Effect of zinc oxid on the bentonite ability for removing Methylene blue from solution

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Abstract:

A batch adsorption system was applied to study the adsorption of methylene blue from aqueous solution by Iraqi bentonite and treated bentonite with different amount of zinc oxide (ZnO). The adsorption capacities of methylene blue onto bentonite were evaluated. The equilibrium between liquid and solid phase was described by Langmuir model better than the Freundlich model. Langmuir and Freundlich constants have been determined. The separation factor or equilibrium parameter, R_L which is used to predict if an adsorption system is favourable or unfavourable was calculated for all cases.

Keyword: Adsorption capacities; Adsorption isotherm; Iraqi Bentonite; Methylene Blue.

Introduction:

The purification of waste water contaminated by hazardous pollutants of inorganic and organic nature is among the serious problems of conservation, especially when such toxic materials (eg. dyes) contaminating the environment even in an insignificant concentration are involved. The elimination of such pollutants from aqueous solution is an important problem not only from a technical but also from an economic point of view. In order to minimize the possible damage to people and the environment, several studies have been conducted around the world [1-4].
Methods for decolorization have therefore become important in recent years.In principle; decolorization is possible with one or more of the following methods: adsorption, precipitation, chemical degradation, photodegradation and biodegradation [5]. Adsorption techniques have proven successful in removing colored organic species, with activated carbon being the most widely used adsorbent due to its high capacity for the adsorption of organic materials [6] · However, due to activated carbon high cost and the difficulty of regeneration, effective adsorbent such as bentonite clay derivatives is needed. Bentonite is important clay having a variety of uses because of its colloidal property when it is mixed with water, swelling in water and in some organo environment and having high plasticity [7]. The industrial application of bentonite dispersions is very wide spread. Bentonite with its higher ion exchange capacity and surface area is used as an industrial raw material in sorptive, catalytic. They are used in different branches of industry, such as in drilling fluids, dyes, pharmaceutical application, paper, cement and ceramics. Bentonite dispersions have the advantage over other clays in being sensitive to surfactants, polymers and electrolytes [8] .The aim of this work was to study the effect of amount of ZnO on the ability of bentonite to

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remove the methylene blue from solution .

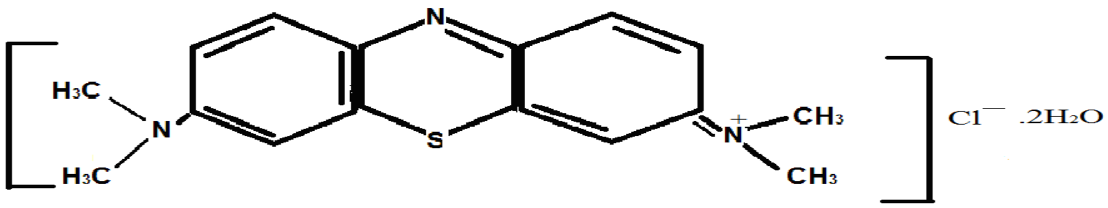
Materials and Methods:

The bentonite clay was supplied from the state company for geological survey and mining-Iraq; the bentonite had the particle size less than 75µm. The molecular formula of bentonite could be written as [9] :

$Mg_2Al_{10}Si_{24}Fe_2O_{60}$ (OH) $_{12}$[Na, K, Ca]

Bentonite which treated with zinc oxid was prepared by mixing 10g of bentonite and different amounts of zinc oxid (99.99% Gold Label FW 81.37, Merck) (1, 0.5, 0.1 and 0.05) g then shaken with 50 ml of distilled water for 24 h at room temperature, and then separated the solution by filtration process and drying in oven at 70 ^{o}C for 48 h.

The dye used was a methylene blue, (crystals, no.M 157/ 15/ 220 from M&B chemical co., of molecular weight 355.90) which correspond to the methylene blue hydrochloride, with $2H_2O$ and the chemical formula is ($C_{16}H_{18}ClN_3S.\ 2H_2O$), and the formula of the methylene blue can be written as:



Stock solution of methylene blue was prepared and then diluted to give standard solutions of appropriate concentration. Batch experiments were conducted in 100 ml round flat bottom flasks and equilibrated using a magnetic stirrer. Then 10 ml aliguots of these standard solutions were placed in flasks and 0.1 g of bentonite powder was added, (the equilibrium contact time was 20 min.). After filtration, the solution of methylene blue in supernatant was analyzed at λmax 660 nm using uv-vis spectrophotometer (SP-3000 plus OPTIMA-Japan). The calibration curve was accomplished by measuring the absorbance of solutions at 660 nm.The plotting of absorbance vs. concentration was shown in Fig. 1. The amounts of adsorption were calculated by basing on the difference of methylene blue concentrations in aqueous solutions befor and after adsorption. The adsorption capacity can be calculated as[10]:

$$\text{Adsorption capacity } (q_e) = \frac{(C_o - C_e)\,V}{W} \qquad \ldots\ldots\ (1)$$

Where C_0 is the initial concentration (ppm), C_e is the final or equilibrium concentration (ppm); V is the volume of the solution (ml) and W is the weight of the bentonite powder (g).

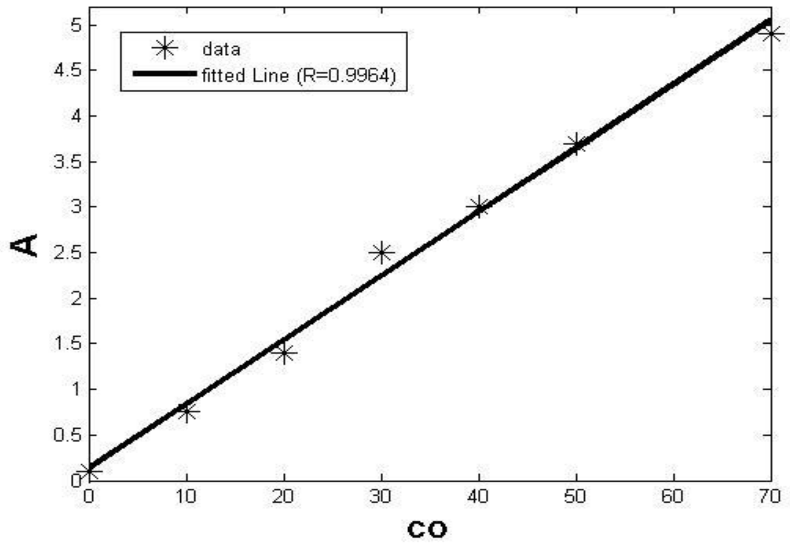


Fig.1- The calibration curve of various methylene blue concentration

Results and Discussion:

Fig. 2 shows the experimental equilibrium isotherms for adsorption of MB on bentonite surface, it show that when the amount of zinc oxide increases the C_e increases and q_e decreases. The results clearly show that the addition of competing components systematically decreases the extent of adsorption.

The experimental values of the isotherm were used in the linear forms of Langmuir equation, which is valid for monolayer sorption . It is given by[11]:

$$C_e/ q_e = C_e/ Q + 1/ Qb \qquad \text{……..(2)}$$

Where Q is the maximum adsorption at monolayer (mg g^{-1}), C_e is the equilibrium concentration of methylene blue (ppm), q_e is the amount of methylene blue adsorbed per unit weight of bentonite powder at equilibrium concentration and b is the Langmuir constant or the adsorption equilibrium constant (ml mg^{-1}) and is a measure of the energy of adsorption. A linearized plot of C_e/ q_e against C_e gives Q and b (Fig. 3). The widely used empirical Freundlich equation basing on sorption on heterogeneous surface given by [11]:

$$\text{Log } q_e = \log K_f + 1/ n \log C_e \qquad \text{………(3)}$$

Where K_f and n are Freundlich constants indicating sorption capacity and intensity, respectively. K_f and n can be determined from a linear plot of $\log q_e$ against $\log C_e$ Fig. 4. The calculated results of the Langmuir and Freundlich isotherm constants and the correlation coefficients R^2 are given in table 2.

Table 2 - Langmuir and Freundlich isotherm constants and correlation coefficients

adsorbent	Langmuir			Freundlich		
	Q(mg g^{-1})	b(ml mg^{-1})	R^2	n	K_f(mg g^{-1})	R^2
Bentonite	357.14	0.451	0.998	-25.510	14.614	0.650
Bentonite + 1g ZnO	131.57	-0.002	0.968	-1.522	89.747	0.973
Bentonite + 0.5g ZnO	222.22	-0.004	0.982	-3.538	28.559	0.906
Bentonite + 0.1g ZnO	125	-0.002	0.943	-1.858	59.799	0.928
Bentonite + 0.05g	416.6	0.0043	0.953	-4.098	13.722	0.391

Basing on Fig. 3 the correlation coefficients R^2 reach to 0.998 in the case of Langmuir isotherm and R^2 was ranging between(0.391-0.973) for Freundlich which means the adsorption oby Langmuir rather than Freundlich. So MB make monolayer on the bentonite surface, and the value of maximum adsorption capacity Q was 357.14mg/g for bentonite and for bentonite with 0.05g of ZnO was 416.6 mg/g. The exponent n was less than zero, an indication of an unfavourable Freundlich adsorption process.

It has been reported that the effect of isotherm shape with a view to predict if an adsorption system is favorable or unfavorable.[12] . The essential features of Langmuir isotherm can be expressed in term of a dimensionless constant separation factor or equilibrium parameter, R_L which is expressed by the following equation: [13]

$$R_L = 1/\ 1+ bC_o \qquad \text{.......... (4)}$$

Here C_o is the initial concentration (ppm), and b is Langmuir constant (ml/ mg). The parameters show the shape of isotherm according to table 3.

Table 3 - Effect of Separation Factor on Isotherm Shape[12]

R_L value	Type of Isotherm
$R_L > 1$	unfavorable
$R_L = 1$	linear
$0 < R_L < 1$	favorable
$R_L = 0$	irreversible

Basing on the effect of separation factor on isotherm shape, the R_L values are in the range of $0 < R_L < 1$, which indicates that the adsorption of MB on bentonite and modified bentonite which treated with 0.05g ZnO are favourable.

The value of R_L for different initial methylene blue concentrations are given in table 4..

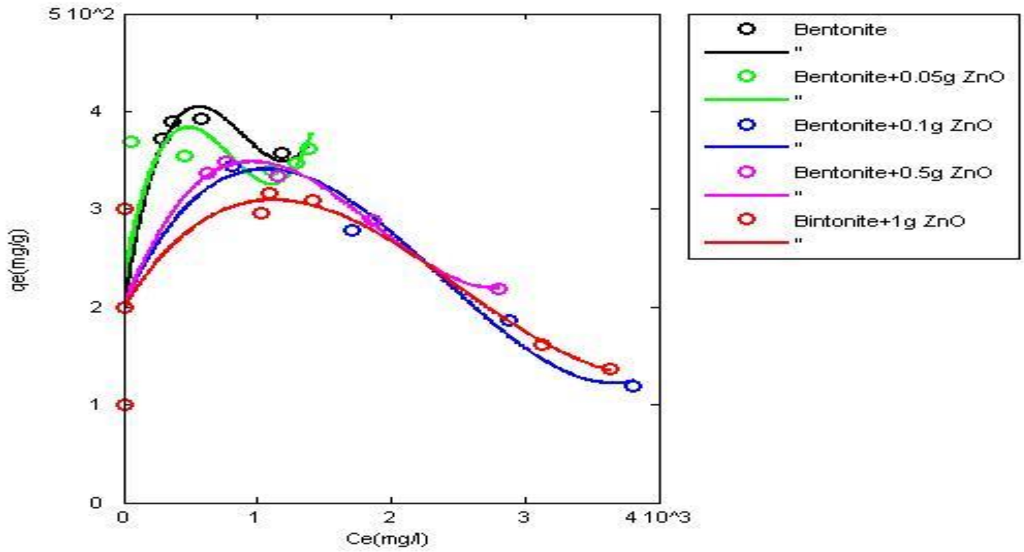


Fig.2 The adsorption isotherm of MB on Bentonite.

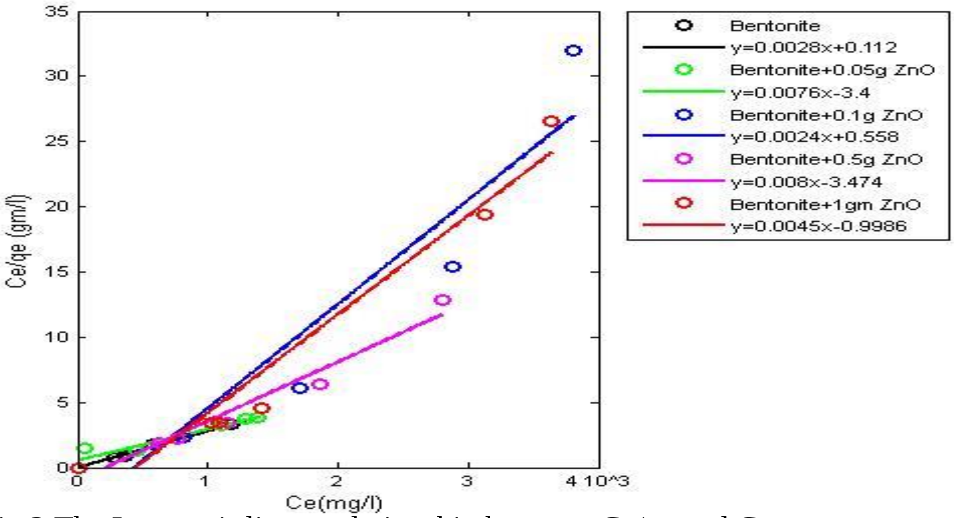


Fig.3 The Langmuir linear relationship between Ce/qe and Ce.

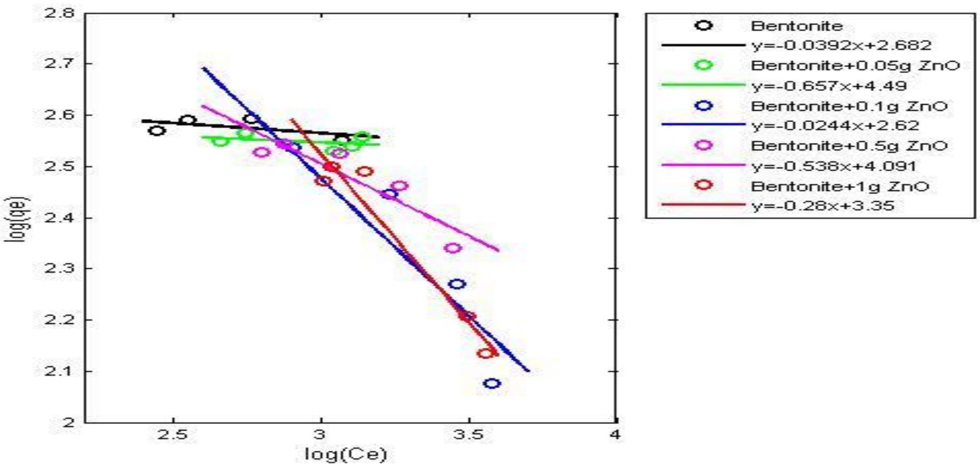


Fig.4 The Freundlich linear relationship between log(qe) and log(Ce).

Table 4 - $R_L$values based on the Langmuir equation

Initial conc. Of MB(ppm)*10^2	R_L value				
	Bentonite	Bentonite+1g ZnO	Bentonite+ 0.5gZnO	Bentonite +0.1gZnO	Bentonite +0.05gZnO
10	0.038	-0.833	-0.285	-0.769	0.188
20	0.019	-0.294	-0.125	-0.277	0.104
30	0.013	-0.178	-0.080	-0.159	0.071
40	0.009	-0.128	-0.058	-0.121	0.054
50	0.007	-0.100	-0.046	-0.095	0.044

Bentonite and bentonite with 0.05 g ZnO can be considered to be microporous ; therefore pores are largely enough to let methylene blue ions through. The mechanism of ions adsorption on porous adsorbents may involve three steps; [14-15] (i) diffusion of the ions to the external surface of adsorbent; (ii) diffusion of ions into the pores of adsorbent; (iii) adsorption of the ions on the internal surface of adsorbent. The first step of adsorption may be affected by MB ions concentration and agitation period. The last step of the adsorption is considered as a rate-determining step and as a relatively rapid process.

Conclusions:

In this study, the capacity of bentonite clay to adsorb Methylene blue ions from aqueous solutions was examined, including equilibrium studies. The adsorption isotherms could be well fitted by the Langmuir equation. The results show that degree of the interaction between the Methylene blue and the bentonite particles depends on the concentration of MB solution and the amount of zinc oxide used with bentonite. When the concentration of MB increases and the amount of zinc oxide increases the value of q_e decrease that means the dimerization of MB or desorption process take places for MB ions (Fig. 2).The value of maximum adsorption capacity Q for modified bentonite with 0.05g ZnO was more ability for removing methylene blue dye.

The results clearly show that the addition of competing components more than 0.05g ZnO systematically decreases the extent of adsorption.

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تاثير اوكسيد الخارصين على قابلية البنتونايت في ازالة المثلين الازرق من المحلول

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الخلاصه:
تم دراسة امتزاز صبغة المثلين الازرق على طين البنتونايت العراقي والبنتونايت المعامل مع كميا ت مختلفة من اوكسيد الخارصين. وقد تم تطبيق متساويات الحرارة للنكماير وفرندلش ومن حساب الثوابت لهاتين المعادلتين تبين تطبيق موديل لانكمايرافضل من موديل فرندلش كما تم حساب معامل الفصل او معامل التوازن(R_L) لكل من البنتونايت والبنتونايت المعامل مع كميات مختلفة من اوكسيد الخارصين حيث من قيم (R_L) تبين ان سطح البنتونايت المعامل مع 0.05غم من اوكسيد الخارصين هو الافضل في قابلية امتزاز صبغة المثلين الازرق من محاليلها.