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PREDICTION OF ADSORPTION EFFICIENCY FOR THE REMOVAL MALACHITE GREEN AND ACID BLUE 161 DYES BY WASTE MARBLE DUST USING ANN

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ABSTRACT

In the present study, batch adsorption studies were performed for the removal of malachite green and acid blue 161 dyes from aqueous solutions by varying parameters such as contact time, waste marble dust amount, initial dye concentration and temperature. The equilibrium adsorption data were analyzed by Langmuir, Freundlich and Temkin adsorption isotherm models. The Langmuir and Freundlich adsorption models agree well with experimental data. The pseudo-second order, intraparticle intraparticle diffusion and Elovich kinetic models were applied to the experimental data in order to describe the removal mechanism of dye ions by waste marble dust. The pseudo-second order kinetic was the best fit kinetic model for the experimental data. Thermodynamics parameters such as ΔG, ΔH and ΔS were also calculated for the adsorption processes. The experimental data were used to construct an artificial neural network (ANN) model to predict removal of malachite green and acid blue 161 dyes by waste marble dust. A three-layer ANN, an input layer with four neurons, a hidden layer with 12 neurons, and an output layer with one neuron is constructed. Different training algorithms were tested on the model to obtain the proper weights and bias values for ANN model. The results show that waste marble dust is an efficient sorbent for malachite green dye and ANN network, which is easy to implement and is able to model the batch experimental system.

Keywords: Waste marble dust, adsorption, malachite green, acid blue, ANN

1. Introduction

Dyes are significant pollutants causing environmental and health problems. Most industries use dyes and pigments to color their products. Today more than 9000 types of dyes have been incorporated in the color index and the biggest consumers of these dyes are textile, tannery, paper and pulp industry, cosmetic, plastics, coffee pulping, pharmaceuticals, food processing, electroplating and distilleries spew, perhaps these are the serious polluters of our environment as far as color pollution is concerned. Due to its complex chemical structure, dye is one of the most difficult constituents in the textile wastewater to treat. The treatment of dye house wastewater constitutes major economical and environmental issues (Thinakaran *et al.*, 2006; Rastogi *et al.*, 2008; Mahmoued, 2010; Alver and Metin 2012). Most of the dyes are stable and has no effect of light or oxidizing agents. They are also not easily degradable by the conventional treatment methods. Removal of dyes from the effluent is a major problem in most of the textile industries. Several biological, physical and chemical methods have been used for the treatment of

the industrial textile wastewater including microbial biodegradation, membrane, coagulation, filtration, complexation, biosorption, oxidation and ozonation. However, most of the above methods suffer from one or more limitations and none of them were successful in completely removing the color from wastewater (Dawood, 2010; Mahmoued, 2010; Nethaji *et al.*, 2010). Among these methods, adsorption process is one of the effective methods for removal dyes from waste influent. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances (Luo *et al.*, 2010; Jayaraj *et al.*, 2011; Rahman *et al.*, 2013). Activated carbon has been used widely in many adsorption applications due to its high adsorption capacity yet commercially activated carbon is expensive. Therefore, many researchers try to search for a low-cost adsorbent substitutable for activated carbon. A low-cost adsorbent is defined as one which is abundant in nature, or is a byproduct or waste material from another industry. Many low-cost adsorbents have been searched by investigators to substitute it. Studies so far have focused on adsorbents such as alumina, magnetite, silica, goethite, bentonite, activated carbon, clay, perlite, zeolite, sawdust, banana and orange peels, fly ash, red mud, waste marble dust, tea industry waste, coffee bean, cement kiln dust, bagasse fly ash, phosphogypsum, sepiolite, bentonite, kaolinite and others (Ahlawat, 2008; Rastogi *et al.*, 2008; Lian *et al.*, 2009; Baek *et al.*, 2010; Dawood, 2010; Mahmoued, 2010, Rahman *et al.*, 2013).

Many rich marble deposits in countries like Portugal, Spain, Italy, Eqypt, Greece, Turkey, Iran and Pakistan are located in Alpine-Himalayan belt. Turkey has numerous marble deposits. Turkey has even more, 40% of total marble reserves in the world. Seven million tons of marble are produced in Turkey annually. In processing marble such as cutting to size and polishing etc. for decorative purposes, marble dust and aggregate are created as byproducts (Celik and Sabah 2008, Gencel *et al.*, 2012). The by-product generated from marble processing is a powdered dust and may represent an environmental problem. At this moment, most of the marble waste is landfilled and alternative solutions are being explored in many countries with the aim to turn marble waste into a sustainable material (Bacarji *et al.*, 2013).

An ANN is a self-adaptive method and has the ability to approximate any reasonable function arbitrarily well. The leraning and generalization ability of an ANN makes it a powerful modelling tool (Haykin, 1999). In the past, ANNs have been successfully employed in the modelling of several processes such as those conducted (Prakash *et al.*, 2008; Yetilmezsoy and Demirel, 2008; Raj *et al.*, 2010; Aber *et al.*, 2009; Sadrzadeh *et al.*, 2008; Elemen *et al.*, 2012; Sinha *et al.*, 2012) The main advantage of the ANN model over traditional methods is that they do not require the complex nature of the underlying process. This modelling tool has not been used yet to model the adsorption of dyes by waste marble dust.

The aim of this study is to evaluate adsorption kinetics, isotherms and thermodynamic parameters of malachite green and acid blue 161 dyes from aqueous solution using waste marble dust. The different parameters influencing the adsorption of malachite green dye ions on marble wastes were optimized and the results are presented in this paper. Also in this work, experimental data were modeled by an ANN to predict removal malachite green and acid blue 161 dyes by waste marble dust.

2. Experimental Procedure

2.1. Adsorbent

The waste marble dust sample used in this study was obtained in wet form as an industrial by product in İstanbul region. The wet waste marble dust was dried up prior to the preparation of the samples. The samples were sievied and those with size (90-125 μm) were used in the experiments. The waste marble dust contains the chemical compounds SiO_2, Al_2O_3, and CaO with minor contents of MgO, Fe_2O_3, K_2O and Na_2O according to XRD analysis. The physical properties and chemical constituents of marble waste is given in Table 1. The crystalline phase composition of the waste marble dust used in this work was characterized by SEM (FEI Quanta 400 MK2) in Fig. 1.

Table 1. Chemical composition (wt. %) of waste marble dust

	Cement kiln dust
SiO_2	13.40
Fe_2O_3	1.80
Al_2O_3	3.30
CaO	43.40
K_2O	0.70
MgO	1.20
Na_2O	0.20
MnO	0.10
TiO_2	0.20
LOI*	35.70

*Loss on ignition

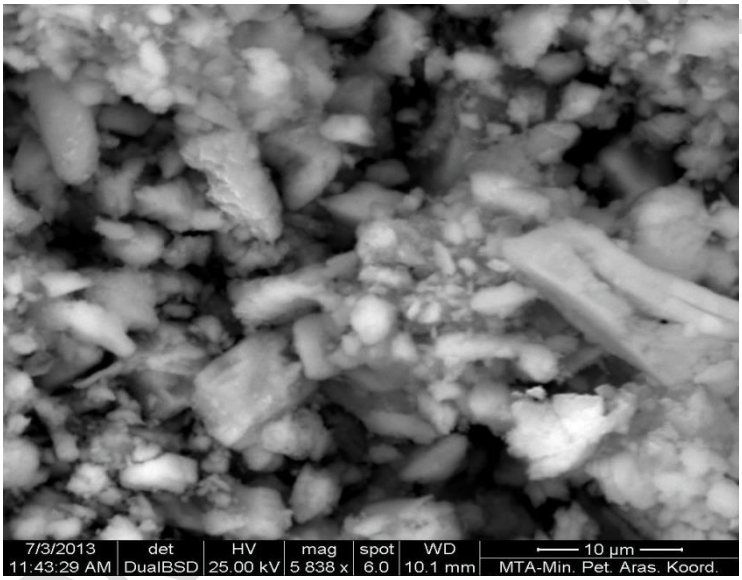


Figure 1. SEM spectrum of waste marble dust

2.2. Adsorbate

The textile dyes; malachite green ($C_{23}H_{26}ClN_2$), acid blue 161 ($C_{20}H_{13}N_2O_5SNaCr_x$) were selected for adsorption studies. The stock solution of 1000 mg l^{-1} was prepared by dissolving accurately weighed amounts of malachite green and acid blue 161 in 1000 ml distilled water. Table 2 shows some properties of textile dyes. The initial pH of solutions was adjusted to the required value by using NaOH or HCl solutions. Malachite green and acid blue 161 concentrations were analyzed by measuring the absorbance values after and before each experiment at 620 nm and 341 nm, respectively.

2.3. Adsorption procedure

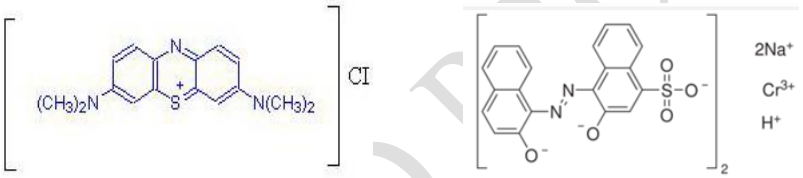
In order to determine the effect of contact time, initial dye concentration, adsorbent dosage, pH and adsorption temperature on malachite green and acid blue 161 dye removal efficiency, batch experiments were conducted. A stock solution 1000 mg l^{-1} of dye was prepared in distilled water and was diluted according to the working concentration. Thermo 10- UV/Visible Spectrophotometer was used at λ_{max} of 620 nm for malachite green and at λ_{max} of 341 nm for acid blue 161 to make the absorbance measurements. The dye solution (50mL) at desired concentration (12.5 and 200 mg l^{-1}), adsorbent dosage (1.25 and 20 g l^{-1}), adsorption tempature (20 °C and 70 °C) and contact time (5 and

240 min) taken in 250 mL erlanmayer flasks was used. pH value of distilled water (pH 6.25) for all adsorption experiments was used. The flasks were kept under agitation in a rotating shaker at 150 rpm for 1 h. The removal efficiency (E) of the waste marble dust on malachite green and acid blue 161 dye was calculated according to the following formula:

$$E(\%)=\frac{C_0-C}{C_0}\times 100 \quad (1)$$

where C_o is the initial concentration of the dye solution and C is the final concentration of the dye solution.

Table 2. Some properties of malachite green and acid blue 161

Textile Dyes Properties	*Malachite green*	*Acid Blue 161*
C.I. No	42000	15706
CAS No	5596-64-2	12392-64-2
Chemical Formula	$C_{23}H_{26}ClN_2$	$C_{20}H_{13}N_2O_5SNaCr_x$
Molecular Weight	364.92	394.40
C.I. Name	Basic Dye	Acid Dye
Molecular Structure		

2.4. Modeling Approach

In literature, many ANN architectures have been used to model engineering problems. The most widely used ANN models among feed-forward models, are the Multi-Layer Perceptron (MLP) and the Radial Basis Function (RBF) models (Haykin, 1999; Elemen *et al.*, 2012; Sinha *et al.*, 2012).

In this study, an ANN was used to predict the percentage of the malachite green or acid blue 161 dyes removal. For this purpose, a three-layer ANN, an input layer with four neurons (e.g. contact time, waste marble dust amount, initial dye concentration and temperature), one hidden layer with 12 neurons, and an output layer with one neuron (e.g. malachite green and acid blue 161 dyes) (4-12-1) is constructed. Different training algorithms are tested on the model proposed to obtain the best weights and bias values for the model. After, the four-layer ANN is evaluated by using the weights and bias values obtained the best training algorithm.

2.5. The ANN Model

In this study a feed-forward MLP with logaritmic sigmoid transfer function (logsig) at hidden layer and output layer was used. Different BP algorithms were compared to select the best suited BP algorithm. The gradient descent bacprobagation with adaptive learning rate algorithm was found as the best. The model and its parameters were determined based on the minimum value of the mean squared error (MSE) of the training and prediction set.

The training and testing data is obtained from the experimental studies. The training data set consists of 40 data items and the validation set consists of 6 data items and the testing data set consists of 8 data item. The range of training, validation, and testing data is shown in Fig.2, Fig.3, Fig.4, and Fig.5, respectively. A small amount of data causes over-fitting problems during neural network training process. The network has memorized the training examples, but it has not learned to generalize to new situations. To avoid this problem a validation data set was used in this study.

If the proposed ANN model is not valid due to transfer functions, other type of transfer functions can be used. If you need more data new experiments should be carried out. The Neural Network Toolbox of Matlab R2011 mathematical software was employed.

3. Results and discussion

3.1. Effect of particle size

To evaluate the effect of particle size on adsorption process, the samples were sieved into the following particle sizes (µm): -500+250, -250+125,-125+90, and -90+60. The adsorption characteristics of waste marble dust with respect to particle sizes are given Fig 2. Fig shows that decreasing in particle size of waste marble dust causes an little increase adsorption loading and adsorption efficiency. Therefore, increase in removal efficiency with decrease in particle size of waste marble dust is not significant.

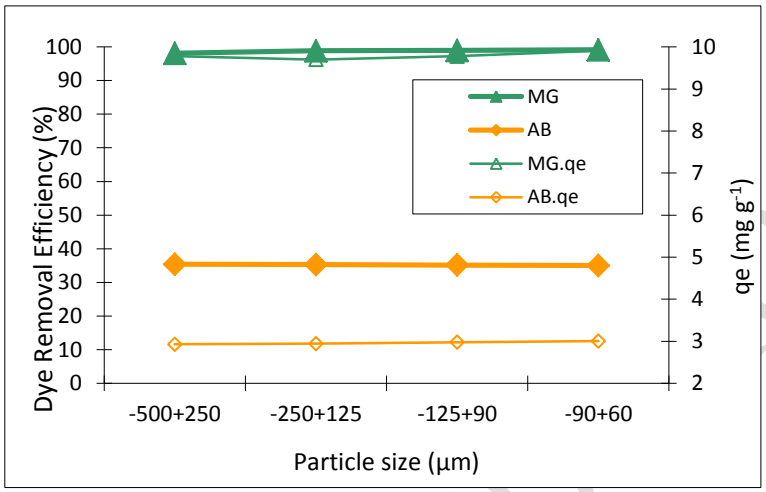


Figure 2. Effect of particle size on malachite green and acid blue 161 adsorption (T: 20 °C, C_o : 50 mg l^{-1}, dosage: 5 g l^{-1})

3.2. Effect of contact time on the removal of malachite green and acid blue 161

The effects of contact time in the range 5-240 min were studied using a constant concentration of malachite green and acid blue 161 dye solution at 20 °C. The removal percentages of the malachite green and acid blue 161 dyes as a function of contact time are shown in Fig 3.

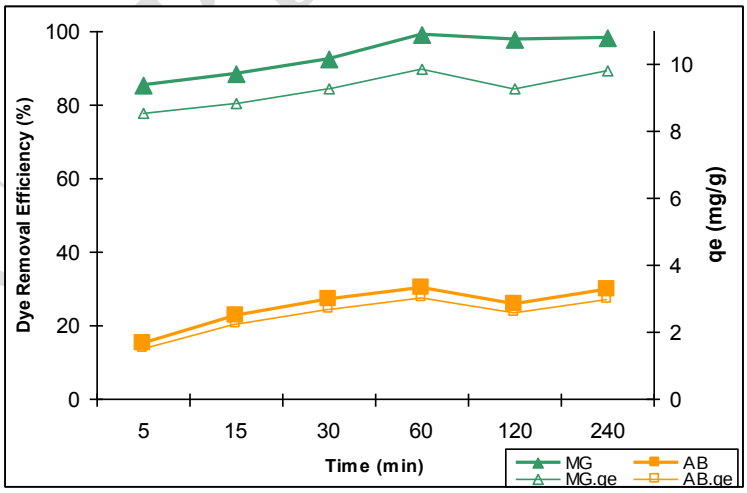


Fig. 3. Effect of contact time on malachite green and acid blue 161 adsorption (T: 20 °C, C_o : 50 mg l^{-1}, dosage: 5 g l^{-1})

The results showed that the removal of malachite green and acid blue 161 dye increases with time rapidly and saturation in about 120 min. The results clearly show that if contact time for waste waste marble dust is increased from 5 to 120 minutes, the removal efficiencies for malachite green and acid blue 161 dye increase from 85.33 % to 98.18 % and 15.29 % to 29.65 %, respectively. However, the adsorption of acid blue 161 dye using waste marble dust is very limited due to the surface of the waste

marble dust and dye molecules having negative charges. It is know that waste marble dust has a negative charged surface, this causes a relatively low adsorption capacity for acidic dyes. As can be seen in Fig.3. malachite green dye have more effective dye than acid blue 161 dye for waste marble dust (Crini, 2006; Kuleyin and Aydin, 2011; Alver and Metin, 2012).

3.2. Effect of waste marble dust amount on the removal of malachite green and acid blue 161

Fig. 4 shows the effect of the amount of waste marble dust dosage on the malachite green and acid blue 161 removal. As the waste marble dust amounts increased, the removal efficiencies increased. The removal efficiencies for 0.125 g l^{-1} of waste marble dust for malachite green and acid blue 161 were found to be 98.78 % and 99.68 %, but as the waste marble dust amounts were increased to 2 g l^{-1}, removal efficiencies were found to be 2.47 % and 48.91 %. These results show that removal efficiency was increased with increasing amount of the waste marble dust.

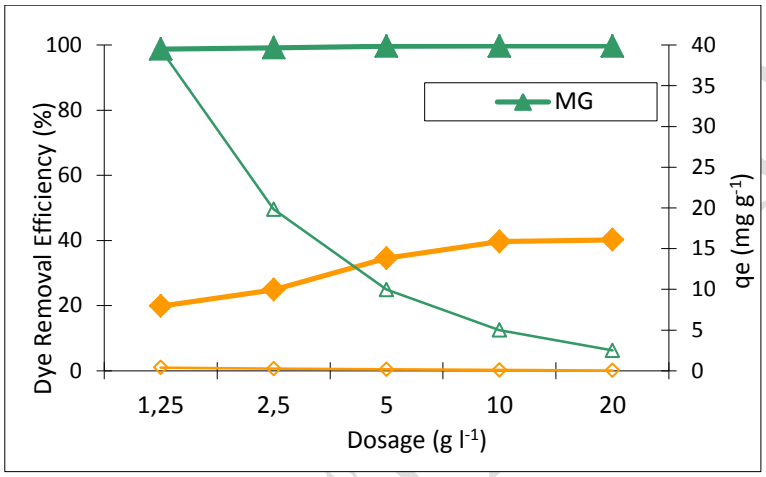


Figure 4. Effect of waste waste marble dust amount on malachite green and acid blue 161 adsorption (T: 20 °C, C_o : 50 mg l^{-1}, time: 1 h)

3.3. Effect of initial dye concentration of malachite green and acid blue 161

The effects of initial malachite green and acid blue 161 concentrations in the range of 12.5 - 200 mg l^{-1} on the adsorption were investigated under the specified conditions.

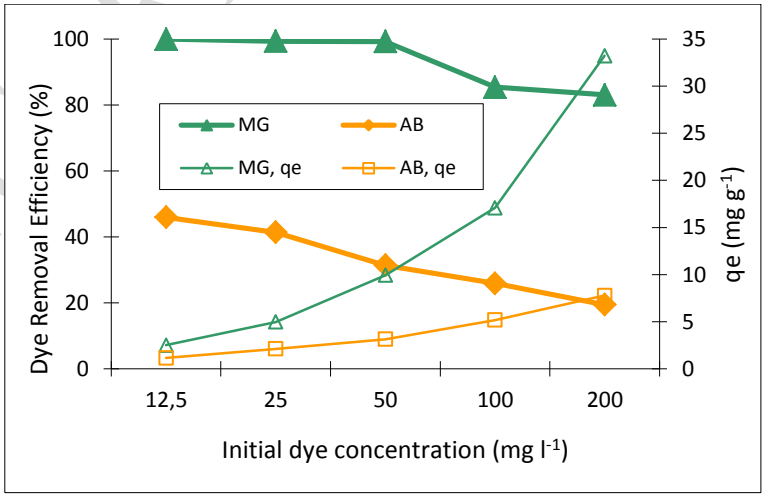


Figure 5. Effect of initial concentration on malachite green and acid blue 161 adsorption (T: 20 °C, dosage: 5 g l^{-1}, time: 1 h)

Fig. 5 shows the adsorption of malachite green and acid blue 161 on waste waste marble dust as an initial dye concentration. The percent adsorption of malachite green and acid blue 161 are inversely

related to the initial dye concentrations. Percentage of malachite green and acid blue 161 removal decreased as its concentration increased at fixed adsorbent dosage. As can be seen from Fig. 5, increasing the dye concentration led to an increase in the dye adsorption by waste marble dust. This can be attributed to the effective pore diffusivity decrease with increasing initial dye concentration. The maximum adsorption capacity of waste waste marble dust was found to be 33.23 mg g^{-1} for 200 mg l^{-1} MG dye concentration and 7.77 mg g^{-1} for 200 mg l^{-1} AB 161.

3.4. Effect of temperature on the removal of malachite green and acid blue 161

The effect of temperature on the malachite green and acid blue 161 adsorption on waste waste marble dust was carried out at 20, 30, 50 and 70 ^{o}C. The results are presented in Fig. 6 From the Fig. 6, the removal of malachite green and acid blue 161 was slightly increases with temperature, which indicates the endothermic nature of the adsorption reaction. At higher temperature, more dye molecules have sufficient energy to undergo an interaction with active sites at the surface. In addition, increasing the temperature was known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle due to the decrease in the viscosity of the solution (Nethaji *et al.*, 2010; Alver and Metin, 2012).

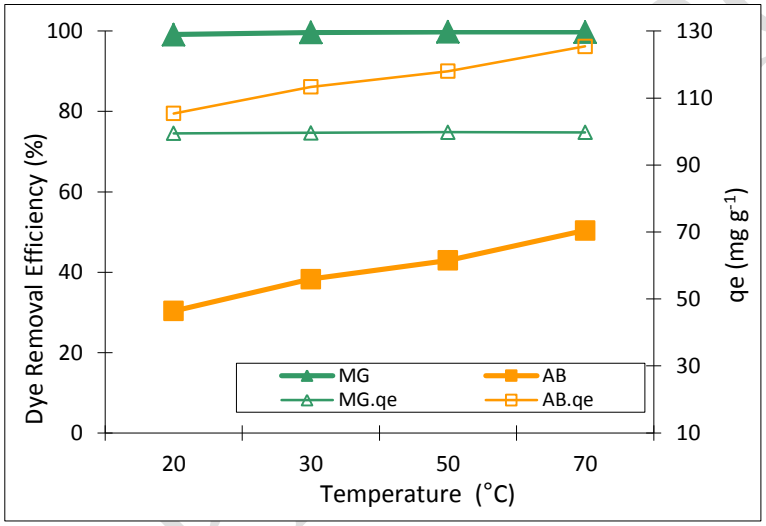


Figure 6. Effect of temperature on malachite green and acid blue 161 adsorption on waste waste marble dust (C_o : 50 mg l^{-1}, dosage : 5 g l^{-1}, time: 1 h)

3.5. Adsorption isotherm models

The successful representation of the dynamic adsorptive seperation of solute from solution on an adsorbent depends upon a good description of the equilibrium separation between the two phases. An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants (Nuhoglu and Malkoc, 2009). The effect of concentration on sorption was applied to different isotherm models to find a suitable model to instruct the further experimental design. Several isotherm equations are available. In this research, in order to determine the mechanism of MB and CV adsorption on the waste waste marble dust the experimental data was applied to the Langmuir, Freundlich, Temkin isotherm equations (Bulut, *et al.*, 2008; Ahmad and Alrozi, 2011).

The Langmuir sorption isotherm is the best known of all isotherms describing sorption and it has been successfully applied to many sorption processes. Thus, the Langmuir isotherm model is given by equation (Hui *et al.*, 2005; Oren and Kaya, 2006);

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (2)$$

where q_e is the equilibrium adsorbed (mg g^{-1}), C_e is the equilibrium liquid-phase concentration (mg l^{-1}), q_m and K_L are the Langmuir constants related to sorption capacity and sorption energy, respectively. The values of q_m (mg g^{-1}) and K_L (mg^{-1}) can be determined from the linear plot of C_e/q_e versus C_e (Fig. 7a). The values q_m and K_L obtained from these plots are listed in Table 3.

Table 3. Constants of adsorption of MG and AB uptake by waste waste marble dust

Dye	Langmuir			Freundlich			Temkin		
	qm	K_L	R^2	K_f	n	R^2	A	B	R^2
MG	4.67	0.883	0.9888	9.45	4.438	0.9568	258.70	2.7146	0.7465
AB 161	10.62	0.0150	0.9636	0.39	1.693	0.9929	0.20	2.0371	0.9467

The Freundlich isotherm is an empirical model that is based on adsorption on heteregenous surface; it is given in Eq. (3),

$$\log q_e = \log K + (1/n)\log C_e \quad (3)$$

where q_e the amount of dye ions adsorbed per gram of adsorbent at equilibrium (mg g^{-1}), C_e is the equilibrium concentration in mg l^{-1}, K is roughly an indicator of the adsorption capacity (mg g^{-1}), n is a characteristic constant for the adsorption system (l g^{-1}).

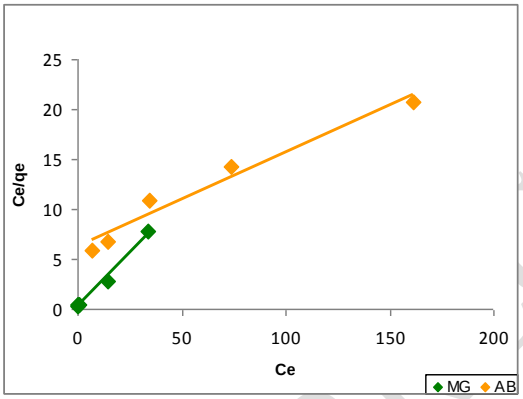


Figure 7a. The Linearized Langmuir isotherm of MG and AB 161 uptake by waste waste marble dust

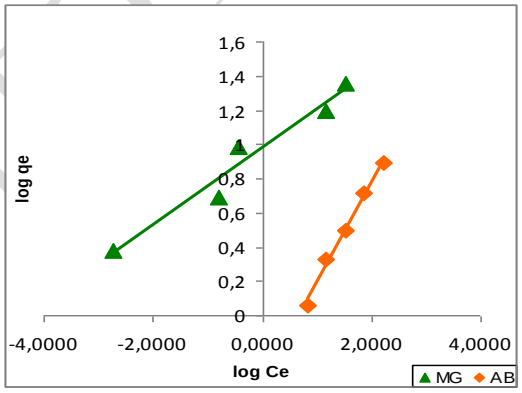


Figure 7b. The Linearized Freundlich isotherm of MG and AB161 uptake by waste waste marble dust

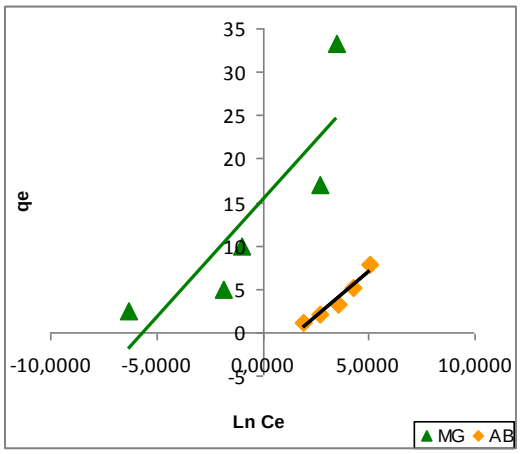


Figure 7c. The Linerized Temkin isotherm of MG and AB 161 uptake by waste waste marble dust

The *n* values between 1 and 10 (i.e., 1/n less than 1) indicate the beneficial adsorption (Fig. 7b). A relatively *n*<<1 indicates that adsorption intensity is favorable over the entire range of concentrations studied, while n>1 means that adsorption intensity is favorable at high concentrations but much less at lower concentrations (Banu and Guclu, 2009; Zhao *et al.*, 2008). For the adsorption of MG and AB 161 on waste waste marble dust , the *n* values were above beneficial adsorption.

The derivation of the Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation. Temkin isotherm model is given in Eq. (4):

$$q_e = (RT/b)\ln AC_e \quad (4)$$

$$q_e = B\ln A + B\ln C_e \quad (5)$$

where B=lnRT/b, q_e (mg g^{-1}) and C_e (mg l^{-1}) are the amounts of adsorbed dye per unit weight of adsorbent and unadsorbed dye concentration in solution at equilibrium, respectively. Also, T the absolute temperature in K and R is the universal gas constant, 8.314 J mol^{-1} K^{-1}. The constant B is related to the heat of adsorption (Fig. 7c).

3.6. Adsorption kinetics

Pseudo-second-order kinetics may be expressed as given by Eq. 6:

$$\frac{dq_t}{d_t} = k_2(q_e - q_t)^2 \quad (6)$$

where k_2 is the rate constant of adsorption, q_e and q_t are the amount adsorbed at equilibrium (mg g^{-1}). Integrating this for the boundary conditions t = 0 to t = t and q_t = 0 to $q_t = q_t$ gives (Eq. 7):

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (7)$$

which is the integrated rate law for a pseudo-second-order reaction. Eq. (7) can be rearranged to obtain (Eq. 8):

$$q_t = \frac{t}{(1/k_2 q_e^2) + (t/q_e)} \quad (8)$$

which has a linear form of (Eq. 9)

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

where k_2 was the rate constant of second-order MG and AB 161 adsorption. Fig. 8a shows the linear plots of t/q_t versus *t*. The correlation coefficients for the second-order kinetic model were higher than 0.999 indicating the applicability of this kinetic model of the adsorption process of MG and AB 161 on waste waste marble dust .

The rate parameter for intraparticle diffusion equation is given using the following equation (Ofomaja, 2008; Zhao *et al.*, 2008) (Eq. 10).

$$q_t = k_{id} t^{1/2} + C \quad (10)$$

where C is the intercept and k_{id} is the intra-particle diffusion rate constant (mg g^{-1} $min^{1/2}$). The plot *q* versus $t^{1/2}$ is given by multiple linear regions representing the external mass transfer followed by intra-particle or pore diffusion. In this model, due to the porous nature of the adsorbent, pore diffusion is expanded to be surface adsorption (Karagöz *et al.*, 2008). Fig. 8b exhibits the intra-particle diffusion model of MG and AB 161 adsorpsion on waste waste marble dust. The intra-particle diffusion rate constants k_{id} and correlation coefficients are presented in Table 4.

The Elovich equation has general application to chemisorption kinetics. This equation has been applied satisfactorily to some chemisorption data and has been found to cover a large range of slow adsorption. The Elovich equation is often valid for systems in which the adsorbing surface is heterogeneous. The rate parameter for the Elovich equation is determined as (Sprynskyy, *et al.* 2005; Cheung *et al.* 2000).

$q_t=\beta \ln(\alpha) +\beta \ln t$ (11)

where α ($mgg^{-1}min^{-1}$) and β (gmg^{-1}) are the equilibrium rate constants for Elovich model. The equation constants can be obtained from the slope and intercept of a straight-line plot of q_t against ln t. The values of constants can be obtained from the slope and intercept of the plots (Fig. 8c). The values of kinetic constants are presented in Table 4.

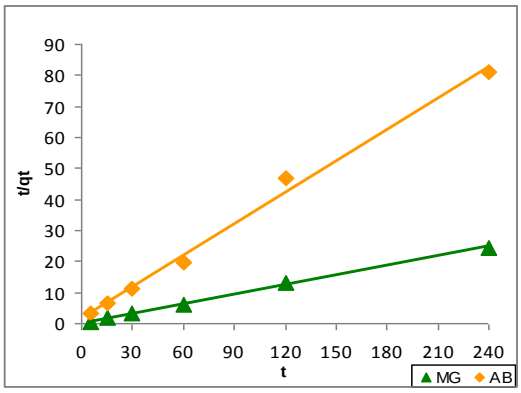


Figure 8a. Linerized pseudo-second-order kinetics plots for MG and AB 161 adsorption

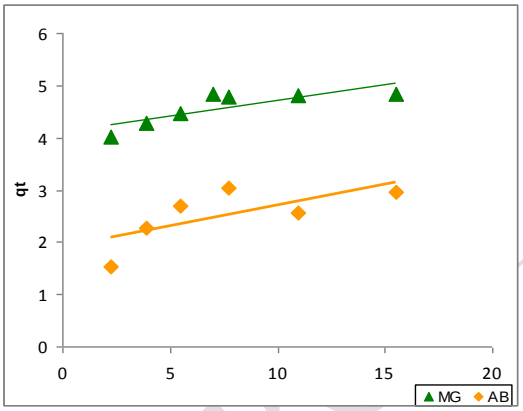


Fig.8b. Linerized intraparticle diffusion kinetics plots for MG and AB 161 adsorption

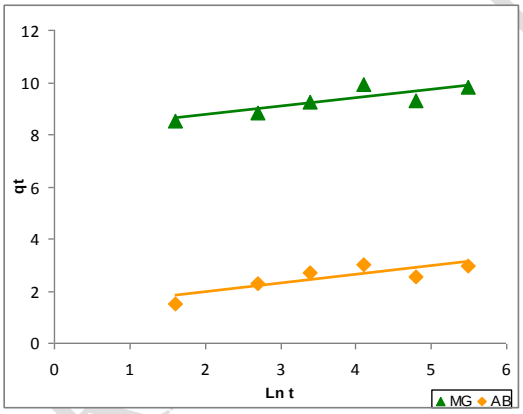


Fig. 8c. Linerized Elovich kinetics plots for MG and AB 161 uptake by waste waste marble dust

Table 4 . The kinetics constants for the removal of the MG and AB 161 by waste waste marble dust

Dye	Pseudo Second Order			Intraparticle Diffusion			Elovich		
	q_e	k_2	R^2	C	k_{id}	R^2	β	α	R^2
MG	9.80	0.061	0.9992	4.133	0.059	0.6448	0.32	$6.6.10^4$	0.7329
AB 161	2.96	0.689	0.9937	1.900	0.079	0.5008	0.33	47.07	0.7189

3.7. Thermodynamic parameters

The adsorption standard free energy changes (ΔG^o) are determined with the following equation (Alpat, S.K. et. al., 2008; Lin J.X. et al,. 2008)

$\Delta G^o= -R\ T\ \ln K$ (12)

where *R* is the gas constant ($8.314x10^{-3}$ kJ K^{-1} mol^{-1}) , T is the temperature (K), and ΔG^o is the free energy of sorption. The equilibrium constant was calculated from:

$K = q_e/C_e$ (13)

where q_e and C_e were the equilibrium concentrations of malachite greenin solution and on the sorbent correspondingly.

The sorption distribution coefficient may be expressed in terms of enthalpy and entropy changes as a function of temperature:

$$\ln K = -\Delta H^o/RT + \Delta S^o/R \quad (14)$$

The enthalpy change (ΔH^o) and the entropy change (ΔS^o) can be calculated from a plot of *lnK* versus 1/T.

The values obtained were given in Table 5. The endothermic nature of process is well explained by positive value of the enthalpy change. The negative value of free energy suggests that the adsorption process is spontaneous and the affinity of the adsorbent for the dye is indicated by the positive value of entropy.

Table 5. Thermodynamic coefficients for MG and AB 161 adsorption on waste waste marble dust

Dye	ΔG^o (kJ mol^{-1})				ΔH^o (kJ mol^{-1})	ΔS^o (kJ mol^{-1} K^{-1})
	20 °C	30 °C	50 °C	70 °C		
MG	-14.36	-15.87	-18.51	-19.31	15.376	0.102
AB 161	-2.69	-3.27	-3.81	-4.61	7.977	0.036

3.8. The Results of the ANN Modeling

The developed ANN model had three layers. The input layers had four neurons as contact time, marble sludge dust amount, initial dye concentration and temperature. The output had one neuron as percentage of the adsorption efficiency for the removal malachite green and acid blue 161 dyes by marble sludge dust. Fig.9 shows the number of neurons in the two hidden layers. It was selected as 12 neurons because of its minimum error values (%) for training and testing sets.

The ranges of operating variables were initial concentration (12.5–200 mg l^{-1}), contact time (5–240 min), temperature (20-70 ^oC), and absorbent dosage (0.0625–1 g l^{-1}). The data were divided into training, validation, and sets. All samples were to be scaled into the 0-1 due to using sigmoid transfer function in the output layer. A regression analysis to show the performance of the network is given Fig. 10.

The performance of the constructed ANN model was also statistically measured by mean squared error (MSE) and the coefficient of determination (R^2) as follows:

$$MSE=\left(\frac{1}{n}\sum_{i=1}^{n}\left(y_i-y_{di}\right)^2\right) \quad (15)$$

$$R^2=1-\frac{\sum_{i=1}^{n}\left(y_i-y_{di}\right)^2}{\sum_{i=1}^{n}\left(y_{di}-y_m\right)^2} \quad (16)$$

where n is the number of points, y_i is the predicted value, y_{di} is the actual value, and y_m is the average of the actual values.

The prediction model was shown that the ANN model was able to predict the adsorption efficiency for the removal malachite green and acid blue 161 dyes by marble sludge dust with R >0.89 and MSE<0.01. These results are quite reasonable and accepted.

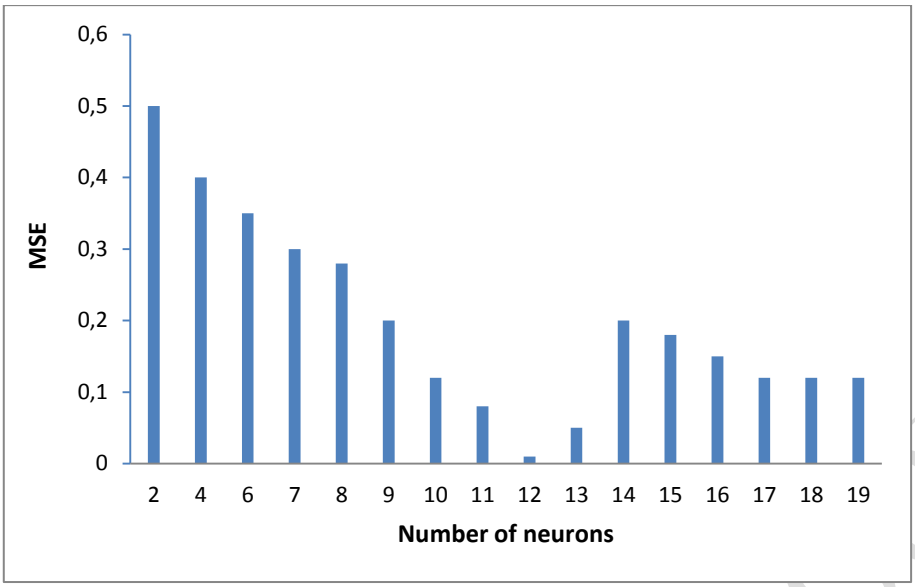


Figure 9. The number of hidden layer neurons in the ANN structure

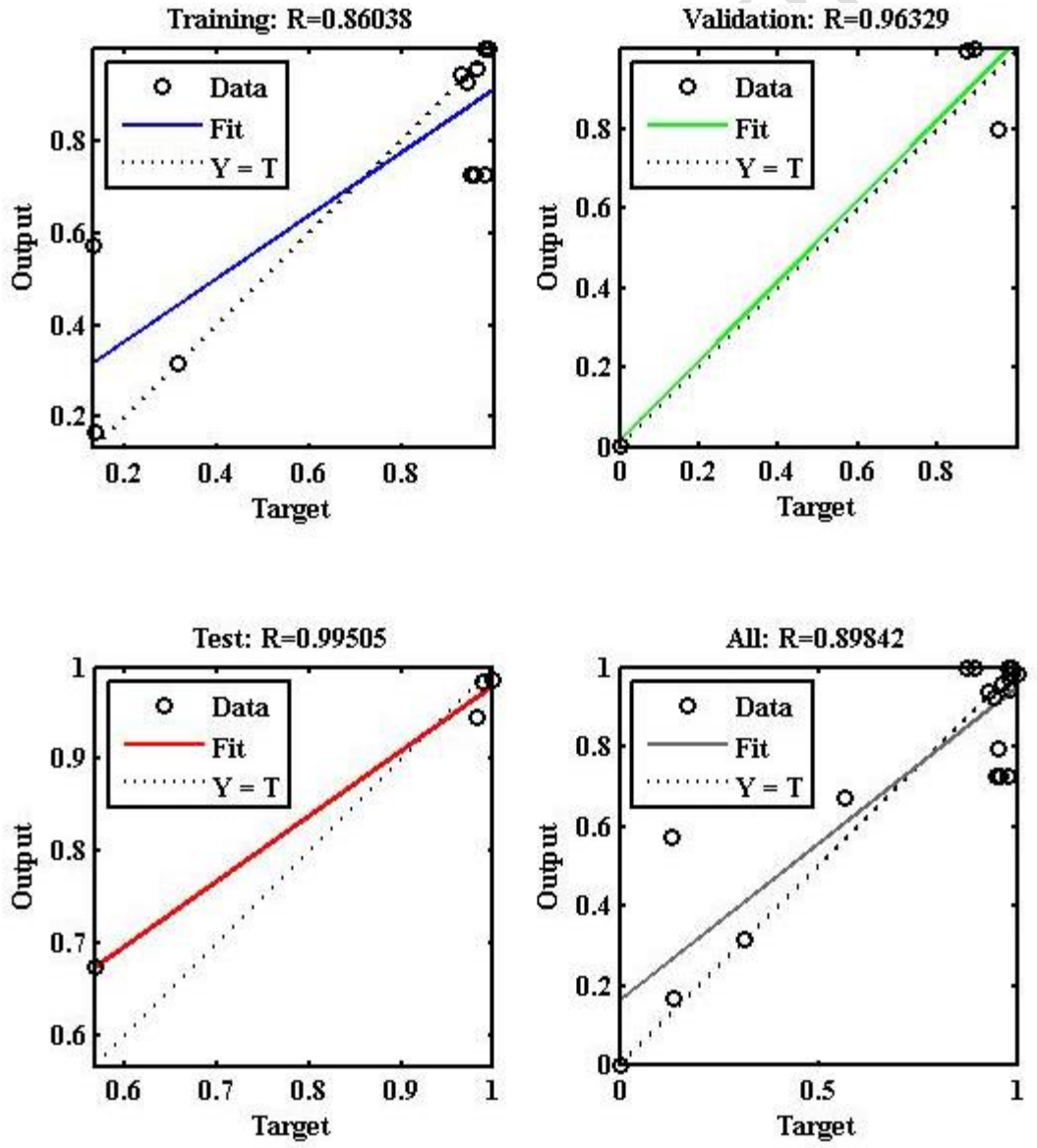


Figure 10. Performance of the ANN model

4. Conclusions

The effect of various operational parameters such as contact time, waste marble dust amount, initial dye concentration and temperature on teh adsorption of malachite green and acid blue 161 dyes was investigated and optimized. The waste marble dust used as a low-cost adsorbent showed a excellent adsorption performance for removal of malachite green dye from aqueous solutions. The maximum adsorption capacity of waste waste marble dust was found to be 33.23 mg g^{-1} for 200 mg l^{-1} MG dye concentration and 7.77 mg g^{-1} for 200 mg l^{-1} AB 161.The adsorption of the basic dye (MG) was better than the adsorption on an acidic dye (AB) on waste foundry sand. ANN model was used some experimental data to predict the response of the experiments at new similar conditions for the problem of malachite green and acid blue 161 dyes removal by waste marble dust. The proposed ANN modelling method also decreases the number of the experiments to remove of the adsorption efficiency for the removal of malachite green and acid blue 161 dyes by waste marble dust. This decreases the cost of the experimental studies.

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