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OPTIMIZATION OF MALACHITE GREEN DYE REMOVAL BY SEPIOLITE CLAY USING A CENTRAL COMPOSITE DESIGN

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ABSTRACT

In this study, a four-factor five-level Central Composite Design (CCD) was applied to develop mathematical model and optimize process parameters for malachite green dye (MG) removal from aqueous solutions using sepiolite. The individual, combined, and quadratic effects of four experimental factors (initial pH of solution, contact time, initial dye concentration, and sepiolite dosage) on dye adsorption were studied. Based on the analysis of variance (ANOVA) results, the order of factors from high to low contribution on removal efficiency was found as initial dye concentration, sepiolite dosage, initial dye concentration*initial dye concentration, sepiolite dosage*sepiolite dosage, and contact time with respect to sum of squares. Optimization results showed that the optimal settings for significant experimental factors were initial dye concentration= 77 mg l^{-1}, sepiolite dosage= 26 g l^{-1}, and contact time= 42 min. At this setting, predicted maximum removal efficiency was over 99%.

Keywords: Adsorption, Central Composite Design, Malachite Green Dye, Optimization, Sepiolite

1. Introduction

Pigment and dyes are widely used in textiles, paper, leather, plastics, rubber, carpet, pharmaceutical, and cosmetic industries (Özdemir *et al*., 2007; Tor and Cengeloglu, 2006). About 10,000 different dyes weighing approximately 0.7 million tons are produced annually for various industrial processes. A considerable percentage of these dyes are released into the effluent during the dyeing process. Direct discharge of these effluents into municipal wastewater plants and/or environment may cause the formation of toxic carcinogenic breakdown products. Over 90% of some 4000 dyes tested in an ETDA (Ecological and Toxicological Association of the dyestuff) survey had lethal dose 50% (LD_{50}) values greater than 200 mg kg^{-1}. The highest rates of toxicity were found amongst basic and diazo direct dyes (Garg *et al*., 2004; Hameed *et al*., 2008; Nethaji *et al.,* 2010; Mona *et al*., 2011). Malachite green (MG), also called aniline green and basic green 4, is a toxic chemical primarily used as a dye. Though the external use of MG as an antiseptic, antibacterial and antiprotozoan agent is well known but its oral consumption is toxic, hazardous and carcinogenic due to presence of nitrogen. Contact to malachite green with skin and eye causes irritation with redness and pain. The available toxicological information reveals that in the tissues of fish and mice MG easily reduces to persistable leuco-Malachite Green, which acts as a tumor promotor. MG has a complicated chemical structure; it is resilient to fading on exposure to light and water and is, therefore, the removal of MG from wastewater before discharging to the environment is necessary and very important (Önal *et al*., 2006; Baek *et al.,* 2010; Ahmad and Alrozi, 2011).

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In order to remove dyes from aqueous solutions, many chemical or biological treatments such as adsorption, coagulation, fenton process, ozonation, electrochemical oxidation, ultrasonic irradiation, and membrane process have been used either individually or together. Adsorption techniques to remove dyes from water have been widely used. It has been found to be an economical and effective treatment method for removal of dyes due to its sludge free clean operation. Adsorption processes using activated carbons have been widely proposed and used for the removal of both organic and inorganic pollutants from aqueous effluents. However, commercially available activated carbons are expensive, and in recent years, a great deal of effort has been put into the proposal and usage of low-cost adsorbents prepared from naturally occurring materials and wastes for the removal of dyes from wastewaters (Ay *et al*., 2009; Uğurlu, 2009; Im *et al*., 2012; Somayajula *et al*., 2012;). In the recent years, for the removal of different type of substances from wastewaters, several materials have been evaluated as adsorbent like silicagel, clay, perlite, zeolite, sepiolite, hydroxyapatite, fly ash, unburned carbon, coir pith carbon, pulp fiber, shale oil ash, silkworm pupa, and others (Lazarevic *et al*., 2007; Şener, 2008; Alpat *et al*., 2008; Neta *et al*., 2011; Singh *et al*., 2011).

The clay mineral sepiolite is currently used as raw material due to its powerful sorbent properties (Rytwo *et al*., 1998). Sepiolite has an open structure exhibiting a microfibrous morphology with a high specific surface area (around 340 m^2 g^{-1}) and a large micropore volume (around 0.44 cm^3 g^{-l}). The sorptive property of sepiolite particularly renders it invaluable as a bleaching, and clarifying agent, filter aid, industrial adsorbent, and a spectrum of uses ranging from cosmetics to paints and even fertilizers. Most of the studies were about the sorption of heavy metal ions, organic molecules and ions, ammonium and phosphate, color, and other undesirable components, dyes, phenol, and lignin (Balci, 2004, Garg *et al*., 2004; Turan *et al*., 2005; Zhao *et al*., 2008; Bingol *et al*., 2010).

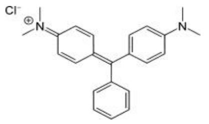
Response Surface Methodology (RSM) is an experimental technique invented to find the optimal response within the specified ranges of the factors. Since “optimal” often implies a minimum or maximum, optimization designs involve at least three levels of each factor so that curvature may be estimated. Central Composite Design (CCD) is one of the most commonly used RSM designs (Im *et al*, 2012; Amani-Ghadima *et al*., 2013). CCD is often used in chemical processes when the design plan calls for sequential experimentation because these designs can incorporate information from a properly planned factorial experiment. In this study, four-factor five-level CCD was used to determine the effects of initial pH of solution, contact time, initial dye concentration and sepiolite dosage on the adsorption process and to find optimum settings.

2. Materials and methods

2.1 Materials

Sepiolite sample used in the experiments was received from Aktaş Lületaşı Co. in Eskişehir, Turkey. Sepiolite was washed thoroughly with double distilled water to remove the dirt and other foreign matter and dried at 70 °C for a period of 3-5 h.

Table 1. Some properties of malachite green dye

Basic Dyes Properties	Malachite green
C.I. No	42000
CAS No	5596-64-2
Molecular Formula	$C_{23}H_{25}ClN_2$
Molecular Weight (g mol^{-1})	364.92
Melting Point	164 °C
C.I. Name	Basic Dye
Molecular Structure	

C.I: colour index

2.2 Methods

The basic dye, malachite green ($C_{23}H_{25}ClN_2$), was selected for adsorption studies.

The stock solution of 1000 mg l^{-1} was prepared by dissolving accurately weighed amounts of malachite green in 1000 mL distilled water. The stock solution was further diluted to obtain desired concentration ranging from 10 to 250 mg l^{-1}. Table 1 shows some properties of malachite green dye. The pH of the solutions was adjusted with HNO_3 and NaOH solutions by using a WTW 330 pH-meter with a combined pH electrode.

2.3. Adsorption procedure

Batch experiments based on CCD were conducted at random to study the effect of the pre-selected four operating variables on the dye removal efficiecy of the sepiolite. For adsorption of the dye on sepiolite, different weighted amounts of the sepiolite (0.5–40 g l^{-1}) were equilibrated with 100 ml of solution initially containing 10–250 mg l^{-1} of the malachite green dye. The pH of the dye solutions was adjusted (2.0-9.0) with HCl or NaOH solutions by using WTW 330 pH-meter with a combined pH electrode. The adsorption experiments were conducted in a bath shaker for 23 °C at 175 rpm at different contact times (5–91 min.). The equilibrated samples were taken out, and the aqueous solution phase was separated from the adsorbent using a centrifuge to make it adsorbent free. The dye concentration in supernetant solution was determined using the UV–visible spectrophotometer at 617 nm. All experiments were conducted in duplicate and the average values were used for data analysis.

The removal efficiency (*E*) of the sepiolite on malachite green dye was calculated according to the following formula:

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

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

2.3 Central Composite Design

Response Surface Methods use specific experimental design combinations to develop mathematical models with linear, quadratic, and interaction terms to find optimum performance from a given set of factors and response variables (DeCarlo, 2007). The two most frequently designs used in response surface modeling are Central Composite Design (CCD) and Box–Behnken Design (BBD). These designs are capable of fitting a second order prediction equation ($\hat{y} = \hat{\beta}_0 + \sum_{i=1}^{k} \hat{\beta}_i x_i + \sum_{i=1}^{k} \hat{\beta}_{ii} x_i^2 + \sum \sum_{i<j} \hat{\beta}_{ij} x_i x_j$) for the response.

CCD consists of cube points for the estimation of linear and interaction effects, center points to check for curvature, and axial points to estimate quadratic terms. Alpha (α) for axial points is the distance of each axial point from the center. A central composite design with five center points and α=2 was used to conduct the experiments (Table 2). After performing the experiments according to the design, removal efficiencies were recorded as response variable. The experimental parameters were analyzed and optimized in the MINITAB 16 statistical software environment.

Table 2. Experimental data set and design matrix

Factors	**Symbols**	**Levels of Factors**				
		−α (−2.000)	**−1**	**0**	**+1**	**+α (+2.000)**
Initial pH	X_1	2.00	3.75	5.50	7.25	9.00
Sepiolite Dosage (g l^{-1})	X_2	0.5	10.375	20.250	30.125	40
Initial Dye Conc.(mg l^{-1})	X_3	10	70	130	190	250
Contact Time (min)	X_4	5	33.75	62.50	91.25	120

Run	X_1	X_2	X_3	X_4	Efficiency (%)
1	3.75	10.375	70	33.75	90.85
2	7.25	10.375	70	33.75	93.10
3	3.75	30.125	70	33.75	98.95
4	7.25	30.125	70	33.75	98.71
5	3.75	10.375	190	33.75	89.85
6	7.25	10.375	190	33.75	90.21
7	3.75	30.125	190	33.75	92.60
8	7.25	30.125	190	33.75	92.10
9	3.75	10.375	70	91.25	97.48
10	7.25	10.375	70	91.25	97.56
11	3.75	30.125	70	91.25	99.57
12	7.25	30.125	70	91.25	99.82
13	3.75	10.375	190	91.25	85.47
14	7.25	10.375	190	91.25	88.45
15	3.75	30.125	190	91.25	89.88
16	7.25	30.125	190	91.25	90.20
17	2.00	20.250	130	62.50	98.17
18	9.00	20.250	130	62.50	99.42
19	5.50	0.500	130	62.50	75.60
20	5.50	40.000	130	62.50	99.69
21	5.50	20.250	10	62.50	98.80
22	5.50	20.250	250	62.50	76.40
23	5.50	20.250	130	5.00	86.12
24	5.50	20.250	130	120.00	98.72
25	5.50	20.250	130	62.50	98.63
26	5.50	20.250	130	62.50	98.65
27	5.50	20.250	130	62.50	98.92
28	5.50	20.250	130	62.50	98.77
29	5.50	20.250	130	62.50	98.83
30	5.50	20.250	130	62.50	98.60
31	5.50	20.250	130	62.50	98.88

3. Results and discussion

3.1 Characterization of the sepiolite

The chemical composition of the sepiolite slag was evaluated by using X-ray Fluorescence techniques (Rigaku ZSX Primus). The chemical composition of the sepiolite is given in Table 3. The BET specific surface area was measured to be 82.35 m^2 g^{-1} from N_2 adsorption isotherms with a sorptiometer (Quantachrome Co., NOVA 2200). In this study, scanning electron microscopy (SEM, Zeiss Supra 50VP) was used for micro-structural investigations. Figure 1 illustrates the SEM analysis of sepiolite.

Table 3. Chemical composition of sepiolite sample (wt%)

Component	wt.%
SiO_2	53.47
MgO	23.55
Al_2O_3	0.19
Fe_2O_3	0.16
CaO	0.71
LOI*	21.49

*LOI: loss of ignition

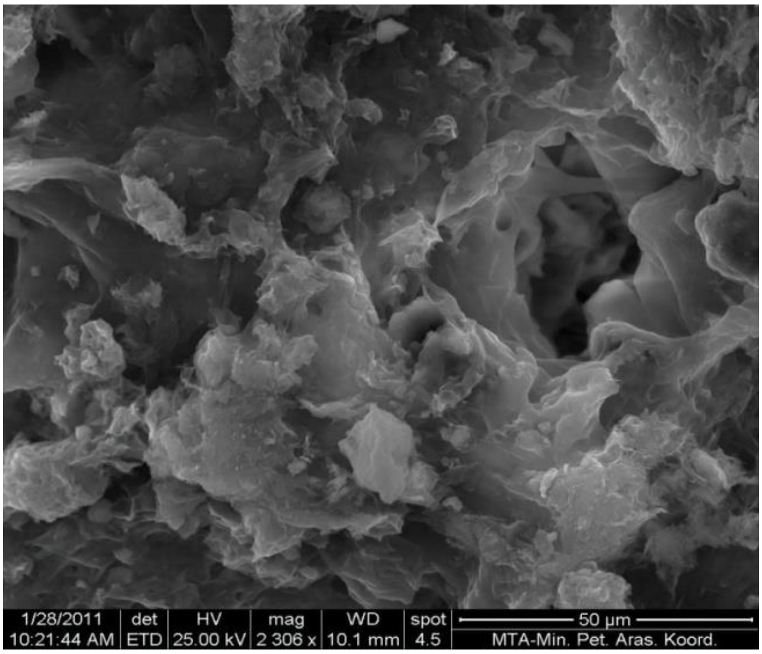


Figure 1. SEM microphotograph of sepiolite crystals with drusy texture

3.2. Statistical Analysis

Estimated regression coefficients and related statistics are given in Table 4. In order to determine which of the effects in the model are statistically significant, *p*- values were used. If the p-value is less than or equal to 0.05 (commonly used α-level), it is concluded that the effect is significant. Since the p-values of X_2, X_3, X_4, X_2X_2 and X_3X_3 are less than 0.05, it was concluded that the effects of these terms are statistically significant.

After identifying a significant set of effects (dosage, concentration, time, squared terms of dosage and concentration), related statistics were then recalculated. Table 5 shows the regression table of the reduced model. This model can be used as the final model to conduct optimization.

Table 4. Estimated regression coefficients

Term	Coef	SE Coef	T	P
Constant	60.4138	15.0573	4.012	0.001
pH	-0.7020	2.9962	-0.234	0.818
Dosage	1.6768	0.4770	3.515	0.003
Concentration	0.1749	0.0793	2.206	0.042
Time	0.3674	0.1656	2.218	0.041
pH*pH	0.1018	0.2123	0.480	0.638
Dosage*Dosage	-0.0254	0.0067	-3.808	0.002
Concentration*Concentration	-0.0007	0.0002	-3.825	0.001
Time*Time	-0.0016	0.0008	-1.972	0.066
pH* Dosage	-0.0211	0.0503	-0.420	0.680
pH* Concentration	0.0005	0.0083	0.059	0.954
pH* Time	0.0022	0.0173	0.127	0.901
Dosage* Concentration	-0.0008	0.0015	-0.522	0.609
Dosage*Time	-0.0017	0.0031	-0.564	0.581
Concentration*Time	-0.0009	0.0005	-1.696	0.109

S = 3.47635 PRESS = 1113.32
R-Sq = 85.26% R-Sq(pred) = 15.12% R-Sq(adj) = 72.36%

Coef: Coefficient SE Coef: Standard Error of Coefficient T: Student's t test P: Probability

Table 5. Estimated regression coefficients for reduced model

Term	Coef	SE Coef	T	P
Constant	76.7678	4.34511	17.668	0.000
Dosage	1.3145	0.27254	4.823	0.000
Concentration	0.1020	0.04723	2.159	0.041
Time	0.0395	0.02431	1.625	0.117
Dosage*Dosage	-0.0244	0.00650	-3.759	0.001
Concentration*Concentration	-0.0007	0.00018	-3.777	0.001
S = 3.42393 PRESS = 744.309				
R-Sq = 77.66% R-Sq(pred) = 43.25% R-Sq(adj) = 73.19%				

The regression equation in Eq. (2) was created using the values found under the coefficients column in Table 5. According to equation (1), dosage (*X*$_2$), and concentration (*X*$_3$) have quadratic effects on removal efficiency, while time only has a linear effect. The relationship between dosage and efficiency, and concentration and efficiency follow a curved line, rather than a straight line. Thus, optimum values of these experimental factors can be found.

$$y = 76.7678 + 1.3145 \cdot X_2 + 0.1020 \cdot X_3 + 0.0395 \cdot X_4 - 0.0244 \cdot X_2^2 - 0.0007 \cdot X_3^2 \quad (2)$$

R-square is a goodness-of-fit-measure, and tells how much of the variability in the dependent variable is explained by the independent variables. The adjusted R-square gives a truer estimate by taking into account the number of independent variables. The value of adj. R- square means that 73.19% of the total variance in the removal efficiency is explained by the experimental factors involved.

The ANOVA results indicate the relative importance of the linear and square sources with respect to the sum of squares (Table 6). The order of factors from high to low contribution on removal efficiency is concentration, dosage, concentration* concentration, dosage*dosage, and time. ANOVA results also show that all the included effects in the model except time are statistically significant at 0.05 level.

Table 6. Analysis of variance for removal efficiency (%)

Source	**DF**	**Seq SS**	**Adj SS**	**Adj MS**	**F**	**P**
Regression	5	1018.54	1018.54	203.709	17.38	0.000
Linear	3	712.44	340.39	113.464	9.68	0.000
Dosage	1	247.3	272.72	272.723	23.26	0.000
Concentration	1	434.18	54.67	54.67	4.66	0.041
Time	1	30.96	30.96	30.963	2.64	0.117
Square	2	306.1	306.1	153.051	13.06	0.000
Dosage*Dosage	1	138.84	165.69	165.692	14.13	0.001
Concentration*Concentration	1	167.26	167.26	167.26	14.27	0.001
Residual Error	25	293.08	293.08	11.723		
Lack-of-Fit	9	284.92	284.92	31.658	62.08	0.000
Pure Error	16	8.16	8.16	0.51		
Total	30	1311.62				

Optimization plot gives the best settings for each factor to specified response. Figure 2 recommends sepiolite dosage at 26 g l^{-1}, initial concentration at 77 mg l^{-1}, and contact time at 42 min. At this setting, the predicted removal efficiency equals to 99.9997% with a desirability value of 0.99973. Since there is only a single response variable, this desirability value is basically the same result with composite desirability.

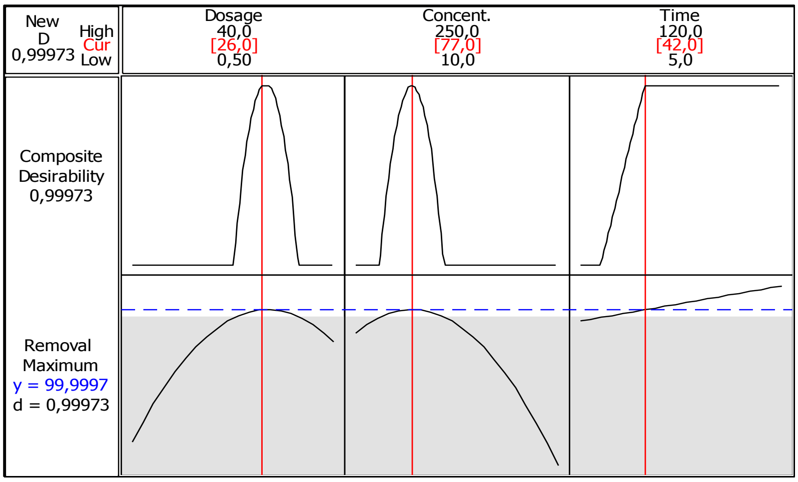


Figure 2. Optimization plot

The contour and surface plots can also be used to visually identify the optimal settings for experimental factors. Since these plots show only two factors at a time, any extra factors are held at a constant level. The contour plot shows multiple combinations of dosage, and concentration that can be used to set the process on target removal efficiency. The surface plot, a three-dimensional wireframe graph, represents the functional relationship between the removal efficiency and the experimental factors, dosage, and concentration.

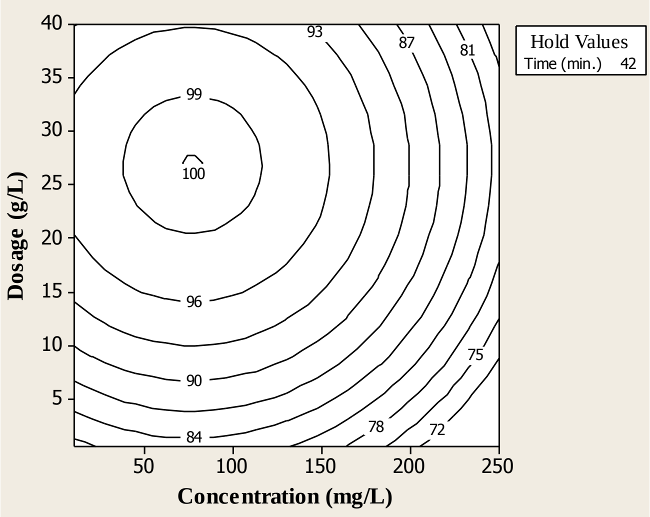


Figure 3. Contour plot of dye removal efficiency

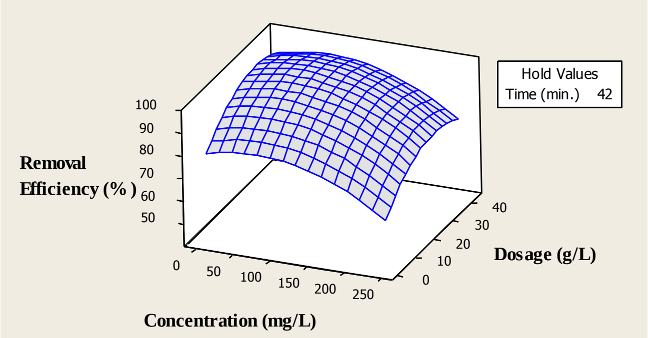


Figure 4. Surface plot of dye removal efficiency

Initial dye concentrations provide an important driving force to overcome all mass transfer resistance of the dye between the aqueous and sepiolite (Mona *et al*., 2011). Sepiolite, which is a kind of fibrous silicate clay mineral, is formed of tetrahedral and octahedral sheets. The systematic inversion of tetrahedral and octahedral sheets in the layer is periodically interrupted and the coordination of terminal octahedral ions is completed with strongly bonded water molecules. This mineral structure results in the adsorption sites with high surface irregularities. The adsorption phenomena for such systems are complex (Balci, 2004).

Figure 3 and Figure 4 shows the adsorption of malachite green at different initial dye concentrations with respect to varying sepiolite dosage. At low concentrations, malachite green ions present in the adsorption medium can interact with the binding sites. At high concentrations (250 mg l^{-1}), because of the saturation of the adsorption sites, the rate constant of dye adsorption onto the sepiolite shows a decreasing trend. It may be noted that initial dye concentration was the most significant component of the regression model for the present application, whereas, the initial solution of pH showed the lowest effect on the dye adsorption efficiency. According to Figure 3 and Figure 4, the maximum efficiency occurs at dosage 26 g l^{-1} and concentration 77 mg l^{-1} when time was kept at 42 min. The predicted maximum efficiency is approximately 99.9% which is the same as the result from the optimization.

4. Conclusions

The present study dealt with malachite green dye removal from aqueous solutions using sepiolite. The performance of sepiolite was modeled and optimized using central composite design. The effects of four important operational parameters including initial pH of solution, contact time, initial dye concentration, and sepiolite dosage were evaluated by the response surface and counter plots. Analysis of variance (ANOVA) showed the relative significance of process parameters in removal process. The quadratic model was analyzed using ANOVA technique. The *F* value of the regression was found to be 17.38 with corresponding *p* value of 0.000. It implies that the model is significant and can appropriately explain the relation between response and independent variables. Initial concentration, dosage, and contact time were found to be as significant factors. The second-order regression model was developed to predict the removal efficiency using Minitab. The optimal conditions to remove malachite green dye removal from aqueous solution at constant temperature of 23 °C, and stirring speed of 175 rpm were found to be contact time 42 min, initial dye concentration 77 mg l^{-1}, and sepiolite dosage 26 g l^{-1}. At these conditions, the predicted maximum removal efficiency (99.9%) was achieved. The present results showed that sepiolite which is received from local resources and low cost materials have a good potential for malachite dye removal from aqueous solution in the industrial application.

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