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REMOVAL COMPARISON OF METHYLENE BLUE DYE BY PUMICE STONE AND POWDER ACTIVATED CARBON FROM AQUEOUS SOLUTIONS

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Abstract

Color material in the effluent of wastewater, will cause harmful effects on aquatic ecosystems. So when discharging wastewater into receiving waters, should be reduced to an acceptable level. The aim of this study is comparison the efficiency of pumice stone and powder activated carbon for the removal of methylene blue dye(MB) from aqueous solutions.

In this study, three variables Including contact time(15, 30, 45,60 and 75 min), adsorbent dosage(0.2, 0.5, 0.8,1.1 and 1.4gr/L) and pH(3, 5, 7, 9 and 11), In removal of methylene blue dye (with the constant initial concentration of 85 mg/L) by pumice and activated carbon powder were investigated. Based on the three variables, 20 of the experiment (Run) for both adsorbents were carried out, and finally, dye concentration was measured by a spectrophotometer at a wavelength of 665 nm.

The results showed that with increasing each variable, the amount of MB dye removal increases. In addition, highest efficiency of pumice and powder activated carbon in removal of MB dye was 82.5% and 100% respectively, that this efficiency was obtained in contact time (75 min), adsorbent dosage (1.4gr/L) and pH (11).

Based on results, it can be concluded that if we can provide optimal conditions for MB dye removal, pumice as an effective absorbent instead of expensive adsorbent activated carbon used to remove cationic dyes from effluent of industrial wastewaters.

Keywords: Pumice stone, Activated carbon, Methylene blue, Aqueous solutions

Introduction

Adsorption process is an efficient method for the removal of organic matter from waste effluents, but this method is not sufficiently applied due to its high initial cost and regeneration system cost. These factors, therefore, move researchers toward adsorbent methods having minimal cost, availability and high efficiency (1).

Scoria powder is proved to be an appropriate method according to low cost, availability and its micro-porous structure and specific surface area, which are avoiding the preliminary step of the calcination, a high energy use. Also, it floats in water owing to its low density. Recently, many researchers used Scoria for removing cadmium, disinfection byproducts, heavy metals, phenol, various dyes and sulfur dioxide from aqueous solution (2-5). Dye is one of the main pollutants generated from chemical industries (e.g. Textile, leather, paper and dye manufacturing industries).

The wide application of dyes generates colored wastewaters which are extremely noxious to the aquatic biota and upset the natural balance in the water resources through reduced photosynthetic activity. Some adverse impacts of dyes on humans (allergy, dermatitis, skin irritation, and cancer) are also reported in the literature (6).Dyes are commonly found in trace quantities at industrial scale and in industrial effluents (7). It is a fact that due their visibility, dyes are recognized easily even at the levels as less as 1 mg/l. Dyes inhibit several biological processes (8). Color of textile effluents escalates environmental problem mainly because of its non-biodegradable characteristics. Thus, the removal of dyes from effluents before they are mixed up with unpolluted natural water bodies is important.

Adsorption, coagulation, flocculation, oxidation, precipitation, filtration, electrochemical processes, etc are the common techniques reported for the removal of dyes from effluents (9).Pumice, which is commonly found in Iran and thus is easily and cheaply accessible, was used in this study as an alternative adsorbent in comparison with powdered activated carbon(PAC), As an efficient adsorbent, to remove of Methylene Blue(MB) from watery decompositions. Pumice is a volcanic stone, which can have an acidic or basic character. Due to its micro porous structure, it has a high specific surface area(10-13). The aim of this study is to compare pumice and activated carbon for the removal of methylene blue dye from aqueous solutions.

Material and Methods

- **Specificationspowderabsorbentpumice**

Several methods such as fourier transform infrared spectroscopy (FTIR), X ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the adsorbent. First, using FTIR Spectrometer (WQF-510) and with a resolution of 4cm^{-1}in the range of 400-4000cm^{-1} by Pellets KBr technique was carried out (Figure 1). As well scanning electron microscopy (SEM) was carried out using a Philips XL30 is shown in Figure 2. Chemical characteristics of pumice stone by XRD method and using XRD Device with model (Shimadzu XRD-6000) was carried out that provided in table 1.

Table-1: The major compounds identified in pumice absorbent by X ray diffraction (XRD).

Compound	Percent
SiO_2	48.79
Al_2O_3	19.6
K_2O	4.4
Fe_2O_3	9.1
CaO	7.9
MgO	8.85
etc.	1.36

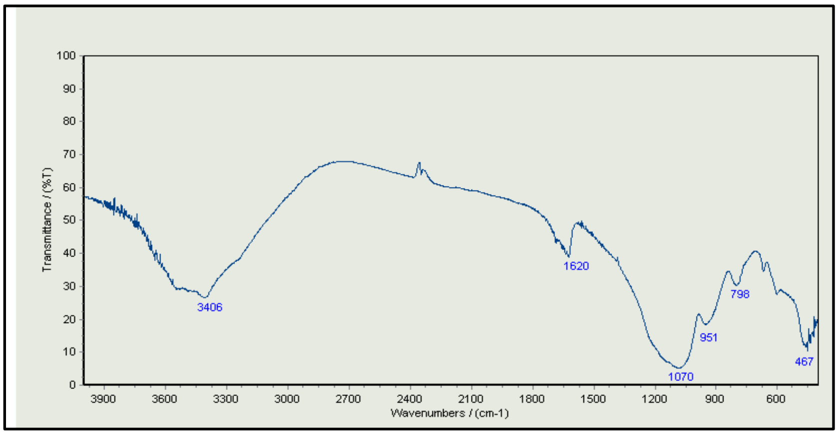

Figure-1. Fourier transform infrared spectroscopy (FTIR) related to Pumice adsorbent.

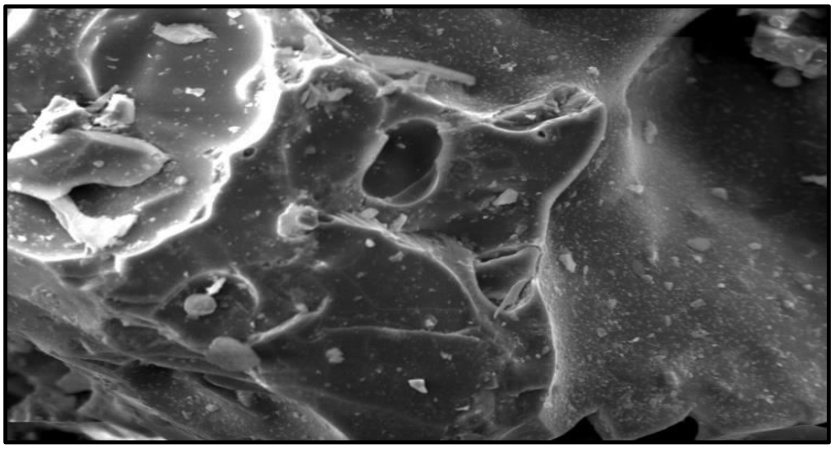

Figure-2. Scanning electron microscopy(SEM) related to Pumice adsorbent

- **Design ofexperiments(determination of sample size):**To determine the number (Run) experiments (required sample size) design of experiments (DOE) software with response surface methodology (RSM) was used. So based on rang of variables (Table 2), required experiments number, 20 Run was obtained (table 3). When determining the experiments Run, central point is in contact time (75 min), adsorbent dosage (1.4gr/L) and pH (11) was considered. In addition initial concentration of MB dye was considered constant level (85 mg/L).

Table-2: Experimental range and level of the independent variables.

Variables	Range and level				
	-α(-1.5)	-1	0	1	+α(1.5)
Contact Time, min	15	30	45	60	75
Adsorbent Dosage, gr/l	0.2	0.5	0.8	1.1	1.4
pH	3	5	7	9	11

- **Sample preparation and conduct experiments**

Inthisstudy, theMethylene Blue Dye with the chemical formula($C_{16}H_{18}N_3SCl$) with molecular weight 319.85gr/mol (Produced by MerckCompany, Germany) was used.For the preparation Stoke concentrations (1000mg / l), the amount of one gram of methylene blue dye carefully weighed with an electrical balance, then was transferred to Erlenmeyer flasks with one liter volume. After that, bydeionized distilled waterwas reachedtovolume1000ml.From preparedstock solution, operational concentration(85mg/L) was prepared. To adjust the pH, NaOH and HCL. After each period of operation, 15 ml of solutionin speed of 200 rpm for 15 minutes was centrifugedand finally dye concentration was measured by a spectrophotometer(Cary 50-Perkin Elmer company) at a wavelength of 665 nm (14).To achieve better results, experiments were repeated three times. At each stage measurement, calibration curve was prepared based on the absorption and standard concentrations of dye.

Results

The highest efficiency of pumice and powder activated carbon in removal of Methylene Blue Dye was 82.5% and 100% respectively, that this efficiency was obtained in contact time (75 min), adsorbent dosage (1.4gr/L) and pH (11). Experimental conditions and results of central composite design is presented in Table 3 and Analysis of variance (ANOVA) for fit of Methylene Blue Dye removal from central composite design after elimination of insignificant model terms is provided in Table 4. The trend of Methylene Blue Dye removal based on variables by Pumice and Activated Carbone showed in figure 3 and figure 4, respectively.

Table-3: Experimental conditions and results of central composite design.

Run	Variables			Responses (Removal of dye, %)			
	Factor1	Factor2	Factor3	Pumice Adsorbent		Activated Carbone	
	A: Contact Time, min	B: Adsorbent Dosage, gr/l	C: pH	Actual	Predicted	Actual	Predicted
1	15	0.2	3	20.5	16.3	39.8	36.81
2	75	0.2	3	22.2	25.78	46.3	45.48
3	45	0.8	7	54.0	52.11	83.1	86.71
4	45	0.8	7	54.0	52.11	85.2	86.71
5	45	0.8	7	54.0	52.11	87.0	86.71

6	75	1.4	11	82.5	87.93	100.0	102.83
7	75	1.4	3	45.5	49.12	69.0	67.86
8	45	0.8	7	54.0	52.11	90.4	86.71
9	15	0.2	11	47.6	55.11	72.2	73.18
10	45	0.8	7	54.0	52.11	92.3	86.71
11	75	0.2	11	65.8	64.59	82.3	82.05
12	45	0.8	9	66.1	61.82	98.4	90.58
13	60	0.8	7	57.4	54.49	87.2	86.57
14	15	1.4	3	34.7	39.64	65.8	65.89
15	45	1.1	7	70.6	57.95	100	95.75
16	30	0.8	7	46.8	49.74	80.7	83.86
17	45	0.8	5	38.6	42.41	62.4	72.75
18	15	1.4	11	78.2	78.45	100.0	100.66
19	45	0.5	7	41.8	46.28	76.5	83.28
20	45	0.8	7	54.0	52.11	89.2	86.71

Table-4: Analysis of variance (ANOVA) for fit of Methylene Blue Dye removal from central composite design after elimination of insignificant model terms.

Parameters	Adsorbents	
	Pumice Adsorbent	Activated Carbone
Modified equations with significant terms	Removal(%)= +52.11+4.74A+11.67B+19.41C	Removal(%)= +80.39+2.71A+12.46B+17.84C
Type of model	Liner	Liner
F value	59.64	15.65
Prob>F	< 0.0001	< 0.0001
Mean	52.12	80.39
SD	5.04	9.33
R^2	0.9179	0.7458
Adj. R^2	0.9025	0.6981
Pred. R^2	0.8525	0.5221
AP	31.766	15.822
PRESS	731.08	2618.84
PLF	0.1334	0.0934

SD: standard deviation, R^2: determination coefficient, Adj. R^2: Adjusted R^2, Pred. R^2: Predicted R^2, AP: Adequate. Precision, PRESS: Predicated residual error sum of squares, PLF: Probability for lack of fit.

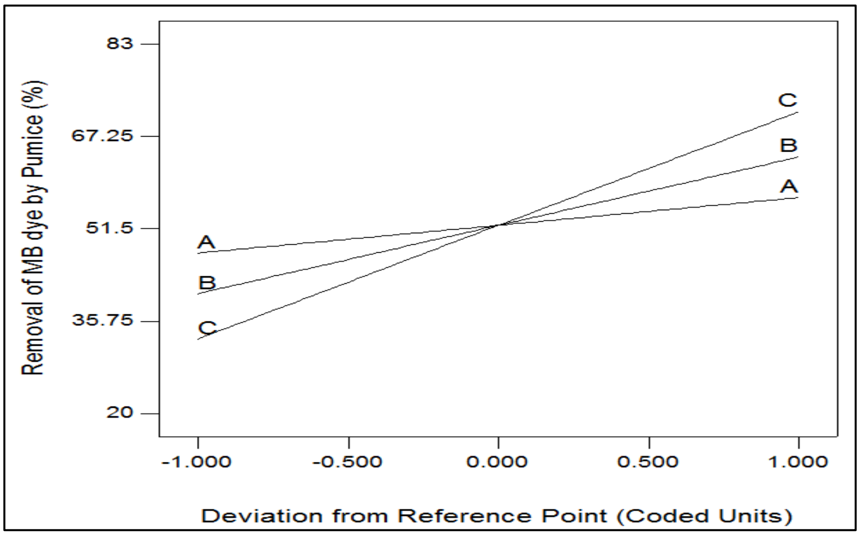

Figure-3.The trend of methylene blue dye removal by Pumice based on variables (A: Contact Time, B: Adsorbent Dosage and C:pH)

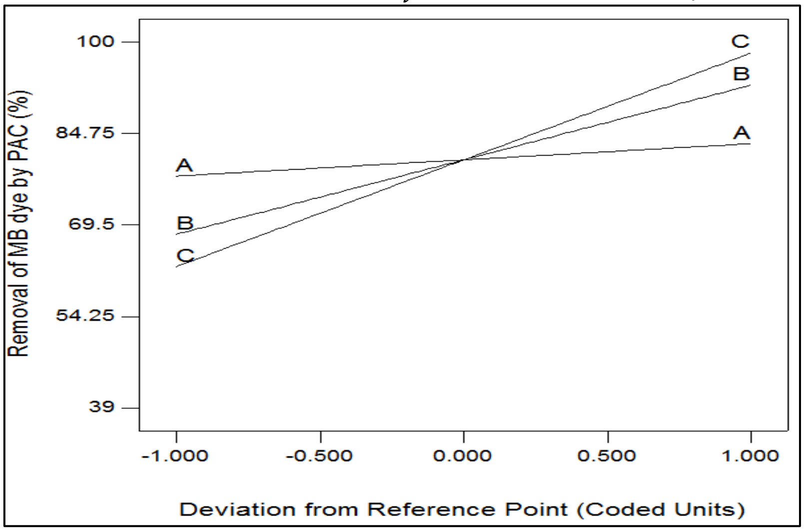

Figure-4.The trend of methylene blue dye removal by Powdered Activated Carbon based on variables (A: Contact Time, B: Adsorbent Dosage and C:pH).

Discussion

The validity of the prediction model is expressed by several parameters such as R2, R2-Adj, Prob> F, AP and PLF (12-10). The results showed that all the above parameters for the model are provided in the appropriate range (Prob>F Less than 0.05 and AP>4). Therefore, this implies the validity of models to predict the amount of dye removal is achieved. In addition, the obtained models show that the overall removal of methylene blue dye (by both absorbent) follows a linear trend.

The effect of contact time, adsorbent dosage and pH on removal efficiency of methylene blue dye by pumice and activated carbon showed that by increasing all three parameter, dye removal will increase. And the most affected was related to pH (Factor C), adsorbent dose (Factor B), and contacted time (Factor A), respectively. The effect of pH factor than other factors (adsorbent dose and contact time) can also be caused by high pH effect on the physical and chemical characteristics of the absorbent and adsorbent (15). Because of increases in pH, adsorbent surface has a negative charge and since methylene blue is a cationic dye (16). So, in the alkaline environment that absorbent surface is more negative charge, as a result, due to electrostatic attraction, the absorption rate of dye more will be (17). On the other hand, the pH above 9, Methylene Blue Dye suffering more chemicals changes, as a result, it also becomes more absorbed (18). Also, results showed a decrease in pH, dye absorption is reduced.

This may be because in the acidic environment due to the production of ion proton (H+), electrostatic repulsion Occurs. So the cationic dye absorption is reduced. Since dominant component of pumice is SiO2, by reducing the pH, this composition of be converted to Si+3 that it also causes electrostatic repulsion and thus reduce the absorption of cationic dye. The poor absorption dye, in acidic environments is due to dye penetration in the adsorbent pores.

In relation to changes adsorbent dosage, the results showed that these changes more evident than the contact time, because with increasing dose, more adsorption sites are available for absorbate (for example: dye) **(19).** But because most absorption occurs in the first few minutes, thus increasing contact time and occupies the site of absorption, the absorption rate absorption gradually decreases and reached to equilibrium.

The results of this study with studies of Santhi et al (20), Seey and Kassim (21) and Sharma (22) are consistent.Results of this study, showed that pH is major effect on the absorption of Malachite Green Dye by activated carbon and also pH factor causing physical and chemical changes on the surface of the adsorbent (20-22). For example, Santhi et al study showed that the highest rate of Malachite Green Dye removal by activated carbon, between pH 3 to 7 is pH = 7(20).

Because at this pH, adsorbent surface is negative charge, thus it is would absorption cationic dye (Malachite Green). But in the low pH due to the predominance of hydrogen ions, the adsorbent surface is positive charge, thus, the electrostatic repulsion, reduce the absorption of cationic dye. Base on the highest efficiency of pumice and powder activated carbon in removal of Methylene Blue Dye was 82.5% and 100% respectively, that this efficiency was obtained in contact time (75 min), adsorbent dosage (1.4gr/L) and pH (11).

Since pumice stone found in abundance in the nature of some parts of Iran and therefore the cost is negligible compared with activated carbon, As a result of having 82.5% removal of dye by pumice compared with 100% the efficiency achieved by activated carbon, can be an acceptable rate of the efficiency.In addition, using various agents (such as metals, variousacids and etc.) can be modified the pumice and increased performance of it.

Conclusion

The results showed that with increasing each variable, the amount of MB dye removal increases. In addition, highest efficiency of pumice and powder activated carbon in removal of MB dye was 82.5% and 100% respectively, that this efficiency was obtained in contact time (75 min), adsorbent dosage (1.4gr/L) and pH(11). Based on results, it can be concluded that if we can provide optimal conditions for Methylene Blue Dye removal, pumice as an effective absorbent instead of expensive adsorbent activated carbon used to remove cationic dyes from effluent of industrial wastewaters.

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