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White Marble as an Alternative Surface for Removal of Toxic Dyes (Methylene Blue) from Aqueous Solutions

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Abstract

The preparation of white marble with HCl activation and its capability to remove toxic dye (Methuen blue MB), from aqueous solutions were reported in this study. The adsorbent was characterized with (FT-IR) Fourier transform infrared spectrophotometer, Several physiochemical parameters like , agitation time, primary concentration dye, adsorbent amount and temperature were studied in a batch-adsorption system. Data appeared of the adsorption of MB dye find to rise with increase in primary concentration dye, and agitation time but reductions with the temperature and mass adsorbent of the method. The concentration of dye was measured before and after adsorption through utilizing UV-Visible spectrophotometer at 663 nm.

Key words: White Marble, Textile Dye, Methylene blue MB, Adsorption isotherm

Introduction

Textile industries discharged a major amount of very colored effluent wastewater , that emitted into rivers or nearby land without any handling because the traditional handling way is so costly. On the other hand the little extensive knowhow don't allow a wishful removal color and need certain dis advantages. Therefore removal color from aqueous solutions is one of the main ecological solutions. Dyes generally need a synthetic origin and compound aromatic molecular structures, that brand them extra stable and extra problematic to dyes biodegrade [1-4]. Methylene blue (MB) is the utmost generally utilized substance of cotton dying, silk and wood [5, 6]. MB needs wider application, that containing wools, paper coloring, temporary hair colorant, cottons dyeing, coating of paper stock, etc. However MB is not powerfully hazardous but on inhalation, it can appear several harmful affects. [7].several way was utilized of removal dyes, one of methods adsorption. Adsorption have been make to be superior to another methods of water re-usterms of primary extensive , pliability and elasticity of design, ease of operation and insensitivity to contaminants toxic [8, 9].

White marble is a kind of rock metamorphic created of limestone that subjected to shrill heat and high pressure down the Earth's crust. Limestone is a rock sedimentary made of shells of corals sea and skeletons (single-cell moss). The essential ingredient of limestone is the calcite mineral. When crystals melt calcite and recrystallize in to great coarser crystals interlocking , the perform carbonate rock define as marble [10-12]. Limestone that is free of contaminations products the shining , pure white marble. The major compound of white marble shown in Table (1). The aim of the study removal of the toxic dye by using white marble by using affect of several factor like agitation time, solution of pH, temperature solution , weight of adsorbent and concentration .

Table 1.: The major composite of white marble through weight percent

Chemical Oxide	Percentage %
Silica	**1.2**
Carbonate of lime	**95.16**
Magnesia Carbonate	**1.2**
Iron Alumina and	**0.5**
Water	**1.94**

Experiment

Methods and Materials

In this study collecting the White marble utilizing in Italia by washing for (5 % HCL) to remove bicarbonate ley of deionized water for several times. at (300 ºC) dry in an oven to one hour till reach weight constant . curt white marble into pieces till give powder and sift to particle size(75 μ) , then kept in the desiccators to utilize . dye methylene Blue Commercial was purchased from industry Textile of Al-Hilla Factory. The chemical structure of dye methylene Blue MB appear in Figure. 1

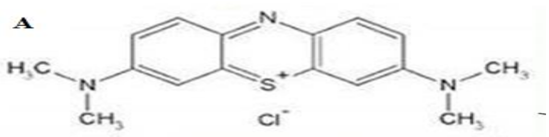

Figure. 1. Chemical structure of Methylene blue (MB)

Effect of several parameters on the adsorption method:

Effect of contact time:

(10mg.L^{-1}) concentration of MB dye with 100ml of solution dye is to be prepared in Erlenmeyer flasks adsorbent concentration (0.5g/100ml) of White marble and preserved into shaker water bath. MB dye concentration determination spectrophotometric ally at the wavelength corresponding to maximum absorbance, λmax, utilizing a spectrophotometer (Apel PD-303 uv (Japan)). The samples with interval time separated by using centrifugation process. The absorbance of the solution is then measured, the MB concentration is to be measured then 24 h until equilibrium will be reaches. A graph is to be plotted with qe vs time. The qe is expressed as[13]:

$$\mathbf{qe} = \frac{(\mathbf{C_0} - \mathbf{C_e}) * \mathbf{V_L}}{\mathbf{m_{gm}}} \qquad (1)$$

Where: qe = Quantity of MB dye adsorbed per unit weight of White marble (mg/g).

C^o= Primary concentration of MB dye (mg/L).
C_e= Equilibrium concentration MB dye (mg/L).
m = mass of White marble (g).
VL= is the volume of solution (L).
The removal E% of MB dye was calculated on the basis of reduction in absorbance at max value of the dye as follows: [14]

$$\textbf{Dye Removal}\ \% = \frac{C_{0}-C_{e}}{C_{0}} * 100 \qquad (2)$$

Where: C_e and C^0 are equilibrium and primary concentrations dye, respectively.

Effect of contact time (5-120) min:

The experiment was carry out through taking (100 mL) samples of concentration (10 mg/L) MB dye in put in conceal flasks and treated 0f (0.5 gm) of weight adsorbent on pH 6 at 25°C.

. ***Effect of temperature [16-50 ºC]:***

The affect of solution temperature was studied through (0.5 g) mass of adsorbent mix with (100 mL) of concentration MB dye rang (2-12mg L^{-1})and the sample was shaking time of one hour at pH 6.

Effect of mass of White marble [0.1-2 g]:

Using several mass of White marble of particle size (75 µ). The concentrations of sample rang (2-12mg/ L) at room temperature of one hour at pH

Effect of acidic treatment.(H2SO4, HCl, and HNO 3)

The study was carried out with different acids such as (H_2SO_4, HCl, and HNO_3), the same process has been done in section 2.1 but with different acids. After this all samples prepared using as adsorbent for two dyes under study (0. 5gm) dose adsorbent White marble of (75µ) average particle size mix by (100 ml)aqueous solution of concentration MB dye rang (2-16) mg.L^{-1} and the sample were shaking time of one hour at (25 ^{0}C) at pH 6.

Effect of particle size (100,200, and 300)

The study was carried out with different particle size (100,200, and 300) mesh (0. 5gm)dose of adsorbent White marble mixing with (100 ml) of (2-12) mg.L^{-1} aqueous solution of dye concentration, and the sample was shaking a period for 1h at a fix temperature (25 ^{0}C) at pH 6.

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RESULTS AND DISCUSSION FT-IR

Analysis

The Fourier transform infrared spectrophotometer of White marble performed before and after dye MB adsorption appeared characteristic bands corresponding to several functional groups. It is appear in Fig.2 that after adsorption of dye MB, a important change in shift or intensity of the present function groups has been observed. Figure. 2 appears new interactions formed among the functional groups of major compound of glass material SiO_2 and the positively charged dye molecules

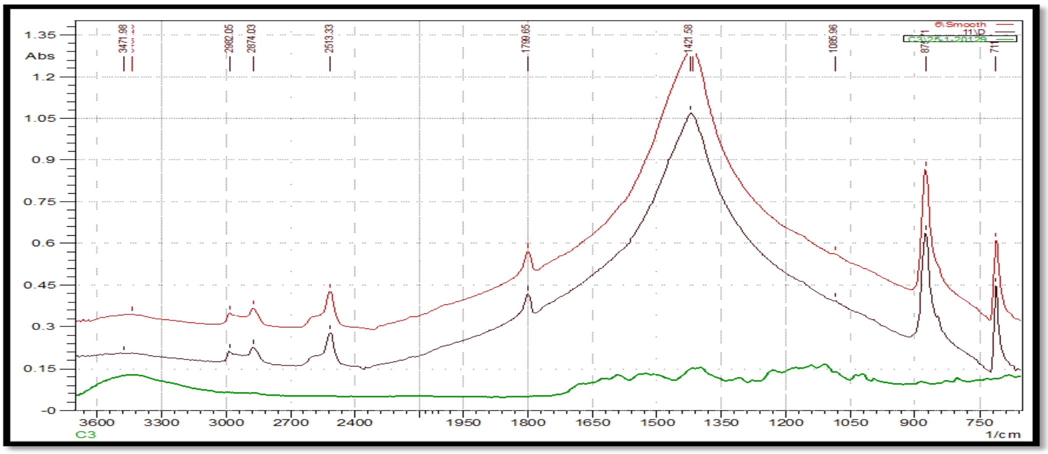

Figure 2: FT-IR spectra for adsorption of MB on the surface of white marble.

Effect of primary dye concentration: and Temperature solution

To determine if the outstanding adsorption method was exothermic or endothermic in nature. The adsorption isotherms was estimated of several MB-adsorbent methods. The removal of Methylene Blue have studied at different temperature (15, 25, and 50 °C). Temperature has a pronounced affect on the adsorption method from the temperature change reason changes in the equilibrium efficiency of the adsorbent for adsorption of particular adsorbate [15, 16]. The uptake of dye lowering with the raise in temperature, signalizing the nature exo-thermic reaction of the adsorption , whereas temperature increases signalize the nature endothermic the reaction of adsorption . It was explained that as the temperature raised , the physical bonding among the organic complexes (counting dyes) and the active sites of the adsorbent weakened. [19-17]

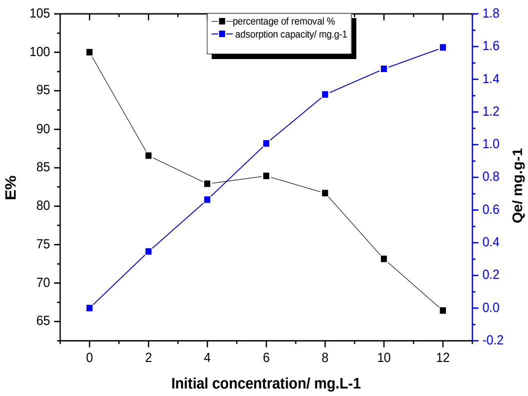

Fig.3: Effect of primary concentration on the removal percent and quantity of adsorbed MB dye on to Wight marble (Exp. Cond,: Temp. = 50°C, agitation time one hour , and solution of pH 6)

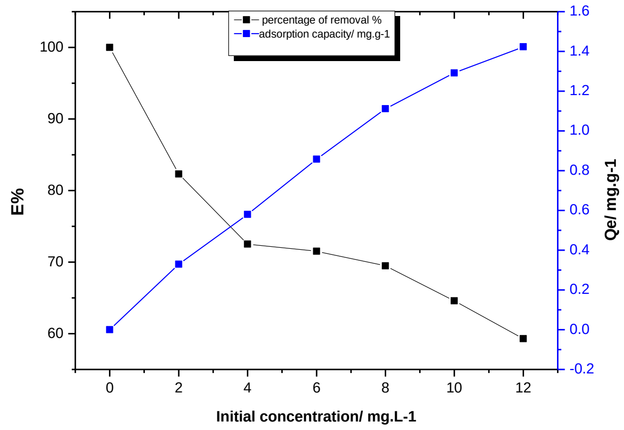

Fig.4: Effect of primary concentration on the removal percent and quantity of adsorbed MB dye on to Wight marble (Exp. Cond.: Temp. = 25°C, agitation time one hour, and solution of pH 6)

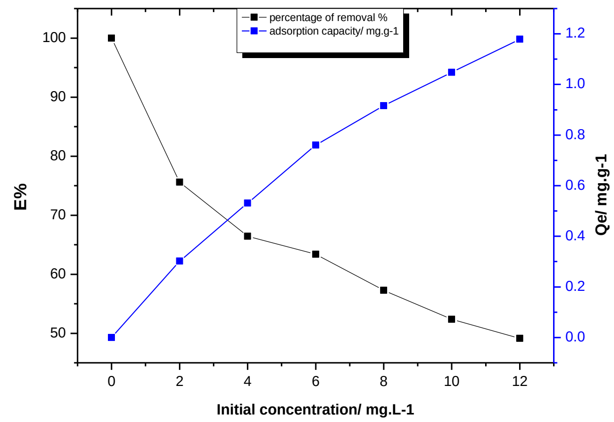

Fig.5: Effect of primary concentration on the removal percent and quantity of adsorbed MB dye on to Wight marble (Exp. Cond.: Temp. = 15°C, contact time one hour , and solution pH 6)

Effect of mass White marble on capacity removal of MB dye :

The solid/solution ratio is an significant parameter estimation the efficiency of a sorbent in a batch sorption was estimated. The affect of sorbent dose on the removal E% of dye Methylene Blue appear in Figur. 6. It followed the predicted pattern of raising removal sorption as the dose was raised . This is possibly because of the resistance to quantity transfer of dye of bulk liquid to the surface of the solid, that becomes significant at great adsorbent loading in which the experiment was conducted [3, 20, 21] . It may be appear the amount of white marble increase with removal of dye Methylene Blue MB increasing . The percentage removal of dye raised once the quantity was changed from 1 - 20 g /L at several concentrations dye MB (2-12 mg/L).[22, 23] The number of active sites obtainable of site adsorption raise through raising the White marble dosage[4]

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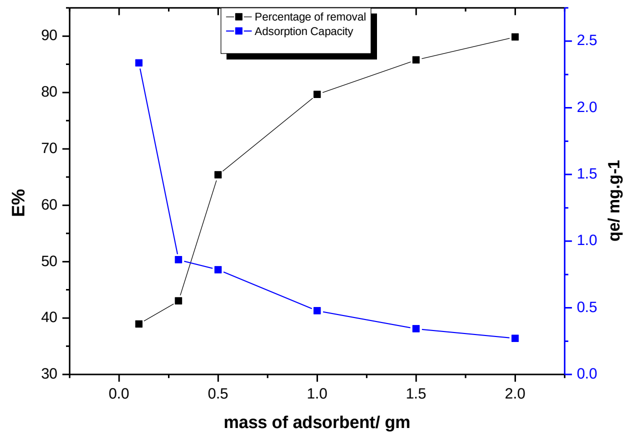

Fig. 6: Effect of amount adsorbent on adsorption dye MB : exp. conditions: Temp. 25°C, solution pH 6, conc. dye 8 ppm .

Effect of acid treatment on the adsorbent surfaces:

The study of the effect of acid treatment was necessary to show the maximum adsorption. The adsorbents were treated by different acids such as (HNO3, H2SO4, and HCl). The results are illustrated in Figures 7

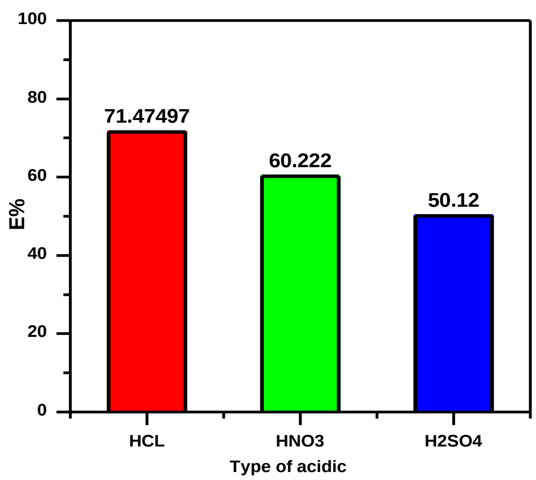

Figure 7: Effect of different acid treatment on the Wight marble for the adsorption of MB dye : exp. conditions: Temp. 25°C, particle size 75 µm , solution of pH 6, conc. dye 8 mg/L ..

It was obvious from the results shown in fig.7 the best removal when the adsorbent treated by HCl, this is may be due to the increased removal caused to re-activated the active sites for adsorbent surface [11].

Effect of Particle Size

The particle size has significant part to show in the quantity of MB dye adsorbed. In the present study particle sizes (100, 200, and 300 mesh) were utilized of the adsorption of dye MB onto white marble results appear in Figur.8

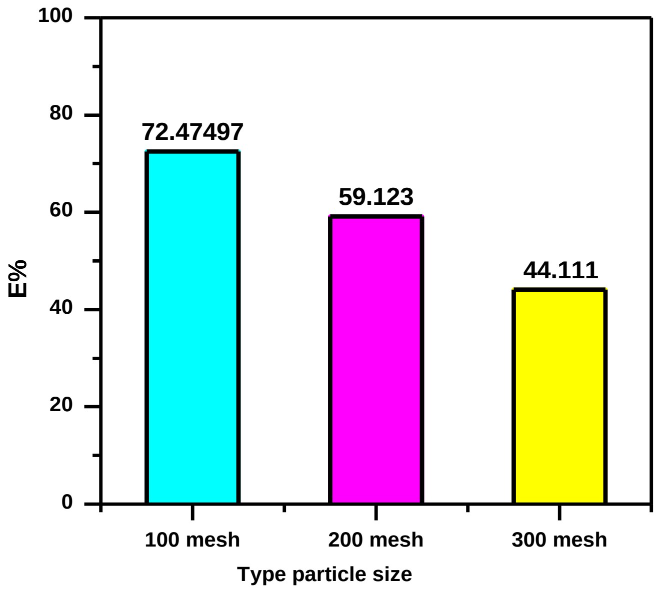

Figure 8: Effect of particle size on the adsorption of MB dye on the surface of white marble exp. conditions: Temp. 25^{o}C, pH 6, dye conc. 8 ppm.

An raise in percentage removal with increasing particle size largely proposes that the molecules of the MB dye do not completely penetrate the particle or partly that the dye molecules preferentially adsorb near the outer surface of the particle [24] .As known the adsorption is restricted to the external surface area of the adsorbent, thus , the lower particle size decrease the external amount transfer resistance and helps adsorbate to enter in to the interior of adsorbent for contacting extra active sites through the adsorption method [25, 26] .

Adsorption Isotherms

Freundlech model:

The empirically derived Freundlich model is defined as follows equation (3) . [27, 28]

$$q_e = K_f C_e^{1/n} \qquad 3)$$

K_f know the adsorption or distribution coefficient and represents the amount of MB dye adsorbed on to adsorbent for unit concentration equilibrium. 1/n is the heterogeneity agent and n is a measure of the deviation of adsorption linearity.[29].The applicability of the Freundlech equation to a particular case is tested via plotting log q_e against log C_e of the logarethmic of Equation 4. [27]

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

Like a plot would yield a straight line through log K_f equal intercept and 1/n equal slope. Results are shown in Figures 5 and the Freundlich constants are illustrated in Table 1:

Langmuir Isotherm:

The isotherm Langmuir is utmost generally utilized of the adsorption of contaminants from liquid solutions [30, 31]. Another equation was derived through Langmuir on the basis of a definite case of the nature of the adsorption method. The Langmuir adsorption model is defined in equation 5 [30, 31]

$$q_e = \frac{q_0 K_L C_e}{1 + K_L C_e} \tag{5}$$

where q_e : Amount adsorbed per unit mass of adsorbent at equilibrium ($mg.g^{-1}$), ($mol.g^{-1}$) C_e : Equilibrium concentration of adsorbate in solution after adsorption ($mg.L^{-1}$), ($mol.L^{-1}$) K_f : Empirical Freundlech constant or efficiency parameter ($L.g^{-1}$) , 1/n : Freundlich exponent , q_0: Empirical Langmuir constant that represents maximum adsorption capacity (mg/g). K_L: empirical Langmuir constant (L/mg) the Langmuir model is limited in its use to adsorption in monolayer. Results are shown in Figures (7)

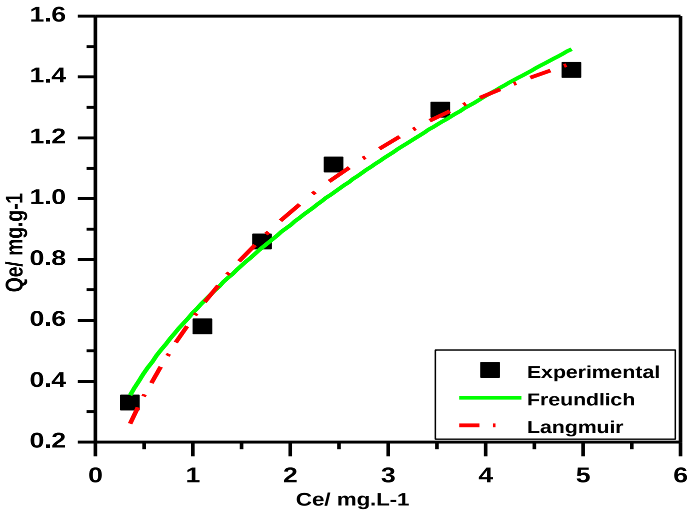

Fig.7. Paracetamol MB dye adsorption model of Different adsorption isotherm nonlinear fit . on *Wight marble* at pH 6, weight dosage 0. 5 gm, 25 °C initial conc. 20mg/L.

Table 2: model of Langmuir and Freundlech, model parameters for MB dye adsorbed on the surface of *Wight marble* at 25 °C.

Isotherm models	Parameters	Paracetamol drug
Langmuir	qm ($mg.g^{-1}$)	2.23771 ± 0.20855
	K_L($L.mg^{-1}$)	0.3731± 0.07196
	R^2	0.98245
Freundlich	K_F	0.6248 ± 0.04195
	1/n	0.5487 ±0.05443
	R^2	0.96944

Conclusion

The adsorption efficiency and E% percentage of color removed increase with increasing contact time, and surface area, and decreasing with raising of primary concentration dye of the dye solution and the adsorption efficiency decreasing with increasing of adsorbent dosage .The adsorption equilibrium of MB dye reaches one hour. Utmost value of adsorption efficiency was found at temperature 50 ^{0}C. Wholly affective factor give good fitting of Langmuir model better than Freundlich model.

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