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Optimization study of adsorption of crystal violet and congo red onto sepiolite and clinoptilolite

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Abstract

The purpose of this study was to investigate the adsorption properties of locally available sepiolite and clinoptilolite materials as adsorbents for the removal of crystal violet and congo red dye ions from aqueous solution. Previous experiments have revealed that two variables, concentration and adsorbent dosage, have a significant effect on removal efficiency. In order to find the set of operating conditions for these variables that result in the best removal efficiency, central composite design of experiments was utilized. The results showed that sepiolite is a suitable material with 99% removal efficiency for the adsorption of both crystal violet and congo red from aqueous solution. However, in spite of clinoptilolite is also a suitable adsorbent for crystal violet, removal efficiency of congo red is rather low.

Keywords: Optimization, dye, removal, sepiolite, clinoptilolite

1. Introduction

Dyeing wastewater discharged into natural receiving waters may make them unacceptable for public consumption. Most of the dyes are stable against photo degredation, bio-degradation, and oxidizing agents. There are several methods for dye removal, such as adsorption, oxidation-ozonation, ultrafiltration, photodegradation, nanofiltration, coagulation-flocculation and biological methods. Among these removal methods, adsorption is an attractive alternative method. Many adsorbents have been tested on the possibility to lower concentrations from aqueous solutions, such as active carbon, peat, chitin, red mud, calcite, clay, natural zeolites, bentonite, sepiolite, montmorillonite, perlite, iron oxide coated sand, birnesite and others. Adsorption is usually related to their specific surface area and porosity. Adsorption is due to presence of active adsorption centers on adsorbent materials surfaces (oxygen atoms in the tetrahedral sheet, water molecules coordinated with the Mg^{2+}, Ca^{2+}, Na^{+} and K^{+}ions at the edge of the structure, and silanol groups caused by the break-up of Si-O-Si bonds). Thus, these materials can be used as an adsorbent to remove basic dye from wastewater (Wang, *et al.*, 2005; Özdemir, *et al.*, 2006; Tor and Cengeloglu, 2006; Bukallah, *et al.*, 2007; Hameed *et al.*, 2008, Lian, *et al.*, 2009; Alpat *et al.*, 2009; Anirudhan and Ramachadran, 2015).

Sepiolite is often found associated with other clay and non-clay minerals such as carbonates, quartz, felsdpar and phosphates. The most important occurrences of sepiolite are found in Vallecas of Spain, Turkey, Madagascar and Tanzania. Sepiolite is a natural clay mineral consisting of magnesium hydro silicate which belongs to the group of silicates with a unit cell formula $Si_{12}O_{30}Mg_8(OH,F)_4 8H_2O$ (Tor, *et al.*, 2009; Uğurlu, 2009; Bingol, 2010). Sepiolite is a fibrous clay mineral that is formed of sheets of tetrahedral and octahedral oxides and it has canal cavities along the fibber. Due to its peculiar structure, sepiolite has considerable high sorption ability and can adsorb up to 200–250 times more water of its own weight. This mineral is widely used to remove undesired components from household and industrial wastewaters and also in various industrial manufacturing processes, such as, some organic matters from wastewater, heavy metals, ammonium and phosphate, color and other undesirable components, dyes, phenol and lignin (Balci, 2004; Turan, *et al.*, 2005; Uğurlu, 2009).

Among the zeolites, clinoptilolite, having the typical chemical formula $Na_6[(Al_2O_3)(SiO_2)30]\cdot 24H_2O$, is the most abundant natural zeolite and is widely used in the world. Clinoptilolite was the prodominant zeolite mineral produced in Turkey. Clinoptilolite has unique properties of high cation exchange capacity and stability to set attrition, which make it higly effective for the removal of toxic pollutantas from water and soils. The primary consuption of the world's largest producers is by the building and construction industry for aggregates and building stone. Other major apllications for clinoptilolite exist in the paper industry which replaces kaolin as a paper filler, and the agricultural industry which uses clinoptilolite as a soil amendment and use an animal feed additive (Zhao, *et al.*, 2008; Rahman *et al.*, 2013; Mirzaei, *et al.*, 2016).

The use of statistical methods to increase productivity and quality and to decrease cost in any industry is increasing. One of the most cost-beneficial of these methods is statistical design of experiments. Experimental Design is a technique of examining controlled changes of experimental factors and the observation of resulting changes in response variable. The main objectives of the experimental approach are 1) to obtain the maximum amount of information by using a minimum amount of resources, 2) to determine which factors shift the average response, and which have little or no effect and 3) To find settings for inputs that optimize the output and minimize the cost, and to validate results (Basu and Wright, 2003; Lakshminarayanan and Balasubramanian, 2009; Mona *et al.*, 2011).

In experimental design studies, when the data set presents curvature, experimental data cannot be described by linear function. In this case, second-order models, Response Surface Methodology (RSM), is used to describe the system studied. The objective of RSM is to optimize response variable which is affected by experimental factors. There are two main types of Response Surface Designs: 1) Central Composite Designs (Coruh and Elevli, 2014; Arslan et al, 2014; Coruh and Elevli, 2015; Çetintaş and Bingöl, 2016) and 2) Box-Behnken Designs (Çoruh et al, 2012; Sisman, 2014; Sisman and Sisman, 2016).

The aim of this study is to investigate the easy and economic removal of crystal violet and congo red from aqueous solutions by adsorption on sepiolite and clinoptilolite. The RSM approach was used to develop the mathematical model and study the interactive effect of process parameters. The present study was aimed at maximizing the removal of crystal violet and congo red dyes using parameter optimization.

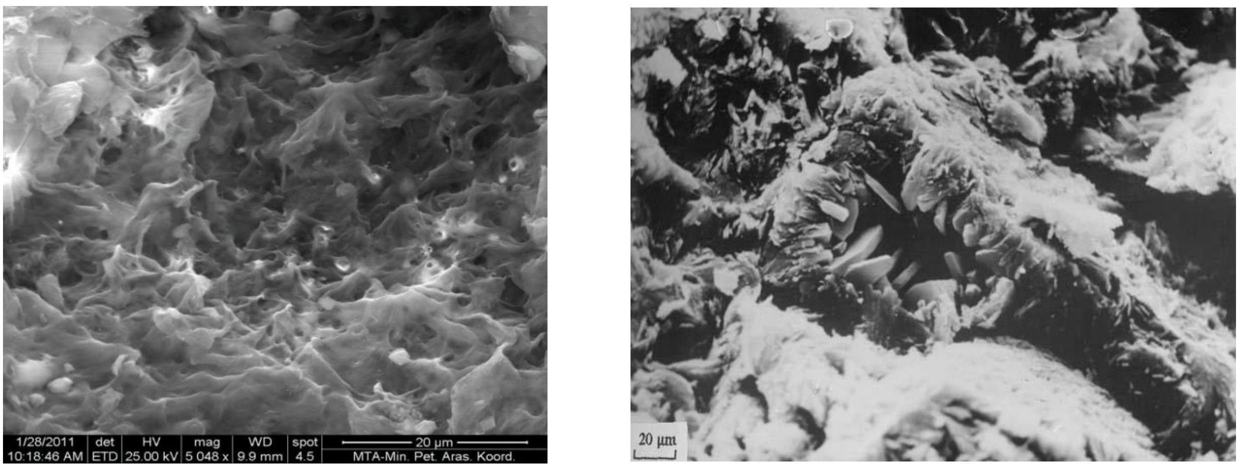
2. Materials and Methods

2.1. Sepiolite

The sepiolite used as an adsorbent was obtained from Eskişehir of Turkey. It was crushed into small pieces from rock form and then powdered in a mortar. Prior to batch adsorption experiments, the adsorbent was washed with distilled water in order to remove the surface dust, and dried at 103 °C. The chemical composition of the sepiolite was evaluated by using X-ray Fluorescence techniques (Rigaku ZSX Primus). The chemical composition of sepiolite included significant levels of SiO_2 (53.47%), MgO (23.557%) and Na_2O (1.40%) while the contents of other metal oxides were approximately 20.0%. The result of BET measurement was found as 82.35 m^2/g for sepiolite. The SEM analysis (scanning electron microscopy) of sepiolite is given in Fig. 1a.

2.2. Clinoptilolite

Clinoptilolite samples used in the study obtained from Manisa-Gördes basin Turkey. The chemical composition of the clinoptilolite was evaluated by using X-ray Fluorescence techniques (Rigaku ZSX Primus). The clinoptilolite contained significant levels of SiO_2 (65.0%), Al_2O_3 (13.7%) and Na_2O (5.6%) while the contents of other metal oxides were less than 13%. The result of BET measurement was found as 54m^2/g for clinoptilolite. The SEM analysis (scanning electron microscopy) of clinoptilolite is given in Fig. 1b. SEM studies show that the former volcanic shards are preudomorfed by aggregates of crystals of clinoptilolite. Clinoptilolite forms euhedral tabular crystals in the inner parts of the shards and sheaf-like fibrous crystals in the other parts. The size of the crystals do not exceed 20 μ across and tend to be 1-10 μ across. The mineralogical analysis clearly show that the former volcanic ash were psedomorphad by crystals of clinoptilolite up to 97 %. Crystal violet and congo red were obtained from Merck.



(a) sepiolite (b) clinoptilolite

Figure 1. SEM microphotograph of sepiolite on clinoptilolite crystals with drusy texture

2.3. Adsorption procedure

The main reason of studying such a large number of variables is to locate the best conditions for best adsorption. To test the conventional methods used to determine the influence of each one of these factors, experiments were carried out by systematically varying the studied factors and keeping constant the others. This should be repeated for every influence factors, resulting in an unreliable number of experiments. Factorial designs are widely used to investigate the effects of experimental factors and the interactions between those factors in a response. The advantages of factorial experiments include relatively low cost, a reduced number of experiments, and increased possibilities to evaluate interactions among the variables (Rytwo, *et al.*, 1998; Im, *et al.*, 2012).

Adsorption studies were carried out under different experimental variables including adsorbent dosage and dye concentration. A stock solutions 1000 mg/L of dyes were prepared in distilled water and was diluted according to the working concentration. Crystal violet and congo red dyes concentration were measured using a UV-Vis Spectrophotometer at λ_{max} of 590 nm and 500 nm, respectively. The dyes solution (100mL) at desired concentration (30 and 300 mg/L) and adsorbent dosage (2 and 20 g/L) taken in 250 mL erlanmayer flasks were used. The flasks were kept under agitation in a rotating shaker at 150 rpm for 2 h. The removal efficiency (E) of the sepiolite and clinoptilolite on crystal violet and congo red dyes were calculated according to the following formula:

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

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

2.4. Central Composite Design

Response Surface Methodology (RSM) consists of a group of mathematical and statistical techniques that are based on the fit of empirical models to the experimental data obtained in relation to experimental design (Bezerra *et al.*, 2008; Amani-Ghadima, 2013). In order to find a suitable approximation for the true relationship between dependent (y) and independent (x_1, x_2, …) variable, below models are used in RSM (Montgomery, 2013):

a) First- order model: In case the response is well modeled by a linear function of the independent variables

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \ldots\ldots \beta_k x_k + \varepsilon$$

b) Second- order model: In case there is curvature in the system

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j + \varepsilon$$

Two very useful and popular experimental designs that allow a second- order model to be fit are Box-Behnken Design (BBD) and Central Composite Design (CCD). When the design plan calls for sequential experimentation, CCDs are often used design because these designs can include information from a correctly planned factorial experiment. One of the major advantages of a CCD is that once the corner points are tested, if curvature is not present then it is not necessary to do the star runs. Unlike the CCD, all of the runs have to be done even if there is no curvature in BBD.

In general, A CCD in k factors requires 2^k factorial runs, 2^k axial runs and at least one center point. Alpha (α) for axial points is the distance of each axial point from the center and calculated by $\alpha = 2^{k/4}$.

3. Results and discussion

In order to find the set of operating conditions for the experimental factors that result in the best removal efficiency, central composite design of experiments was utilized. Table 1 shows the factor levels and complete design matrix. After performing the experiments according to the design with two replicates, removal efficiencies were recorded as response variable. The experimental parameters were analyzed and optimized in the MINITAB 16 statistical software environment.

Table 1. Factor levels and design matrix for CCD

Experimental Factor		Symbol	Levels of Factors			
			Low Level (-1)		High Level (+1)	
Concentration (mg/L)		X_1	30		300	
Adsorbent Dosage (g/L)		X_2	2		20	
Run	X_1	X_2	Average Removal Efficiency (%)			
			CV_Sep	CR_Sep	CV_Clino	CR_Clino
1	30	2	90.00	77.30	60.25	24.15
2	300	2	24.60	33.20	23.20	14.80
3	30	20	99.90	97.80	99.25	84.75
4	300	20	98.40	92.85	81.55	41.45
5	30	11	99.35	97.40	99.90	64.75
6	300	11	90.05	80.75	50.98	28.37
7	165	2	47.55	36.10	21.23	11.85
8	165	20	99.60	97.50	97.05	52.40
9	165	11	98.30	86.40	77.10	30.80
10	165	11	98.40	83.90	76.30	31.20
11	165	11	98.70	94.80	73.50	34.90
12	165	11	98.40	84.50	75.90	32.40
13	165	11	98.40	86.10	72.60	31.50
Factors: 2, Replicates: 2, Total Runs: 26				Cube Points: 8, Center Points in Cube: 10 Axial Points: 8, Alpha: 1		

Table 2. Estimated Coefficients and Models for Removal Efficiency

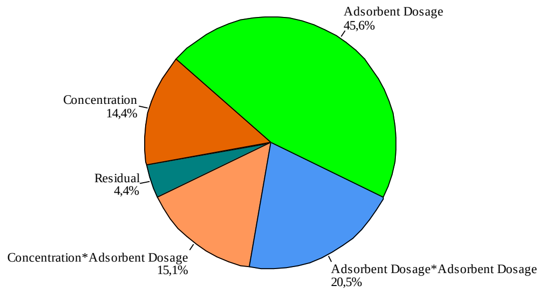
	Term	Coef	SE Coef	T	P
Crystal Violet_Sepiolite	Constant	78.1879	4.53120	17.255	0.000
	Concentration	-0,2387	0.02040	-11.703	0.000
	Adsorbent Dosage	5.9657	0.64354	9.270	0.000
	Adsorbent Dosage* Adsorbent Dosage	-0.2555	0.02573	-9.929	0.000
	Concentration* Adsorbent Dosage	0.0131	0.00154	8.527	0.000
	S = 5.29869 PRESS = 1030.92				
	R-Sq = 95.63% R-Sq(pred) = 92.35% R-Sq(adj) = 94.79%				
	$\hat{y}_{\text{Crystal Violet / Sepiolite}} = 78.1879 - 0.2387.x_1 + 5.9657.x_2 - 0,2555.x_2^2 + 0.0131.x_1.x_2$				
Congo Red_Sepiolite	Term	Coef	SE Coef	T	P
	Constant	67.3630	4.91136	13.716	0.000
	Concentration	-0.2620	0.04714	-5.559	0.000
	Adsorbent Dosage	5.9574	0.70706	8.426	0.000
	Concentration* Concentration	0.0003	0.00013	2.189	0.041
	Adsorbent Dosage* Adsorbent Dosage	-0.2121	0.02875	-7.376	0.000
	Concentration* Adsorbent Dosage	0.0081	0.00159	5.058	0.000
	S = 5.47325 PRESS = 1123.74				
	R-Sq = 94.62% R-Sq(pred) = 89.90% R-Sq(adj) = 93.27%				
	$\hat{y}_{\text{Congo Red / Sepiolite}} = 67.3630 - 0.2620.x_1 + 5.9574.x_2 + 0.0003.x_1^2 - 0,2121.x_2^2 + 0.0081.x_1.x_2$				
Crystal Violet_Clinoptilolite	Term	Coef	SE Coef	T	P
	Constant	43.9542	5.21256	8.432	0.000
	Concentration	-0.1280	0.01657	-7.723	0.000
	Adsorbent Dosage	6.3107	0.86461	7.299	0.000
	Adsorbent Dosage* Adsorbent Dosage	-0.1411	0.03764	-3.748	0.001
	S = 7.75022 PRESS = 2111.92				
	R-Sq = 91.61% R-Sq(pred) = 86.59% R-Sq(adj) =90.46%				
	$\hat{y}_{\text{Crystal Violet / Clinoptilolite}} = 43.9542 - 0.1280.x_1 + 6.3107.x_2 - 0,1411.x_2^2$				
Congo Red_Clinoptilolite	Term	Coef	SE Coef	T	P
	Constant	27.8486	2.80816	9.917	0.000
	Concentration	-0.2303	0.02659	-8.663	0.000
	Adsorbent Dosage	3.5193	0.18961	18.560	0.000
	Concentration* Concentration	0.0006	0.00007	8.433	0.000
	Concentration* Adsorbent Dosage	-0.0070	0.00096	-7.311	0.000
	S = 3.28380 PRESS = 379.178				
	R-Sq = 97.65% R-Sq(pred) = 96.07% R-Sq(adj) = 97.21%				
	$\hat{y}_{\text{Congo Red / Clinoptilolite}} = 27.8486 - 0.2303.x_1 + 3.5193.x_2 + 0.0006.x_1^2 - 0.0070.x_1.x_2$				

The main goal of RSM is to create a predictive model of the relationship between the factors and the response. The coefficients in Table 2 were used to develop this model that can be used to find the optimal response within specified ranges of the factors. The quadratic terms in these equations model the curvature in the true response function. It should be noted that only statistically significant terms ($p<0.05$) were included in models. According to the analysis results, over 90% of variability in removal efficiency is explained by the studied experimental factors.

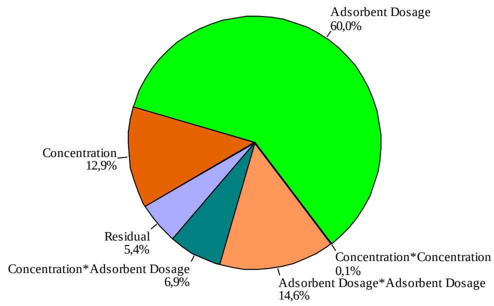
A pie chart can be used to graphically display proportion of total variance that is attributable to each effect. The entire circle represents the total sum of squares. Pie Charts in Fig.2 displays the relative importance of the first-order, second-order and interaction sources with respect to sum of squares. The most significant term for all four models is adsorbent dosage accounting for over 45% of the variability. The order of factors from high to low contribution on removal efficiency are adsorbent dosage and squared term of adsorbent dosage for sepiolite, and adsorbent dosage and concentration for clinoptilolite. The increase in the dye sorption with increasing the sorbent dosage can be ascribed to the greater surface area and the accessibility of more adsorption sites (Im *et al.*, 2012; Gottipati *et al.*, 2010; Hameed *et al.*, 2008).

A contour plot is produced to visually display the region of optimal factor settings (Lakshminarayanan and Balasubramanian, 2009). It shows how a response variable relates to two experimental factors and is useful for establishing desirable response values such as removal efficiency. Points that have the same response are connected to produce contour lines of constant responses. From these figures, it is possible to determine optimal experimental factors. For example, for reaching 99% removal, it is necessary to set adsorbent dosage at 6-19 g/L

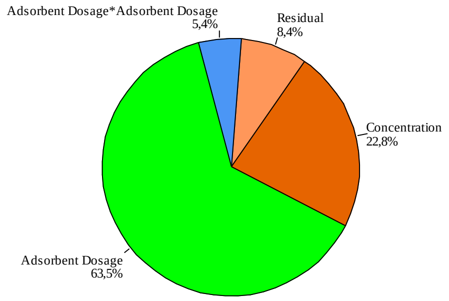
(Fig. 3a), 10-19 g/L (Fig. 3b) and higher than 14 g/L (Fig. 3c). In case of congo red adsorption onto clinoptilolite, it is not possible to reach over 80% removal efficiency. Besides, it appears that maximum removal can be achieved by setting concentration lower than 75 mg/L (Fig. 3b) and lower than 100 mg/L (Fig. 3c). Fig. 3a indicates that several combinations of concentration and adsorbent dosage will result in acceptable removal efficiency.



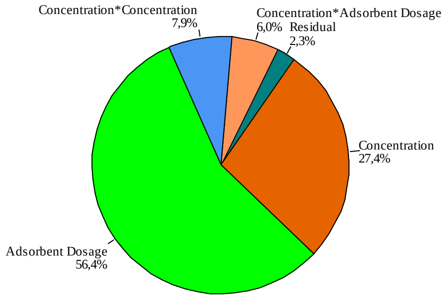
a) Crystal Violet_Sepiolite



b) Congo Red_Sepiolite



c) Crystal Violet_Clinoptilolite



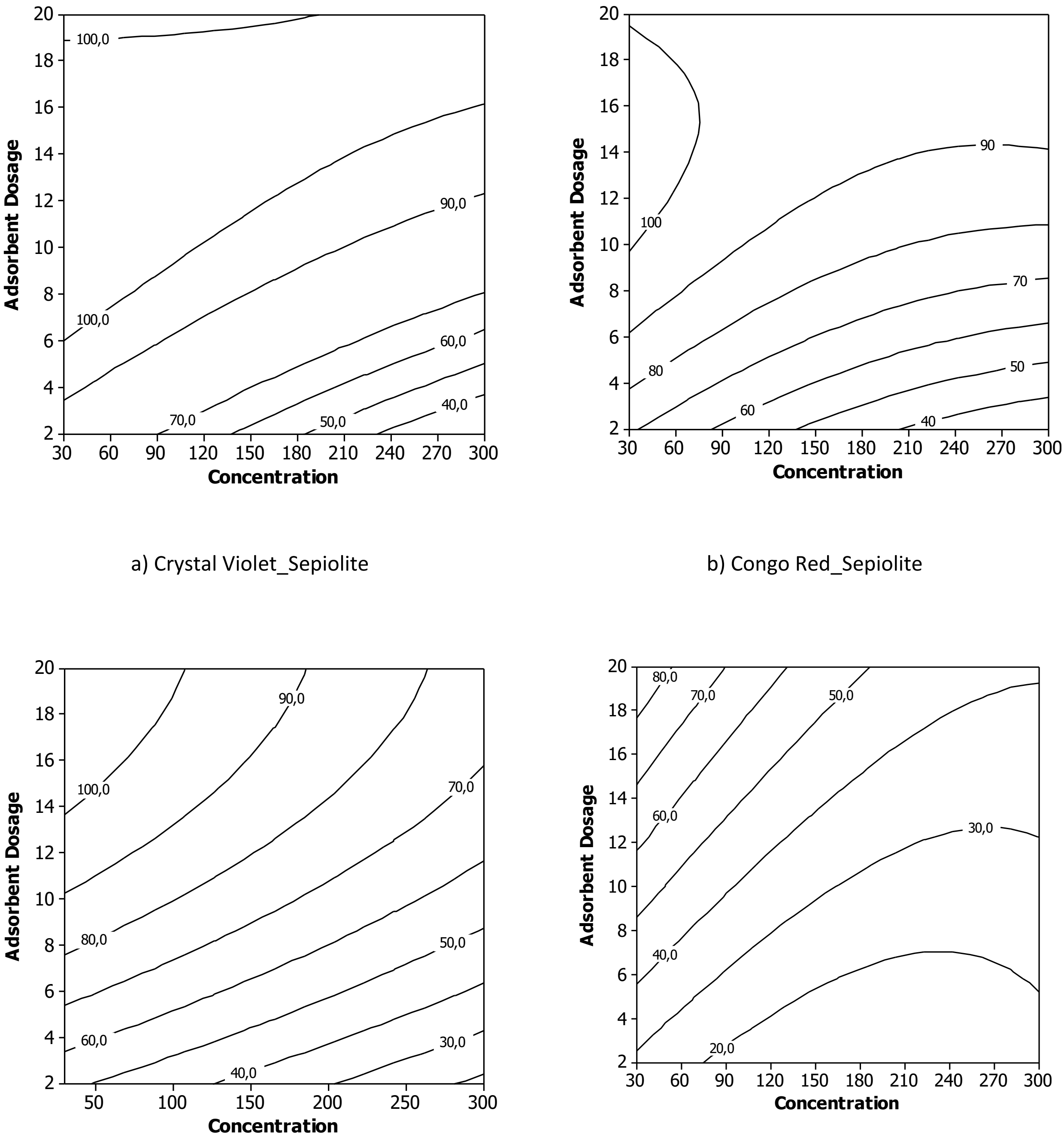
d) Congo Red_Clinoptilolite

Figure 2. Pie chart of sum of squares sources

The response can also be represented graphically in the three- dimensional space to help visualize the shape of response surface. Surface plots in Fig.4 shows quadratic effect in both experimental factors since response surfaces exhibit curvature. Removal efficiency can be maximized by setting concentration and adsorbent dosage. If concentration is hold constant, removal efficiency increases as adsorbent dosage is increased. Initial dye concentrations provide an important driving force to overcome all mass transfer resistance of the dye between the aqueous and adsorbent materials. 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. Removal results presented in present study are in good agreement with the adsorption studies found in literature (Mirzai *et al.*, 2016; Çoruh and Elevli, 2015; Rahman *et al.*, 2013).

4. Conclusion

The purpose of experimental design is to characterize, predict, and then improve the behavior of any system or process. In this study, CCD was applied to explore the optimal conditions for crystal violet and congo red removal from aqueous solutions by sepiolite and clinoptilolite. The effect of initial dye concentration and adsorbent dosage were examined. Results of the obtained models indicated that adsorbent dosage had the highest importance effect on removal efficiency. Dye removal efficiency of 99 % was observed at optimum points except for congo red adsorption onto clinoptilolite. Dye removal efficiencies were improved by increasing of adsorbent dosage and initial dye concentration. These results are in good agreement with the previous studies. The results of present investigation show that sepiolite and clinoptilolite can be used as low cost adsorbents for removing the dye ions from aqueous solution.



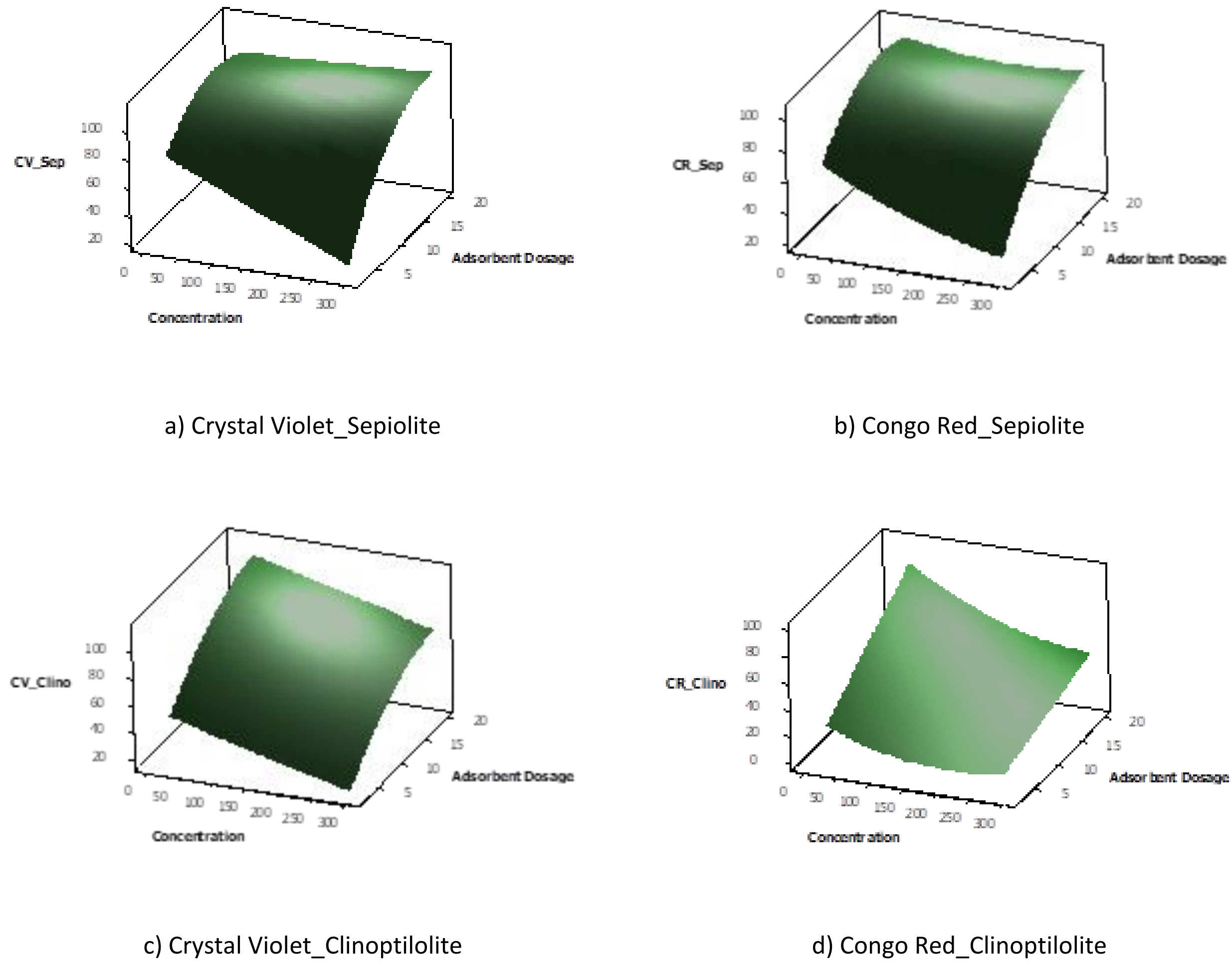
a) Crystal Violet_Sepiolite

b) Congo Red_Sepiolite

c) Crystal Violet_Clinoptilolite

d) Congo Red_Clinoptilolite

Figure 3. Contour plots



a) Crystal Violet_Sepiolite b) Congo Red_Sepiolite

c) Crystal Violet_Clinoptilolite d) Congo Red_Clinoptilolite

Figure 4. Surface plots

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