) shows that the adsorption intensity attains a more non-uniform distribution.

The linear representation of pseudo-first-order and pseudo-second-order for both models predicted and experimental are shown in Fig. 15 (A-D), while the R^2 values and constants are included in Table 4. It is clear from both the experimental and ANN model prediction that MO adsorption onto DSAC/Fe was best defined by the pseudo-second-order kinetic model. Table 4 illustrates that the correlation coefficient R^2 for the pseudo-second-order kinetic (Experimental: 0.8945 and ANN Model predicted: 0.8749) equation was higher than pseudo-first-order (Experimental: 0.828 and ANN Model predicted: 0.7972) and that the calculated q_e values were in a tolerable agreement with the corresponding experimental values. Both these results affirm that the adsorption data were well characterized by the pseudo-second-order kinetic model. Both experimental and model-predicted data agree with each other. The adsorption rate is proportionate to the square of the number of vacant adsorption sites.

Figure 15: Kinetic study on removal efficiency of MO: (A) ANN Predicted Pseudo first order Kinetic Model (B) Experimental Pseudo first order Kinetic Model (C) ANN Predicted Pseudo second-order Kinetic Model (D) Experimental Pseudo second-order Kinetic Model

Table 4: Kinetic Models and Parameter Estimation for MO removal onto DSAC/Fe

Kinetic Model	Type	Model Constants	R ²
Pseudo first order	Experimental	q _e = 5.453 mg/g k ₁ = 0.413 h ⁻¹	0.828
	ANN Model Predicted	q _e = 4.909mg/g k ₁ = 0.395 h ⁻¹	0.7972
Pseudo second order	Experimental	q _e =56.17 mg/g k ₂ = 0.01523 g/mg h	0.8945
	ANN Model Predicted	q _e =53.47 mg/g k ₂ = 0.0119 g/mg h	0.8749

Table 5: Comparative Analysis of prepared Activated Carbon

Source of AC	SSA (m ² /g)	Kinetic Study	Isotherm Study	Dye	Removal Efficiency (%)	Reference
Digital versatile discs (DVDs)	659 (CNTs/DVDs AC)	Pseudo-second-order	Langmuir	Acid Orange 7	92.63	Noorimotlagh et al. 2019
Iranian milk vetch	565	Pseudo-second-order	Langmuir	Acid orange 7	87.90	Noorimotlagh et al. 2015
Granular activated carbon (GAC) commercial	-	-	Langmuir	Synthetic arsenate	close to 100% with pH less than 6	Chang et al. 2010
Commercial AC	-	Pseudo-second-	-	Methylene Blue	98%	Shah et al. 2015

		order				
Synthetic activated carbon	-	Pseudo-second-order	Langmuir	Nitrate adsorption	56.7	Kalantary et al. 2016
Spherical granular activated carbon	500	Pseudo-first-order	-	Methylene Blue	90.0	Kadirova et al. 2014
Milk vetch	-	Pseudo-second-order	Langmuir	4-chlorophenol	89.52	Noorimotlagh et al. 2016
Granular activated carbon commercial	-	Pseudo-second-order	Langmuir	methylene blue and Acid Orange 7	-	Nourmora di et al. 2015
<i>Date Stones</i>	<i>738.65</i>	<i>Pseudo-second-order</i>	<i>Freundlich Isotherm</i>	<i>Methyl Orange</i>	<i>76.6 at 2 pH</i>	<i>Present Study</i>

4. Conclusion

From the above study, it is evident that the activated carbon-containing oxides of iron can absorb methyl orange from wastewater. All the characterizations (SEM, XRD, FTIR, and BET) indicate the morphological and chemical changes of the prepared activated carbon. The SSA of DSAC was 1031.46 m²/g while that of DSAC/Fe was 738.65 m²/g. Although, there was a reduction in surface area the, removal efficiency of DSAC/Fe was better due to the presence of iron oxides. The ANN model developed in the study can predict almost accurately the removal efficiency of MO dye in any parameter condition. From the parameter study, both experimental and model-predicted values illustrate that the removal efficiency decreases with the increase in initial dye concentration. The highest removal was obtained at 2pH. The adsorption process follows the Freundlich isotherm and pseudo-second-order kinetic model. The adsorption rate is proportionate to the square of the number of vacant adsorption sites. From the thermodynamic study, the

positive worth of ΔH° indicates the energy-absorbing nature of the surface assimilation method and the process is endothermic in nature. The low values of each ΔG° (-200 to 0 kJ/mol) and ΔH° correspond to physical surface assimilation.

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