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Optimization of methylene blue adsorption by pumice powder

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Abstract. The main objective of this study is to evaluate adsorptive removal of Methylene Blue (MB) dye from aqueous solution using pumice powder. The effects of pH, adsorption time, agitation speed, adsorbent dose, and dye concentrations on dye adsorption were investigated. Process kinetics and isotherm model constants were determined accordingly. The results showed that adsorbent dose, dye concentration and agitation speed are the important parameters on dye adsorption and the removal of MB did not significantly change by varying pH. A total adsorption process time of 60 min was observed to be sufficient to effectively remove 50 mg/L MB concentration. The MB adsorption data obeyed both pseudo first order and second order kinetic models. Adsorption of MB by pumice fitted well both Langmiur and Freundlich isotherms ($R^2 \geq 0.9700$), except for 150 rpm agitation speed that system fitted only Langmiur isotherm. The results of this study emphasize that pumice powder can be used as a low cost and effective adsorbent for dye removal.

Keywords: adsorption; dye; pumice; kinetics; methylene blue; surface chemistry

1. Introduction

Dyes are widely used in textiles, pulp mills, leather, dye synthesis, printing, painting, photography, food and plastics industries and most of them are resistance to removal with biological treatment systems (Kaykıoglu and Gunes 2015, Cifci and Meric 2015a). There have been registered more than 100,000 commercial dyes and more than 7×105 tons of paints per year in the world (Malakootian *et al*. 2014). Most of the dyes are known to be toxic or carcinogenic and they reduce light transmittance in the aquatic environment. Thus, discharge of textile wastewater in the environment is harmful (Meric *et al*. 2005, Cebeci and Güler 2012) and advanced treatment methods are required to remove color and toxic content before discharge. Flocculation-coagulation, adsorption, chemical oxidation, advanced oxidation processes (such as ozone, H2O2, Fenton and photocatalysis) have been attempted to remove color from textile wastewater (Somasekhar *et al*. 2012). Adsorption process is one of the effective methods due to its significant advantages such as low maintenance costs and easily operation. It also proves high removal efficiency for most of the dyes (Sulak and Yatmaz 2012). Although activated carbon is the widespread used adsorbent it is expensive. Therefore, studies with low cost adsorbents such as

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bentonite, pumice, wood ash, rise husk have been intensed for color removal (Yavuz and Gode 2008, Sulak and Yatmaz 2012, Sepehr *et al*. 2014, Panuccio *et al*. 2009, Haibati *et al.* 2014, Kaykioglu and Gunes 2015).

Methylene blue (MB) is used in wide applications such as cotton or wool dyeing, paper coating, temporary hair coloring (Wu *et al.* 2009). Due to its strong adsorption capacity onto solids, MB is often used as a model compound for the color removal studies including adsorption process (Hameed *et al*. 2007, Yu *et al*. 2012). MB has not been reported to pose poisonous effect to human beings, however it may cause other adverse effects such as feature eye burns with contact, nausea, vomiting and diarrhea when taken by mouth, shortness of breath by breathing, and tachycardia, cyanosis (Senthilkumaar *et al*. 2005, Liu *et al*. 2012).

Pumice, a volcanic stone, is an intensive porous material with an average porosity of 90% (Asgari *et al*. 2012, Calabro *et al*. 2012). As a cheap adsorbent, pumice has become insentively used in the adsorption of heavy metals and dyes (Akbal 2005b, Heibati 2014, Sheng *et al*. 2009, Cifci and Meric 2015b). Besides, removal of phosphorus, fluoride, calcium using pumice was found to be quite effective (Karimaian *et al*. 2013, Sepehr *et al*. 2013a, 2013b, 2014, Panuccio *et al*. 2009, Akbal 2005a, Gode and Moral 2008, Yavuz *et al*. 2008, Asgari *et al*. 2012). Adsorption of MB by pumice (Akbal 2005a) and modified pumice (Baghapour *et al*. 2013, Derakhshan *et al*. 2013, Heibati *et al*. 2014) has been previously studied. However, those studies investigated limited process conditions such as unique initial MB concentration or agitation speed. Because the concentrations of MB in industrial wastewaters vary in a wide range there is a need to investigate the process performance varying process conditions.

The purpose of this study was to investigate the adsorption capacity of the MB dye using a natural pumice powder. Key parameters affecting process efficiency such as agitation speed, initial MB concentration, adsorption time, adsorbent dosage and pH of the solution were studied. Process efficiency was determined by means of MB concentration. Surface characterization of pumice powder was performed using SEM-EDX and FTIR analysis. Model coefficients of Langmuir, and Freundlich isotherms as well as pseudo first order and second order kinetics were determined.

2. Materials and methods

2.1 Chemicals and solutions

A stock solution (200 mg/L) of cationic organic dye Methylene Blue (MB) (Merck, Cat No: 1.05045.0100) was provided from was prepared using distilled water and conserved refrigerated at +4°C. Stock solution was ultrasonicated for 10 minutes and stirred for 24 h for homogenization. All chemicals used in the experiments were of analytical grade.

Pumice powder was kindly supplied from Nevşehir (Mid-Anatolia), Turkey. Particle size of pumice powder is in the range of 0-125 microns.

2.2 Adsorption experiments

Adsorption experiments were performed using 100 mL volume flasks active volume of 50 mL. MB concentration, adsorption time, adsorbent concentration and solution of pH were investigated as the key process parameters effecting removal efficiency of the adsorption processes.

Initial MB concentration was ranged from 10 to 150 mg/L at 250 rpm agitation speed, pH 4 and

2.5 g pumice dose while adsorption time was prolonged from 0 to 120 min. The amount of adsorbent varied between 0.5 and 5 g at 50 mg/L MB concentration, pH 4 and three agitation speeds of 150, 200 and 250 rpm. pH of the MB solutions was adjusted to 3-11 by 1 N H_2SO_4 and 1 N NaOH addition. During investigation of pH effect on adsorption process the conditions were selected as 50 mg/L MB, 2.5 g pumice dose and 250 rpm agitation speed. To define the removal efficiency in this study, samples were taken at defined time intervals. Adsorption time was selected as 60 min and samples were taken after 10-20-30-40-50 and 60 min of agitation. Later, they were centrifuged for 5 minutes at 4000 rpm to separate the pumice powder from the solution. MB concentration was determined in those centrifuged supernatants.

2.3 Analysis

The concentration of MB was measured by Shimadzu UV-Visible spectrophotometer (Shimadzu UV-2401) at 664 nm wavelength which is λ_{max} of MB. The pH measurement of samples was carried out using a pH meter (WTW pH 315i).

Surface properties and chemical characterization of pumice was performed using electron scanning microscope (SEM)-energy dispersive X-ray analyzer (EDX) (FEI-QUANTA FEG 250) operated at 5 kV accelerating voltage of 5 kV at a constant magnification of 2500x. Characterization capabilities of EDX are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray emission spectrum. Fourier Transform Infrared Spectroscopy (FTIR) (Bruker VERTEX 70 ATR) was obtained in the range of 400 to 4000 cm^{-1} to see the chemical structure of pumice.

3. Results

3.1 Characterization of pumice powder

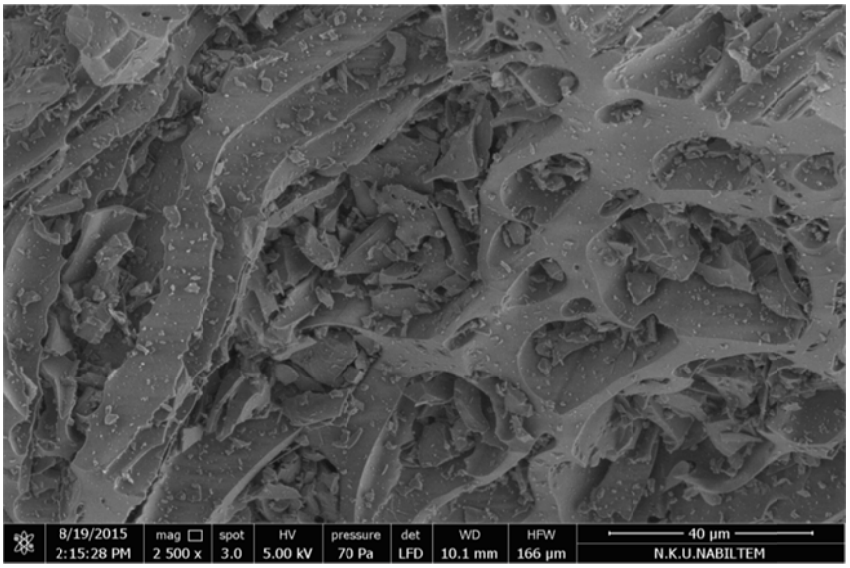
Chemical characterization of pumice powder is given in Table 1. According to SEM-EDX analysis, pumice mainly contains 61.25% SiO_2, 23.45% Al_2O_3, 7.72% K_2O, 4.84% Na_2O and 2.75% Fe_2O_3. These components of pumice were in the range of previous literature studies as seen in Table 1. Details of EDX spectra are given in supplementary Fig. 1.

Table 1 Chemical properties of pumice powder (%w/w) obtained by EDX

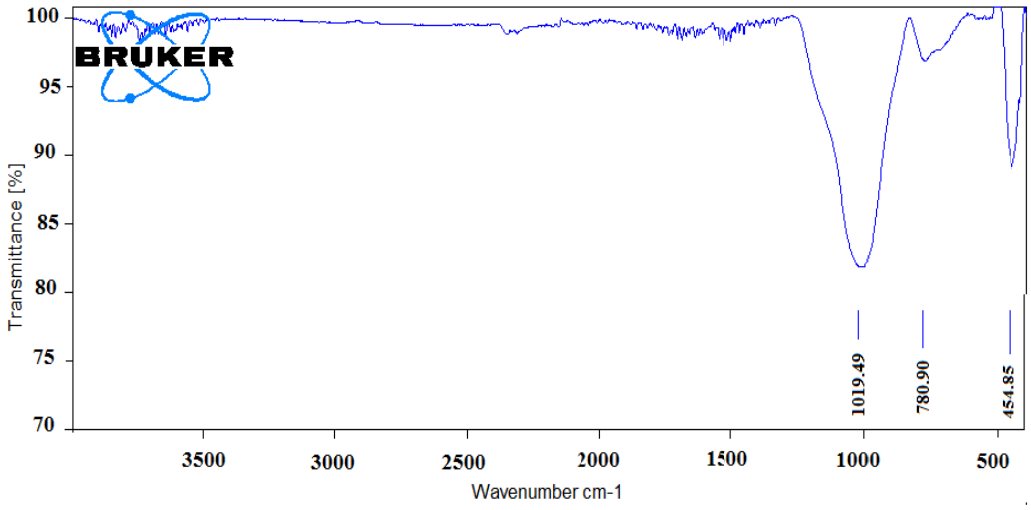
Chemical Composition	Sepehr *et al*. 2014	Kitis *et al*. 2005	Akbal 2005a	Derakhshan *et al*. 2013	In this study
SiO_2	63.5	59-74	63.0-70.4	69.8	61.3
Al_2O_3	17.2	13.5-16.6	14.6-16.3	12.4	23.5
K_2O	2.2	2.8-5.4	3.3-4.4	4.5	7.7
Na_2O	2.0	3.7-5.2	3.6-3.7	3.6	4.8
Fe_2O_3	2.9	1.4-4.8	1.5-3.3	1.9	2.8
TiO_2	0.4	0.1-0.6	0.15-0.75	1.5	-
CaO	3.2	1.2-4.6	0.8-2.65	1.7	-
MgO	1.0	0.4-1.8	0.1-0.8	0.12	-

SEM and FTIR analysis of pumice are given in Figs. 1(a) and 1(b). Looking at SEM analysis, pumice was observed in irregular shapes, porous rich and rough surface indicating a high adsorption capacity (Karimaian *et al*. 2013).

Three main peaks are seen as 1020, 780 and 455 in the FTIR spectra screened between 450-4000 cm^{-1} wavenumber ranges. The peak at ~1020 cm^{-1} could be the Si-O-Si symmetric stretching vibration due to the groups of $(SiO_4)_2$ (Karimaian *et al*. 2013). The peaks at ~780 cm^{-1} and ~455 cm^{-1} could be vibration of Si-O-Si bond (Sepehr *et al*. 2013b). Also, small peaks between 1600 and 1650 cm^{-1}, between 3400 and 3500 cm^{-1} are shown OH bond vibrations to the presence of water molecules (Sepehr *et al*. 2014).



(a) SEM



(b) FTIR

Fig. 1 SEM (a) and FTIR (b) analysis of pumice powder used in this study.

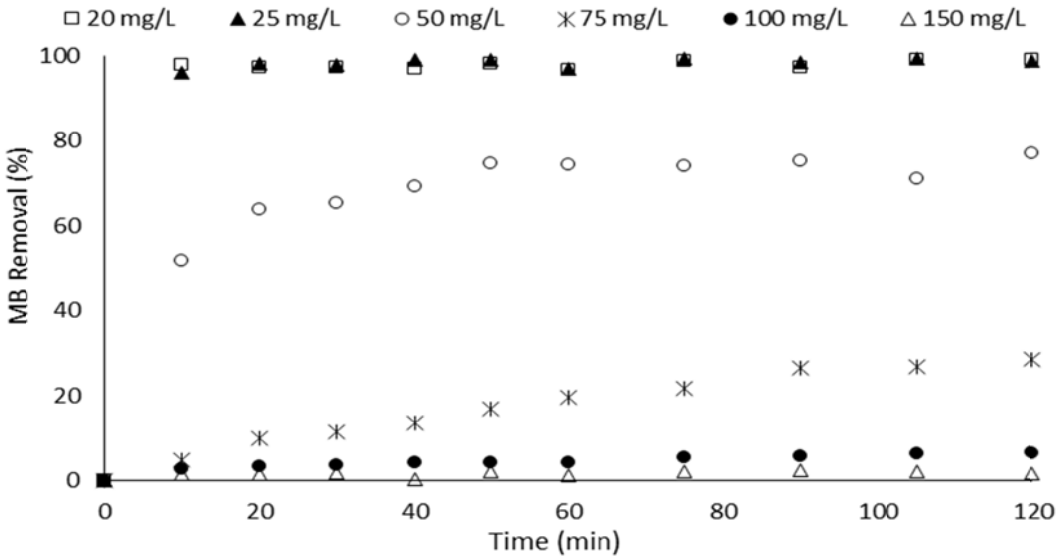


Fig. 2 Time-dependent change of the MB removal efficiencies at various initial MB concentrations (Pumice dose: 2.5 g, agitation speed: 250 rpm; pH:4)

3.2 Effect of adsorption time on MB removal

The effect of adsorption time on removal of MB at 10-150 mg/L initial concentrations is shown in Fig. 2. A range of 95-100% MB removal is reached in 10 min during the removal of 0-25 mg/L MB initial concentrations. In the case of 50 mg/L initial MB concentration, a 74% MB removal was obtained in 60 min and the efficiency did not change much from 60 to 120 min when a 77% MB removal was obtained. Despite the MB removal decreased at 75 mg/L MB concentration, a 29% MB removal is achieved in 120 min adsorption time. According to the results obtained, 50 mg/L MB concentration and 60 min adsorption time are assessed to be suitable for further experiments.

3.2 Effect of agitation speed and adsorbent dose on MB removal and kinetics

To investigate the effects of agitation speed and adsorption dose, the experiments were conducted at three shaking speeds (150, 200 and 250 rpm) and different dose of pumice powder (0.1-5.0 g) at 50 mg/L initial MB concentration (Fig. 3). Agitation speed is an important parameter due to the effect of the boundary layer thickness and surface of the pumice particle (Gupta *et al*. 2011, Bulut and Karaer 2015). When the agitation speed increased, mass transfer resistance of the boundary layer decreased and for the reason that the diffusion rate or the uptake rate of pollutant onto the adsorbent surface increased (Shawabkeh 2009). Despite low MB removal observed at 150 rpm agitation rate, increasing the agitation speed to 200 and 250 rpm, a 97% MB removal was obtained at 4 g pumice dose. However, the adsorption capacity reached at maximum level at a lower pumice dose of 2.5 g and it decreased after 2.5 g pumice dose application. The boundary film layer decreases with increasing the agitation and this causes the higher film transfer coefficient (Bulut and Karaer 2015). However, the film layer thickness did not change significantly

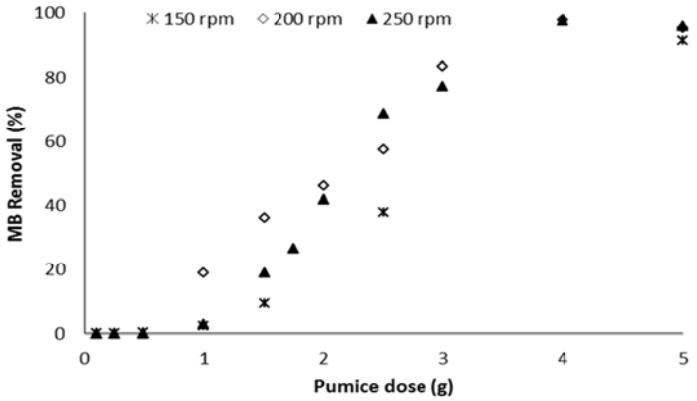


Fig. 3 Change of adsorption capacity at different agitation speed and pumice dose (MB concentration: 50 mg/L, pH:4, adsorption time: 120 min)

at higher of pumice dose of 4 g and as a result of this the agitation speed did not affect the adsorption efficiency.

As seen in Fig. 3, removal of MB by adsorption process increased up to 97% with increasing pumice dose up to 4 g at 250 rpm agitation speed due to its high surface area and active sites on the surface (Fig. 1). The maximum adsorption capacity of 0.69 mg/g pumice powder was obtained at 2.5 g pumice dose and 250 rpm agitation speed where a 69% MB removal was obtained in 60 min adsorption time.

Pseudo first Eq. (1) and second Eq. (2) order kinetics were examined at different agitation speeds following the equation

$$\ln(q_e - q_t) = lnq_e - (k_1 * t) \quad (1)$$

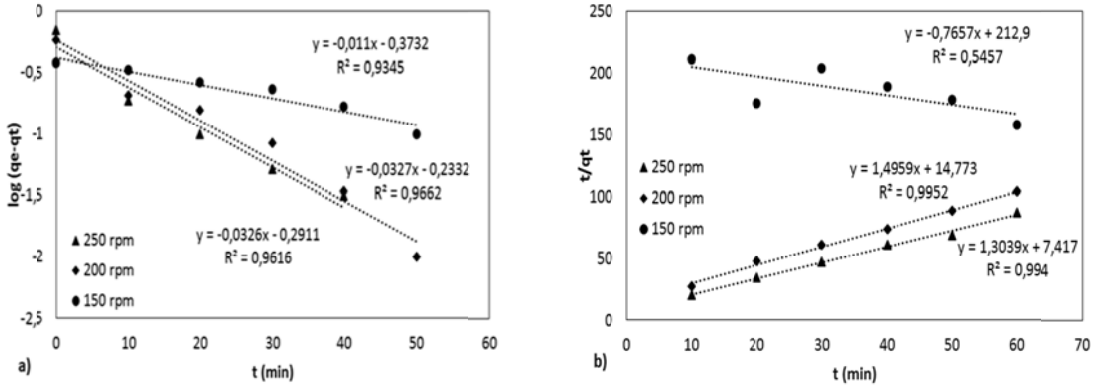
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

where q_e (mg/g) is the amount of MB adsorbed at equilibrium, q_t (mg/g) is the amount of MB adsorbed at any time, t (min) is at any time, k_1 (1/min) is the equilibrium rate constant of pseudo first order adsorption, k_2 (g/mg.min.) is the equilibrium rate constant of pseudo second order adsorption.

A lower k_1 constant is obtained at agitation speed of 150 rpm than 200 and 250 rpm. Accordingly, k_1 values are very close to each other as 0.0327 and 0.0326 g/mg.min at 200 and 250 rpm, respectively (Fig. 4). The lowest k_2 constant was obtained at 150 rpm but the R^2 is lower than 0.55, highest k_2 constant was obtained as 1.4959 g/mg.min at 200 rpm agitation speed. When examined the pseudo-first-order kinetics, despite the k_1 constant increase with increasing the pumice dose up to 2.5 g, k_1 value began to fall after the 2.5 g pumice application (Fig. 5). Optimum parameters were defined to be 2.5 g pumice dose, 250 rpm agitation speed to obtain the highest k_1 and k_2 values in the studied experimental conditions.

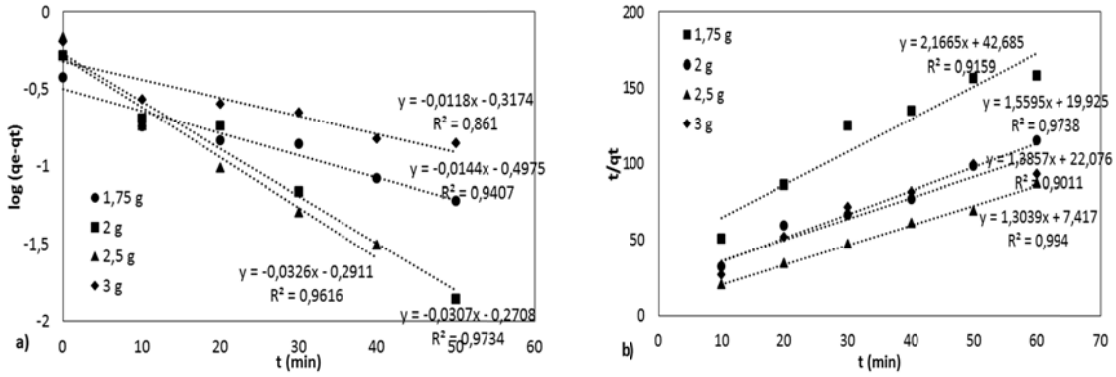
3.3 Effect of initial MB concentration on adsorption process efficiency and kinetics

Effect of MB concentration on the adsorption is seen in Fig. 6. Adsorption time is selected as 60 min. Close to a 100% MB removal was observed in 60 min adsorption time up to 25 mg/L



(a) first order kinetics (b) second order kinetics

Fig. 4 Kinetics evaluation at the conditions of different agitation speeds (MB concentration: 50 mg/L, pumice dose: 2.5 g, pH:4)



(a) first order kinetics (b) second order kinetics

Fig. 5 Kinetics evaluation at different pumice doses (MB concentration: 50 mg/L, agitation speed: 250 rpm, pH:4)

initial MB concentration. The removal efficiency decreased to 74% at 50 mg/L initial MB concentrations and it continued to decrease up to 20% when the initial MB concentration increased to 75 mg/L.

Pseudo first order and second order kinetics at different MB concentration are given in Fig. 7. The k_1 kinetic constant decreased with increasing concentration of MB and at 10, 50 and 75 mg/L MB concentrations, k_1 values were obtained 0.0303, 0.0326 and 0.0158 g/mg.min., respectively. Maximum k_2 constants was obtained at 10 mg/L MB concentrations as 6.2827 g/mg.min and k_2 value is decreased in parallel to increase of MB concentration.

3.4 Effect of solution pH on MB removal and kinetics

The effect of solution pH on MB adsorption with the pumice powder between pH 3-11 is given in Fig. 8, the change of the pH does not appear to have much effect on the adsorption of MB on

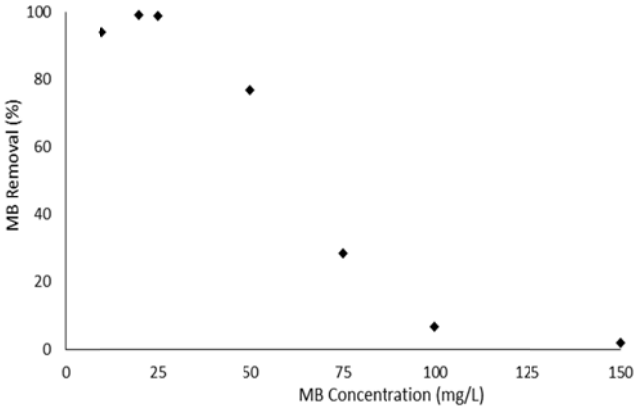
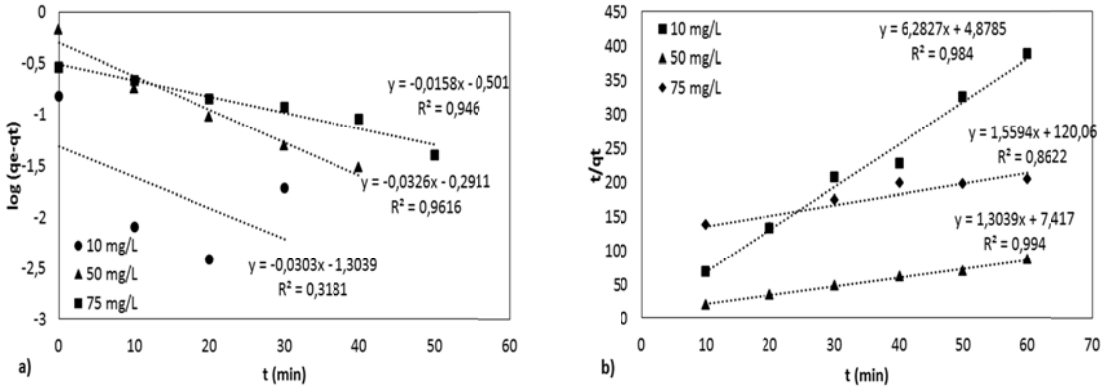


Fig. 6 Effect of MB concentration on MB adsorption (Pumice dose: 2.5 g, agitation speed: 250 rpm; pH:4)



(a) first order kinetics (b) second order kinetics

Fig. 7 Kinetics evaluation in different MB concentrations (Pumice dose: 2.5 g, agitation speed: 250 rpm, pH:4)

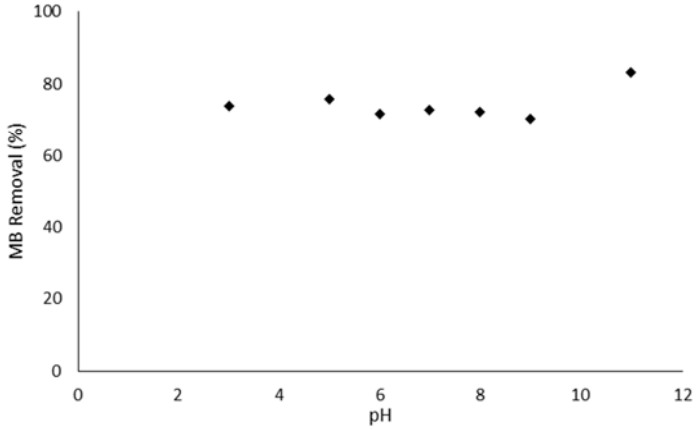
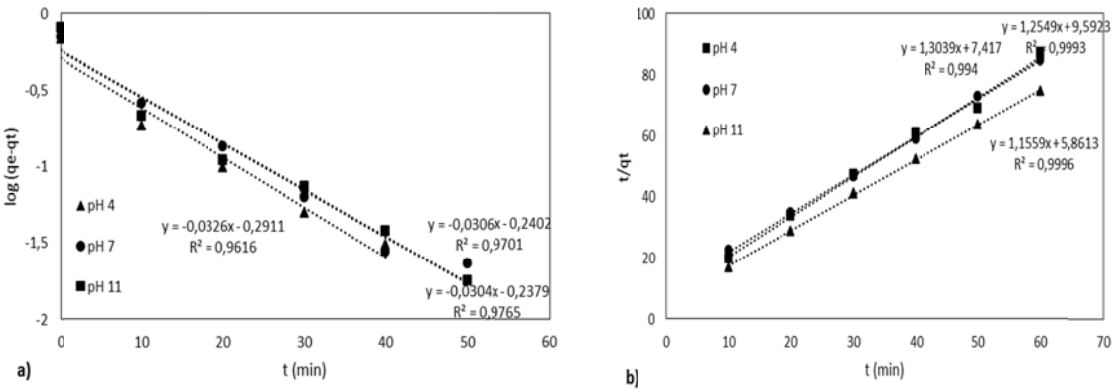


Fig. 8 Effect of pH on MB removal by adsorption (Initial MB concentration: 50 mg/L; Pumice dose: 2.5 g, agitation speed: 250 rpm)



(a) first order kinetics (b) second order kinetics

Fig. 9 Kinetics evaluation at varying pH values (Pumice dose: 2.5 g, agitation speed: 250 rpm, Initial MB concentration: 50 mg/L)

pumice powder. At the end of the 120 min adsorption time, the MB removal was between 70-76%, while pH was in the range of 3-9 and the highest MB removal was observed as 83% at pH 11. In parallel to MB removal, when the pH was between 3 and 9, k_1 value was not changed significantly. The maximum k_1 constant was obtained at pH 11 as 0.0326 g/mg.min, while the minimum k_2 value was 1.1559 g/mg.min. Derakshan *et al*. (2013) calculated similar results that k_1 value was reported as 0.037 g/mg.min at 50 mg/L initial MB concentration, 100 rpm agitation speed, pH 10 and 60 min. adsorption time.

3.5 Langmiur and Freundlich Isotherms

Langmiur Eq. (3) and Freundlich Eq. (4) Isotherms, as the most applied methods and well fitted the experimental data, were also calculated at different agitation speeds according to equations

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \tag{3}$$

$$lnq_e = lnK_f + \frac{1}{n}lnC_e \tag{4}$$

where q_e (mg/g) is the amount of MB adsorbed per unit mass of adsorbent at equilibrium, and C_e (mg/L) is the equilibrium concentration of MB; K_L is the equilibrium constant (L/mg), $q_{\max}$ is theoretical maximum adsorption capacity (mg/g), K_f (l/mg) isotherm constants, and n intensity of the adsorption.

Results showed that adsorption capacity increased with the increase in the agitation speed. Adsorption capacity ($q_{\max}$) was calculated to be 0.045, 0.217, 0.362 mg/g at 150, 200 and 250 rpm, respectively as shown in Table 2. Calculated R_L values varied in the range of 0-1 for Langmiur Isotherms that it indicated a good adsorption capacity of pumice in this study. Comparing the correlation coefficients of Langmiur and Freundlich isotherm, it is seen from Table 2 that high R^2 regression values in both isotherms were obtained.

3.6 Evaluation of the effects of chemical composition and particle size on MB remoal by pumice

Table 2 Model coefficients in Langmiur and Freundlich isotherms at different agitation speeds by pumice/modified pumice

Dye Types	Agitation Speed	Langmiur Isotherms				Freundlich Isotherms			References
	(rpm)	q_{max}	K_L	R_L	R^2	n	K_F	R^2	
MB	150	0.045	0.035	0.362	0.8921	0.837	27.89	0.9958	In this study
	200	0.217	0.073	0.214	0.988	0.907	17.01	0.9771	
	250	0.362	0.134	0.130	0.9873	1.613	3.78	0.9894	
MB[1]	100	15.87	0.132	0.131	0.9920	2.18	3.45	0.9990	Derakhshan *et al*. 2013
Reactive Blue 5	-	1.67-4.65	0.077	0.999	0.8450	-	-	-	Heibati *et al*. 2014
MB	200	-	-	-	-	0.211-1.613	0.201-0.509	0.98-0.99	Akbal 2005b

[1]by modified pumice with hydrochloric acid

Table 3 Comparison of the parameters of MB adsorption by pumice/modified pumice

Parameter	Baghapour *et al*. 2013	Derakhshan *et al*. 2013	In this study
Adsorbent type	Modified Pumice[1]	Modified Pumice[1]	Pumice
MB Concentration (mg/L)	30-60	50	50
Adsorbent Dose (g)	0.2	0.2	2.5
Adsorption Time (min.)	120	120	60-120
Agitation Speed (rpm)	100	100	250
pH	10	10	11
MB Removal (%)	76-85	92.3	83
Si Content (%)	-	70	61.25
Pumice particle size (mikron)	-	0.2	0-125

[1]Modified pumice with hydrochloric acid

Table 3 compares optimum process condition of MB adsorption by pumice. At the same initial MB concentration process conditions varied among the studies. More than ten times of pumice is needed to obtain competable removal compared to modified pumice use. The content of SiO_2 should influence the efficiency. Indeed, it was reported in the study of Akbal (2005), second order kinetic contact (k_2) values were calculated as 8.052 g/mg.min and 3.982 g/mg.min for SiO_2: 70.4% and SiO_2: 63% contents respectively. Lower SiO_2% content in our study can be figured out to be responsible of the use of higher dose of pumice. In this point a principle role of particle size to affect the removal efficiency should be kept in mind as in the study of Derakhshan *et al*. (2013).

Surface modification influences process efficiency, thus a lesser amount of adsorbent can be used. For instance, a 87.72 mg/g adsorption capacity of Cr(VI) by pumice could be increased up to 105-107 mg/g with its modification by $MgCl_2$ or ZVI (Sepehr *et al*. 2014, Liu *et al*. 2015).

In conclusion, the price of pumice was reported to be lower (about 100 times cheaper than that of chitin, chitosan and activated carbon), thus it makes the pumice very attractive adsorbent among other the cheapest adsorbents such as bentonite, clinoptilolite and charcoal that were found to have lower adsorption capacities of Cr(VI) (Sepehr *et al*. 2014, Liu *et al*. 2015).

4. Conclusions

In this study, Methylene Blue (MB) removal by pumice powder adsorption is investigated under varying process conditions of pH, agitation speed, MB doses and pumice doses. SEM and FTIR analyses were performed to evaluate the structure of pumice while process efficiency was evaluated by means of colour removal measured at maximum absorbance of MB.

The results showed that all conditions investigated affected process efficiency. Accordingly, approximately 100% MB removal was attained up to 25 mg/L initial MB concentration. However, the MB removal efficiency decreased with the increasing initial MB concentration. There was no significantly change in the removal of MB during 60-120 minutes of adsorption, thus, 60 minutes were assessed to be suitable adsorption time for the removal of MB. Although pH was observed less influencing parameter of removal efficiency of MB, the highest MB removal efficiency (83%) was obtained at pH 11. Additionally, the agitation speed was found to be important in MB removal by pumice adsorption. Meanwhile, Both Langmiur and Freundlich isotherms well fitted the removal of MB by pumice adsorption. In conclusion, composition (such as $\%SiO_2$ or modification component) and particle size of pumice are important factors influencing positively adsorption process efficiency.

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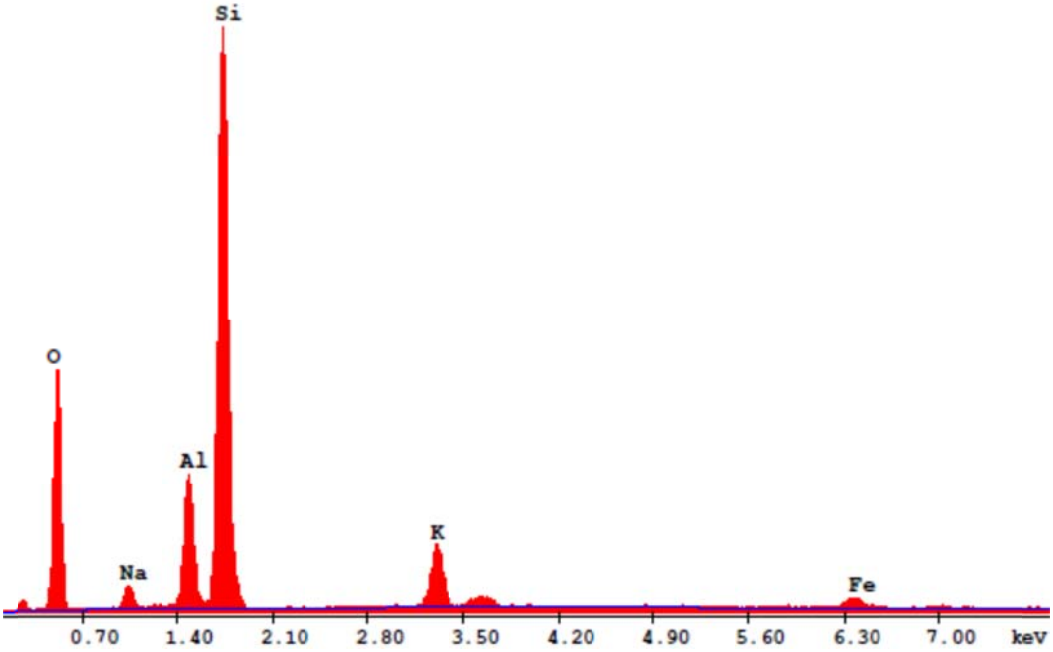
Appendix



Supplementary Fig. 1. EDX spectra of pumice powder used in this study