

# Central Composite and Factorial Design of Experiments for Textile Dye Removal from Solution by Pumice, KOH-Pumice, HCl-Pumice, Kaolinite, KOH-Kaolinite, HCl-Kaolinite Clays

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## Abstract

The pollution of surface waters by the textile dye-containing wastewaters causes to an increasing concern throughout the world. Methyl violet is a toxic, mutagenic and harmful textile dye against humans. Clays are cheap and vast adsorbents in the nature. Methyl violet dye removal from solution was studied by raw pumice and raw kaolinite using the central composite experimental design method. Firstly, raw kaolinite and raw pumice were tested for the dye adsorption and then capacities of raw kaolinite and raw pumice were aimed to increase by KOH and HCl modification. The experimental parameters studied for the central composite design were initial pHs (2-10), adsorbent amounts (0.2-1 g/50 mL) and initial concentrations (100-500 mg/L). In central composite experimental design of raw kaolinite and raw pumice, the all parameters were found as statistically unimportant for kaolinite and pH, pH-pH, concentration-concentration parameters were found statistically important and other parameters were unimportant for raw pumice. Maximum capacities for raw pumice and raw kaolinite were calculated as 7.15 and 18.31 mg/g, respectively. The dye removal of KOH-pumice and KOH-kaolinite were not high from raw pumice and raw kaolinite. HCl modified kaolinite and pumice were ineffective for dye removal. Kinetics of dye removal by raw kaolinite fitted to the pseudo second order model. pH<sub>pzc</sub> values of raw pumice and raw kaolinite were found as 6, respectively. Dye removal was obtained as 90% for 50 mg/L dye concentration by kaolinite. Raw kaolinite was determined as the most effective adsorbent for dye concentrations especially below 100 mg/L.

**Keywords:** Kaolinite, modified-kaolinite, methyl violete removal, modified-pumice, pumice, Optimization

## 1. Introduction

The raising population of humans necessitates to growing industrialization in food and textile industries which produce a huge amount of dye containing wastewater. Some dyes are toxic for humans, animals, soil microorganisms and plants according to their chemical ingredients. Worldwide, it is estimated that 700,000 tons of dyes are generated annually, and 12.5 % of them are inappropriately disposal into aquatic resources [1]. Textile industry wastewaters contain high dye residue, dense color, high BOI and COD [2]. Biological processes like activated sludge, trickling filter, anaerobic digestion are not effective to most of dyes due to dye toxicity for microorganisms. But, physicochemical methods such as adsorption,

coagulation, electrocoagulation, electrooxidation, fenton oxidation-coagulation, biosorption generally have gave good results for dye removal [2,3-7]. Among the mentioned methods, adsorption method in which vast and cheap adsorbents are used has come forward in the last fifty years. Dye removal by adsorption can be realized by clay minerals [8]. Kaolinite and pumice clay minerals are present in vast amounts as pure in their pits and they may be used widely in adsorption investigations for heavy metal and dye treatment from wastewaters. Pumice is highly porous igneous rock, usually containing 67–75% SiO<sub>2</sub> and 10–20% Al<sub>2</sub>O<sub>3</sub>, with a glassy texture [9]. The pumice is used as abrasive material in cleaning and polishing and as light construction material [9]. The total amount of world pumice deposits is sixteen billion tons and the reserves

are hosting in ABD, Turkey, Italy, Greece, Spain, France, Yugoslavia and Germany [9]. Kaolinite is a phyllosilicate clay mineral with the formula of  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  [10]. It is a layered silicate mineral, forming one tetrahedral layer of silica bounded to octahedral layer of alumina by oxygen atoms [10]. The chain like connection of these layers occurs by hydrogen bonds [10]. The adsorption of dyes on clay minerals occurs by interaction on positive surface Si and Al cations and further interaction with  $\text{Si}=\text{OH}$  and  $\text{Al}=\text{OH}$  functional groups [10]. Dye binding realizes at surface of clay and if the clay pores are enough for dye molecule entrance, also dye binding occurs at interior of pores of clay. Textile dye types are reactive dyes, direct dyes, acid dyes, all-purpose dyes, natural dyes, VAT dyes, disperse dyes and azoic dyes. The surface of clay minerals shows different affinity properties for adsorption of different dyes. For instance, while cationic molecules of a cationic dye are adsorbed on negative surface, anionic molecules of an anionic dye are adsorbed on positive surface. Thus, modification of clay surface sometimes becomes necessary. In this study, methyl violet, a cationic dye, adsorption was aimed to increase on kaolinite and pumice surface by modification by KOH and HCl solution. Since methyl violet is cationic dye and requires to negative surface, but sometimes hydrogen bonds at pHs (3-6) may increase the cationic dye adsorption as has been in present study results. Full factorial experimental design by the Minitab 16.0 programme uses surface, counter and optimization graphs. It requires low experimental run.

Optimization study for experiments of adsorption can be done by various computer programmes. Minitab 16.0 computer program is one of the choices for optimization of adsorption data. Central composite experimental design is a tool of Minitab 16.0 programme. This optimization method uses a wide experimental matrix for optimization. This method enables a regression model and Anova analysis. Regression model is used for data estimation of operation of adsorption reactors and Anova analysis gives the confidence factor to understand the statistically important parameters. Also, central composite design method uses surface, counter and optimization graphs for data and parameter analysis [11]. Factorial design requires the low experimental runs and gives linear relationship between parameter levels changing from low value to high value.

In this study, methyl violet, a cationic dye, removal from solution was studied by using kaolinite and pumice clay minerals. Optimization by central composite experimental design was done using Minitab 16.0 programme. After determination of capacities of these mineral, their surfaces were modified by KOH and HCl solutions and it was expected to increase of capacities. The reason of selection of this dye and minerals was wide usage of dye in textile and wide presence of adsorbents in open pits in Turkey. Modified adsorbents were studied using factorial experimental design except

acid modified clays. From the preliminary experiments, the acid modified clays were found as ineffective; therefore their results were not given completely.

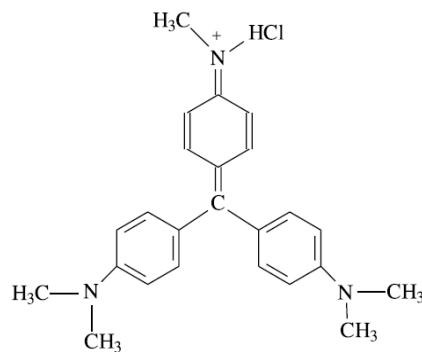
## 2. Materials and Method

### 2.1 Adsorption Experiments for Central Composite Design in Dye Removal by Raw Kaolinite and Raw Pumice Clays

Methyl violet dye is a cationic dye. The open formula of methyl violet is given in Figure 1. The stock dye solution was prepared as 1,000 mg/L and the studied solutions were prepared from this stock solution. Adsorption experiments were carried out according to experimental matrix obtained from Minitab 16.0 programme. Firstly, 15 solutions for raw kaolinite and raw pumice clay minerals in central composite design were prepared at different concentrations, pHs and adsorbent amounts for 50 mL solutions. Then, prepared solutions were located to temperature controlled incubator shaker. Adsorption reactions of kaolinite and pumice clay minerals were conducted at 3 hours, 100 rpm and 20 °C. After reaction, 5 mL solution samples were taken and centrifugated at 3,000 rpm during 3 minutes. The supernatant samples of 1 mL were diluted and measured by using UV-visible spectrophotometer at 584 nm wave length. pH of solutions was adjusted using diluted HCl and KOH solutions. Automatic pipettes were used for adjustment and taking of solutions. A pH meter was used for pH measurements and a magnetic stirrer was used for dye solution preparation. Experiments were conducted with kaolinite and pumice at <850 µm particle size. A time span of 3 hours was found as enough for equilibrium between dye and raw pumice and raw kaolinite. The point of zero charge (pHpzc) values of both raw clays were measured for pHs of 2, 4, 6, 8, 10, 12. The pHpzc experiments were carried out for 50 mL solution, 1.5 g raw clay, 20 °C and 3 hours interaction by temperature controlled incubator shaker. The used pumice was from Tatvan and kaolinite from Balıkesir cities in Turkey. Adsorbent capacity and removal percentages were calculated using following equations.

$$\eta = \frac{(C_0 - C) \times 100}{C_0} \quad (\text{Eq.1})$$

Here,  $\eta$  is removal percentage (%).  $C_0$  and  $C$  are initial and treated solution dye concentrations (mg/L).



**Figure 1.** Chemical structure of methyl violete (MV) dye.

$$Q_e = \frac{(C_0 - C) \times 50}{1,000 \times W} \quad (\text{Eq.2})$$

Here,  $Q_e$  is adsorption capacity (mg/g).  $C_0$  and  $C$  are initial and treated solution dye concentrations (mg/L).  $W$  is adsorbent amount (g) in 50 mL.

## 2.2 Modification Experiments of Clay Minerals by KOH and HCl

For modification of kaolinite and pumice clay minerals, 200 g clay with <850  $\mu\text{m}$  particle size was treated with 10 g KOH/1,000 mL pure water solution during 20 minutes. The equilibrium pHs of this clay-base solution mixtures were 13.34 for kaolinite and 13.37 for pumice. The modified clay minerals were filtered with filter paper and dried during 23 hours at 103  $^\circ\text{C}$  and sieved to <850  $\mu\text{m}$  particle size. The theoretical pHs of base solution was calculated as 13.25, therefore, the modification by base was low or never happened. For HCl modification of pumice and kaolinite, 25 g of clays were modified with 10 mL concentrated HCl (37%) in total 250 mL pure water mixture during one hour while content was being stirred. After modification, solutions were filtered with Whatman filter paper and dried in an oven during 5 hours at 103  $^\circ\text{C}$ .

## 2.3 Factorial Design Experiments for Dye Removal by KOH and HCl Modified Clays

$2^2$  factorial experimental design was applied to KOH-pumice, KOH-kaolinite, HCl-pumice and HCl-kaolinite. The experimental parameters were 20  $^\circ\text{C}$ , 1.5 g adsorbent amount, 3 hours, 100 rpm, 50 mL solutions. The intervals of parameters were pH (4, 8) and concentration (200, 400 mg/L). Experiments were carried out by temperature controlled incubator shaker. The experimental procedure was the same of raw pumice and raw kaolinite. The HCl modified kaolinite and pumice gave the low adsorption capacities and therefore their results were not given.

## 3. Results and Discussion

### 3.1 Central Composite Design of Dye Removal by Raw Kaolinite and Raw Pumice

The low and high levels of parameters are given in Table 1. Fifteen different experimental runs were realized for raw kaolinite and raw pumice minerals by using central composite design. For this purpose, the experimental parameters were initial pHs (2-10), concentrations (100-500 mg/L), and adsorbent amounts (0.2-1 g/50 mL). Central composite design is a widely used approach for data optimization for maximum output. Central composite design uses face centered or face centered plus axial and center points for analysis cage matrix. Also, minimum two and maximum ten factors can be used for statistical analysis in central composite design. Central composite design uses counter graphs and surface graphs for data analysis. Central composite design analysis gives regression model coefficients for model formation and Anova analysis gives confidence constants for determination of statistically meaningful parameters. The regression model equation can be adjusted in the program (Minitab 16.0) as linear, linear plus squares, linear plus interactions or full quadratic [12]. The regression models for kaolinite and pumice can be given as follows in full quadratic form:

$$\text{Kaolinite (mg/g)} = -20.3363 + 0.6469 \cdot \text{pH} + 33.9572 \cdot \text{AA} + 0.0951 \cdot \text{C} + 0.1680 \cdot \text{pH} \cdot \text{pH} - 18.9759 \cdot \text{AA} \cdot \text{AA} + 0.000 \cdot \text{C} \cdot \text{C} + 0.1381 \cdot \text{pH} \cdot \text{AA} - 0.0088 \cdot \text{pH} \cdot \text{C} - 0.0627 \cdot \text{AA} \cdot \text{C} \quad (\text{Eq.3})$$

$$\text{Pumice (mg/g)} = 11.5716 - 3.5036 \cdot \text{pH} + 15.6403 \cdot \text{AA} - 0.0568 \cdot \text{C} + 0.2910 \cdot \text{pH} \cdot \text{pH} + 2.2724 \cdot \text{AA} \cdot \text{AA} + 0.0001 \cdot \text{C} \cdot \text{C} - 1.2429 \cdot \text{pH} \cdot \text{AA} + 0.0042 \cdot \text{pH} \cdot \text{C} - 0.0343 \cdot \text{AA} \cdot \text{C} \quad (\text{Eq.4})$$

Here, pH is solution pH, AA is adsorbent amount (g/50 mL) and C is concentration (mg/L).

The all parameters were found as statistically unimportant for raw kaolinite. pH,  $\text{pH} \cdot \text{pH}$ ,  $\text{C} \cdot \text{C}$  parameters were found statistically important and other parameters were unimportant for raw pumice. Uncodded factors (i.e. real values of factors) were used in analysis of data. The selection of full quadratic equation for model was due to high correlation coefficient. Experimental matrix was given in Table 2. Anova analysis was given in Table 3.

**Table 1.** The low and high values of parameters in central composite design for raw kaolinite and pumice.

Parameters	-2	-1	0	1	2
<b>Kaolinite</b>					
pHs	2	4	6	8	10
Adsorbent (g/50 mL)	0.2	0.4	0.6	0.8	1
Concentration (mg/L)	100	200	300	400	500

<b>Pumice</b>					
pHs	2	4	6	8	10
Adsorbent (g/50 mL)	0.2	0.4	0.6	0.8	1
Concentrations (mg/L)	100	200	300	400	500

by solid-to-ion equilibrium. While sometimes capacities increase at low adsorbent amounts, the capacities sometimes remain constant from low adsorbent amount to high adsorbent amount. For instance, boron adsorption remained constant by increasing resin and alunite amount [13,14]. The reason of high adsorption capacity of middle adsorbent amount was probably due to solid-to-dye equilibrium [13,14]. This also may be related kaolinite surface zeta potential. Further, this was probably due to adsorbent amount-pH interaction. Dye dissociation or aggregation at low pHs might caused to easily or aggregation adsorption, respectively [15,16]. Sodium ions in methyl violet dye molecules exchanged with probably hydrogen atoms at low pHs by dissociation and dye molecules might aggregated with hydrogen atoms. Thus, aggregated dye molecules adsorbed on clay surface a bit high at low pHs.

### 3.2 Adsorbent Amount-pH Effect for Kaolinite

According to results given in Figure 2 (Surface plots), dye removal by kaolinite increased at both minimum pH and maximum pH for middle adsorbent amount. At high pH values, adsorbent surface gained more negative charge and cationic dye easily adsorbed but at low pH values, adsorbent surface gained positive charge and cationic dye molecules attached to surface by hydrogen bound [2]. Pollutant adsorption on adsorbent is related

**Table 2.** Experimental matrix in central composite design for dye removal by raw kaolinite and pumice (20 °C, 100 rpm, 50 mL, 3 hours, <850 µm particle size).

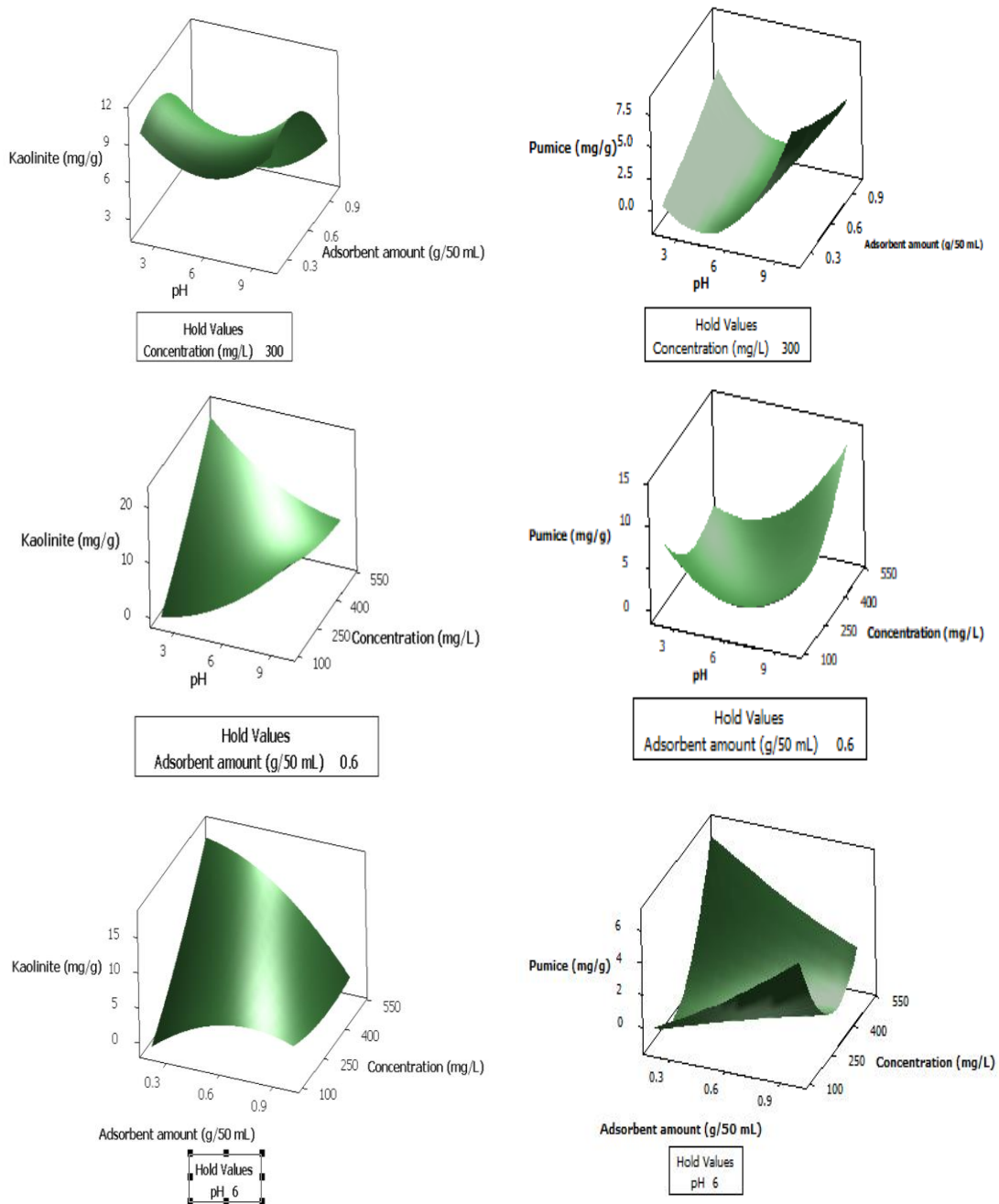
Run	Parameters			Responses			
	pH	AA	C (mg/L)	Kaolinite (mg/g)	Kaolinite Estimation (mg/g)	Pumice (mg/g)	Pumice Estimation (mg/g)
1	4	0.4	200	3.66	2.67	0.00	0.10
2	8	0.4	200	10.10	6.50	0.88	1.43
3	4	0.8	200	3.47	2.35	3.22	2.71
4	8	0.8	200	4.17	6.40	1.64	2.05
5	4	0.4	400	18.31	9.63	0.00	1.36
6	8	0.4	400	11.74	6.43	3.79	6.04
7	4	0.8	400	7.13	4.30	0.00	1.23
8	8	0.8	400	6.76	1.31	2.27	3.92
9	2	0.6	300	9.09	7.30	1.68	2.75
10	10	0.6	300	10.69	8.15	7.15	6.77
11	6	0.2	300	4.04	4.72	0.25	0.22
12	6	1	300	4.29	-0.72	0.00	0.71
13	6	0.6	100	5.30	4.10	2.02	2.54
14	6	0.6	500	11.36	5.97	4.97	5.66
15	6	0.6	300	6.82	5.04	0.00	0.10

pH is solution pH, AA is adsorbent Amount (g/50 mL), C is concentration (mg/L)

**Table 3.** Anova analysis of dye removal by raw kaolinite and pumice in central composite design.

Parameters	Kaolinite		Pumice	
	Constant	p	Constant	p
	R-Sq=74.70%		R-Sq= 91.36%	
	R-Sq(pred)=0.00%		R-Sq(pred)=18.46%	
	R-Sq(adj)=29.16%		R-Sq(adj)=75.30%	
Constant	-20.3363	0.519	11.5716	0.251
pH	0.6469	0.881	-3.5036	0.037
AA	33.9572	0.445	15.6403	0.264
C	0.0951	0.298	-0.0568	0.071
pH*pH	0.1680	0.548	0.2910	0.014
AA*AA	-18.9759	0.499	2.2724	0.786
C*C	0.000	0.797	0.0001	0.032
pH*AA	0.1381	0.966	-1.2429	0.240
pH*C	-0.0088	0.211	0.0042	0.073
AA*C	-0.0627	0.354	-0.0343	0.125

pH is solution pH, AA is adsorbent amount (mg/50 mL), C is concentration (mg/L)



**Figure 2:** Surface plots of dye adsorption on kaolinite and pumice clays.

### 3.3 Concentration-pH Effect for Kaolinite

According to results given in Figure 2 (Surface plots), dye removal increased with low pH and high concentration for kaolinite mineral. At low pHs, kaolinite surface gained positive charge and probably cationic methyl violet dye molecules attached to kaolinite surface by hydrogen bounds. At high concentrations, kaolinite surface was loaded by dye

molecules as a result of driving force of high dye concentration. Similar result for high concentration was reported in methyl violet dye adsorption on clinoptilolite and boron adsorption on alunite [2,14].



### 3.4 Concentration-Adsorbent Amount Effect for Kaolinite

According to results given in Figure 2 (Surface plots), kaolinite mineral showed high capacity for methyl violet dye at low adsorbent amounts and high concentrations. At low adsorbent amounts, dye concentration gradient on low adsorbent amount was high and therefore, more dye molecules adsorbed on kaolinite mineral. At high concentrations, the driving force of dye molecules caused to more dye adsorption on kaolinite mineral [2,14].

### 3.5 pH-Adsorbent Amount Effect for Pumice

According to results given in Figure 2 (Surface plots), methyl violet dye adsorption on pumice mineral increased at low and high pHs. Also, dye removal remained constant for adsorbent amount from low value to high value. At high pHs, pumice surface gained more negative charge and more dye adsorbed on pumice. The reason of constant pattern of adsorption capacity for all adsorbent amounts was thought that the dye adsorption on pumice was related with dye-to-solid equilibrium [13,14,17]. Low pHs probably increased the surface hydrogen bonds that increasing dye adsorption. Because methyl violet dye adsorption increased at low pH. This is also be related with pH-adsorbent amount interaction. While dye adsorption increased at low pHs with increasing adsorbent amount, at high pHs, adsorbent amount was ineffective.

### 3.6 Concentration-pH Effect for Pumice

According to results given in Figure 2 (Surface plots), methyl violet dye adsorption capacities increased at high pHs and high concentrations. At high pHs, surface of pumice mineral was more negative for dye adsorption and at high concentrations, dye was adsorbed at high amount on pumice as a result of high concentration driving force [2,14]. Again, low pHs increased the capacity due to hydrogen bonds.

### 3.7 Concentration-Adsorbent Amount Effect for Pumice

According to results given in Figure 2 (Surface plots), methyl violet dye adsorption increased at low adsorbent amount and high concentration. At low adsorbent amounts and high concentrations more dye molecules penetrate to pumice surface due to high driving force [2,14].

### 3.8 Factorial Design of Experiments for Methyl Violet Dye Removal by KOH-Kaolinite and KOH-Pumice

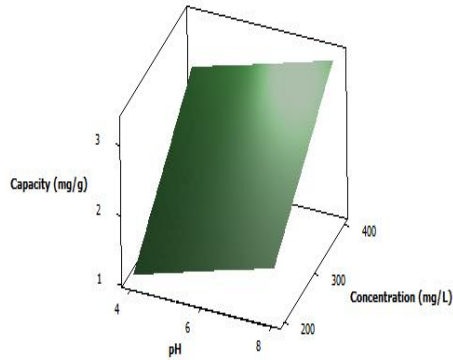
Generally clay surfaces gain negative charge by base modification and they show high affinity against cationic dye like methyl violet. Thus, in this study, kaolinite and pumice clay minerals were modified by KOH solution. Modification experiments were carried

out 200 g clay/10 g/L KOH solutions. After treatment of dye solutions with raw kaolinite and raw pumice by central composite design, the conducting of experiments by factorial experimental design for KOH-kaolinite and KOH-pumice would be practical in respect to time, cost and experimental number. Central composite design has required 15 experimental runs, but factorial design has required total 4 experimental runs for two factors and two levels. In the factorial design, concentrations (200 and 400 mg/L) and pHs (4 and 8) were applied. Factorial design is quite advantageous when compared with central composite, taguchi or classical single parameter experiments in respect to cost, time, experiment number and effort. On the other hand, central composite design is superior than factorial design in respect to wide experimental matrix. Factorial design and central composite design give statistically importance of main and interaction effect of parameters using Anova analysis. Both of the approaches use confidence factor (p) and regression model constants for Anova analysis. Also, Student-t test can be obtained from these statistically optimization methods. Generally, when the p values are low and Student-t test results are high, the importance of parameters is high [14]. The experimental matrix and response for factorial design is given in Table 4. The model constants are given in Table 5. According to Anova analysis, the all parameters are insignificant for KOH-kaolinite and KOH-pumice (coded factors and was not given). The surface plots of factorial analysis for KOH-kaolinite and KOH-pumice showed that high initial solution pHs and concentrations increased the capacities for modified kaolinite and pumice. The regression model are given in follows:

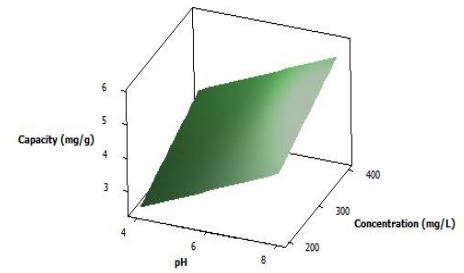
$$\text{Kaolinite (mg/g)} = -0.7375 + 0.458750 * \text{pH} + 0.006675 * \text{C} \quad (\text{Eq.5})$$

$$\text{Pumice (mg/g)} = -1.0875 + 0.15625 * \text{pH} + 0.007825 * \text{C} \quad (\text{Eq.6})$$

Here, pH is solution pH. C is concentration (mg/L). Models were developed according to uncoded factor values. The modification of raw pumice and raw kaolinite with HCl solution did not remove methyl violet dye. Therefore their removal results were not given in this study. Surface plots for factorial design were given in Figure 3 and 4.



**Figure 3:** Surface plots of dye adsorption on KOH-kaolinite.



**Figure 4:** Surface plots of dye adsorption on KOH-pumice clay.

**Table 4.** Experimental matrix in factorial design for optimization and responses (20 °C, 100 rpm, particle size<850 µm, adsorbent 1.5 g/50 mL, 3 hours).

Experimental Parameters				Dye Removal	
Adsorbent	Run	C	pH	Adsorption Capacity (mg/g)	Estimation Adsorption Capacity (mg/g)
Kaolinite	1	200	4	2.02	2.43
	2	200	8	4.68	4.27
	3	400	4	4.18	3.77
	4	400	8	5.19	5.60
Pumice	1	200	4	1.45	1.10
	2	200	8	1.38	1.73
	3	400	4	2.32	2.67
	4	400	8	3.64	3.29

pH is solution pH, C is concentration (mg/L).

**Table 5:** Factorial fitness to dye removal from water (Uncoded).

Parameters		Regression Model Constants
Kaolinite	Model Constant	-0.7375
	pH	0.458750
	Concentration	0.006675
Pumice	Model Constant	-1.0875
	pH	0.15625
	Concentration	0.007825

**Table 6:** Fitness of kinetic data to models for raw kaolinite (Natural pH, 25.7 °C, 1,000 rpm, 100 mg/L, 500 mL, 5 g kaolinite).

Kinetic Models	Coefficient of determination values (R <sup>2</sup> )
Zero-order	0.339
First-order	0.344
Second-order	0.351
Pseudo-second-order	1

### 3.9 Kinetics of dye removal by kaolinite using linear analysis

The determination of kinetics of (ad)sorption is an important way of operation and modeling of batch and column reactors because optimum operation time and reaction degree are determined by kinetic analysis [18]. While the reaction is free from the concentration, the

reaction degree is zero order and for dependence of reaction to concentration, reaction degree can be first order or second order. Also, generally adsorption kinetic

data are described by pseudo-first-order and pseudo-second-order models. The model equations are as follows [19]:

$$\left(\frac{dC}{dt} = -kC^n\right) \quad (\text{Eq.7})$$

The zero-order kinetic model is as follows.

$$C = C_0 - kt \quad (\text{Eq.8})$$

The first-order kinetic model is as follows.

$$\ln(C) = \ln(C_0) - kt \quad (\text{Eq. 9})$$

The second-order kinetic model is as follows.

$$\frac{1}{C} = \frac{1}{C_0} - kt \quad (\text{Eq.10})$$

Here,  $C_0$  is the initial dye concentration (mg/L),  $C$  (mg/L) is the dye concentration at time  $t$  (min) and  $k$  is the rate constant ( $\text{min}^{-1}$ ).

The Ho's pseudo second order kinetic model is given as follow [20].

$$\frac{t}{qt} = \left(\frac{1}{k_2 qe^2}\right) + \left(\frac{t}{qe}\right) \quad (\text{Eq.11})$$

Where,  $k_2$  is the rate constant of the pseudo-second-order equation ( $\text{g/mg min}$ ).  $qe$  is the theoretically sorbed amount at equilibrium ( $\text{mg/g}$ ).  $qt$  is the sorbed amount at any time  $t$  ( $\text{mg/g}$ ). Fitness of the equations is determined from coefficient of determination values. Fitness of kinetic data to the pseudo-second-order model was given in Table 6. Comparison of adsorbents and kinetic data were given in Figure 5 and 6, respectively.

Adsorption capacities of raw and modified kaolinite clays are about near each other, therefore optimum adsorbent was determined as raw kaolinite. Also, raw kaolinite had high capacity from raw pumice and modified pumice. Acid modified pumice and kaolinite did not adsorb methyl violet dye at important amount. The reason of adsorption capacity decrease of KOH-kaolinite from raw kaolinite might be due to calcination of KOH-kaolinite at  $103^\circ\text{C}$ . Thus, probably surface hydroxyl groups were deteriorated for dye adsorption. Also, acid modification probably deteriorated structure of pumice and kaolinite and dye adsorption did not occur. That is, surface functional groups of kaolinite and pumice by acid modification were shredded. On the other hand, raw pumice and raw kaolinite surface gained to high positive charge for cationic dye by acid modification and adsorption did not realize. On the other hand, base modification of raw kaolinite was poor for strong dye adsorption.

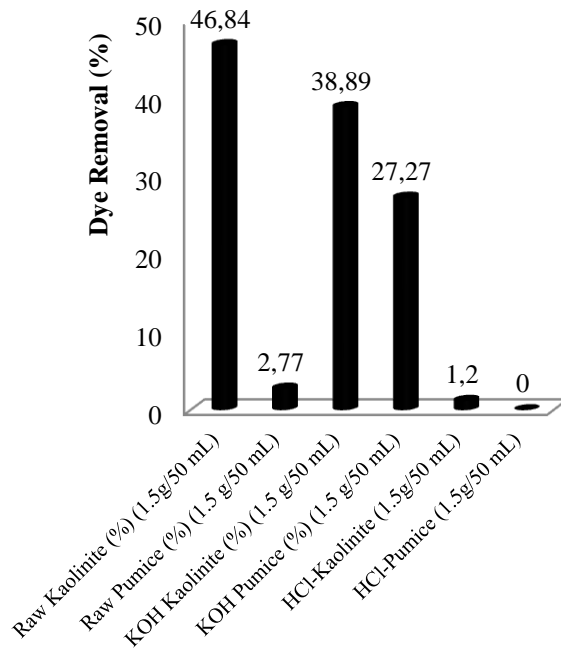


Figure 5. Comparison of adsorbents (Eq.9)

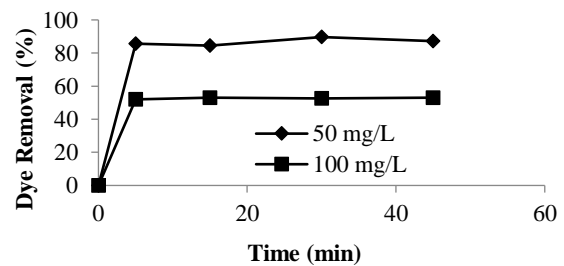


Figure 6: Kinetic data for raw kaolinite (Natural pH,  $25.7^\circ\text{C}$ , 1,000 rpm, 50 and 100 mg/L dye, 500 mL, 5 g kaolinite)

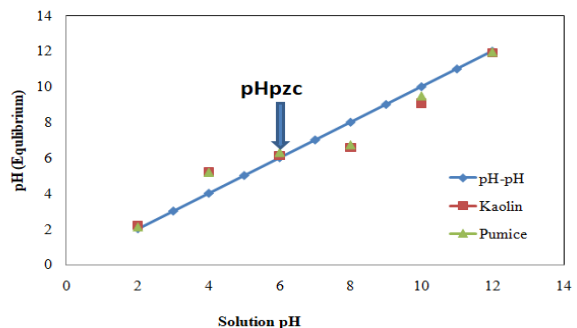


Figure 7. pHpzc values for raw kaolinite and pumice.



### 3.10 XRD and pH<sub>pzc</sub> (point of zero charge) Analysis of Adsorbents

pH<sub>pzc</sub> values for raw kaolinite and pumice were determined as about 6 and given in Figure 7. About below pH (6), raw pumice and kaolinite surface gained positive charge and above pH (6), raw pumice and kaolinite surface gained negative charge in aqueous medium. XRD pattern of raw pumice and kaolinite are given in Figure 8-9. As can be seen in Figure 8-9, the pics are belonging to typical pumice and kaolinite.

### 4. Conclusion

In this study, methyl violet dye removal by raw kaolinite and raw pumice was aimed from solutions by applying optimization technique. The results can be summarized as follow.

Kaolinite clay showed highest performance than pumice but its capacity was thought to increase with base (KOH) modification. Modification did not so increase the capacity for pumice and kaolinite.

Maximum capacity for raw pumice and raw kaolinite was calculated as 7.15 and 18.31 mg/g, respectively.

Optimization for raw pumice and raw kaolinite showed that the all parameters were found as statistically unimportant for kaolinite. pH, pH\*pH, C\*C parameters were found statistically important and other parameters were unimportant for pumice.

It was seen that low and high pH-middle adsorbent amount, low pH-high concentration and low adsorbent amount-high concentration interactions increased the capacity of kaolinite. High pH-low adsorbent amount, high pH-high concentration and low adsorbent amount-high concentration increased the capacity of pumice.

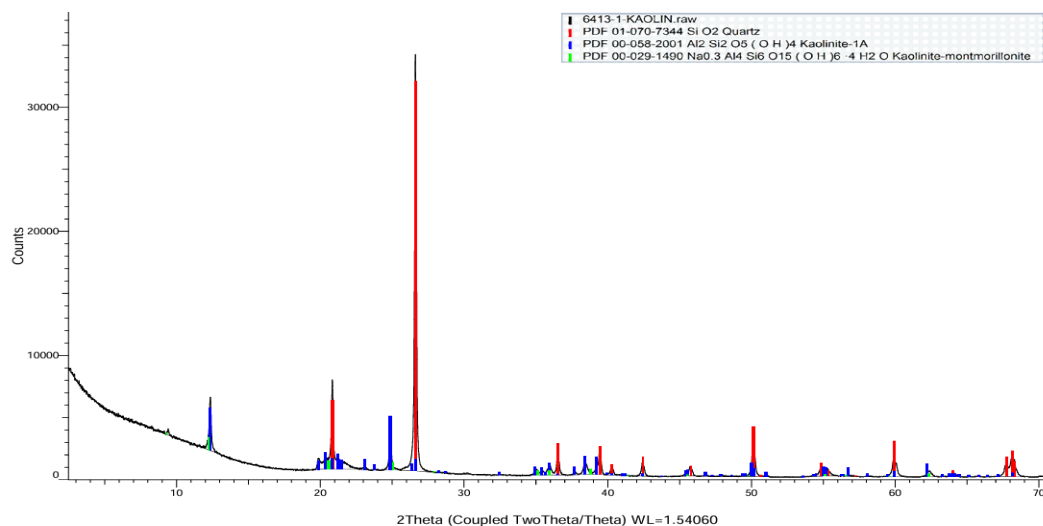


Figure 8. XRD pattern of kaolinite

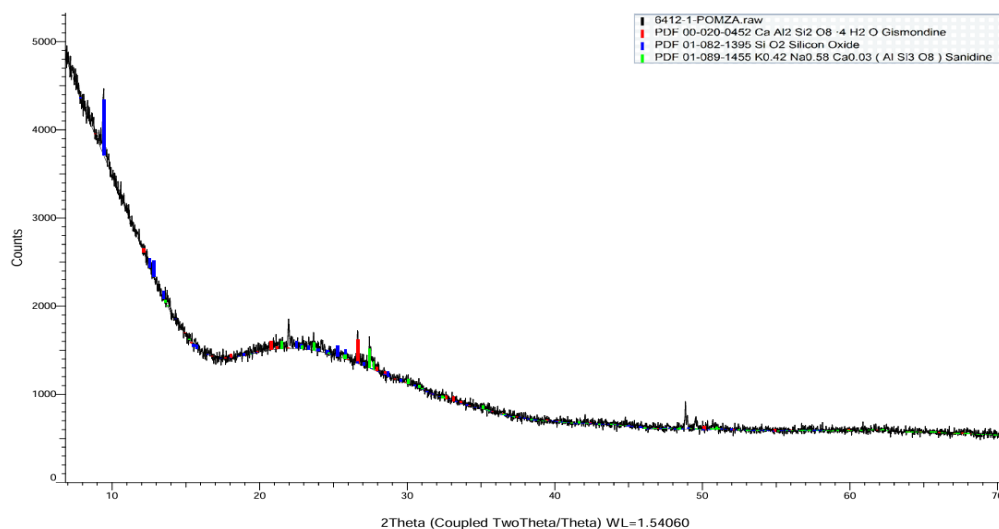


Figure 9. XRD pattern of pumice

Factorial design of dye removal by KOH-pumice and KOH-kaolinite showed that high concentration and pH increased the capacity. The kinetics of dye removal by raw kaolinite fitted to the pseudo second order model. Dye removal was achieved effectively by raw and modified kaolinite mineral. pH<sub>pzc</sub> values for raw kaolinite and raw pumice were determined as about 6. Acid modification was not effective for dye removal. Raw kaolinite removed methyl violet dye at 90% extent for 50 mg/L concentration.

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