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Effect of Various Factors on the Adsorption of Methylene Blue on Silt Fractionated from Bijoypur Soil, Bangladesh

Zaker Y., Hossain M.A.* and Islam T.S.A.
Department of Chemistry, University of Dhaka, Dhaka-1000, BANGLADESH

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Abstract

Silt obtained from the fractionation of Bijoypur (Netrokona, Bangladesh) soil having the particle size (53 – 140 µm) was used as an adsorbent for the removal of Methylene Blue (MB) from aqueous solution. The effect of various factors (pH, temperature and adsorbent dose) on adsorption of MB on silt fraction was investigated. The effect of pH shows that the amount adsorbed increased with the increase of pH of solution. The equilibrium adsorption isotherms were analyzed by Langmuir and Freundlich equations. Both Langmuir and Freundlich models can describe the adsorption equilibrium but the Langmuir model shows better agreement. The amount adsorbed increased with the increase of temperature suggests the formation of dimer in the contact region. SEM micrographs and differential molar isosteric heat of adsorption (ΔH) calculated at different surface coverage, indicate that the surface is heterogeneous having energetically different adsorption sites. Values of n calculated from Freundlich plots indicate that adsorption of MB on silt is spontaneous. At high surface coverage, the differential heat of adsorption versus surface coverage plot shows maximum value indicating the occurrence of structural rearrangement in the adsorbate. With the increase of adsorbent dose, amount adsorbed increased due to the increased surface area of adsorbent.

Keywords: Methylene blue, Silt, pH, temperature, Langmuir and Freundlich isotherms, ΔH, Adsorbent dose, Structural rearrangement.

Introduction

Some physico-chemical methods such as adsorption, degradation, decolorization, coagulation, reverse osmosis etc have been developed to remove dyes from wastewater[1-15]. Adsorption has received considerable attention for color removal from waste waters by fixed bed column process[16] as it offers the most economic and effective method. Many investigators have been showing interest to study dye removal using low cost adsorbents like fly ash, coal, peat, sawdust and wood in recent years because of their local availability. Use of clay materials[1], rice husk[2], coconut coir[3], banana pith[4], wheat straw[5], sugarcane baggase[6], caladium bicolor (wild cocoyam) biomass[7], used tea leaves[8], ghassoul (natural clays from Atlas mountain of Morocco)[9], Neem husk[10], cow dung[11], Sargassum muticum[12], natural zeolites[13] have been found highly effective, eco-friendly and cost effective. Adsorption of industrially important dyes namely Bromophenol blue, Alizarin red, MB, Ericrome black-T, Phenol red, Malachite green and Methyl violet from aqueous media on activated charcoal were studied[17]. Effect of initial dye concentration, agitation time, pH and temperature on adsorption of MB on ghassoul was investigated[10]. Adsorption isotherms and adsorption kinetics, effect of sorbent physico-chemical characteristics (pH, cation exchange capacity, ionic strength, surface area), temperature, adsorption of volatile compounds, presence of a co-solvent, association with dissolved organic matter, sorbent concentration for sorption of organic pollutants by natural sorbents (soils, sediments, clays, humic materials, and dissolved organic matters) were reviewed[18]. Batch adsorption experiments were carried out to investigate effect of several parameters e.g. initial dye concentration, pH, temperature and contact time for the sorption of Congo red, Malachite green and Rhodamine B dyes onto acid activated carbon[19]. The biosorption of reactive dye from aqueous solutions using the activated sludge was studied using a batch system with respect to the initial pH, temperature, amount of adsorbent and the pre-treatment of the adsorbent. Both the Freundlich and Langmuir isotherm models could describe the adsorption equilibrium of the reactive dye onto the activated sludge with the Langmuir isotherm showing the better agreement. First- and second-order kinetic models were used to investigate the adsorption mechanism[20].

Out of three fractions of Bijoypur soil (sand, silt and clay), sand has the lowest adsorptive property[21]. Many investigators studied the adsorptive property of clay[22]; but the adsorptive property of silt has not been thoroughly investigated. The present investigation aims at the detailed study of equilibrium adsorption of dye on silt. The present study was carried out to investigate the effect of different factors e.g. pH, temperature and adsorbent dose on the adsorption of MB on silt. The objective was to study whether the adsorption process can be described by Langmuir and Freundlich models, to determine thermodynamic parameters and the change of surface morphology by SEM.

Material and Methods

Silt was fractionated from Bijoypur (Netrokona) soil. In our present investigation, titrometric method[23] was used for fractionation of Bijoypur soil into sand, silt and clay on the basis of particle size. Fractionated silt was characterized by LIBS, FT-IR, SEM, XRD and pH_{zpc}[24].

The adsorption experiment was carried out at pH 7.0 with MB of concentration 5.0×10^{-5} M at 30°C. 0.1 g of silt was taken in each of 6 bottles containing 40 mL MB solution. The bottles were shaken in a thermostatic mechanical shaker (SWB-20, HAAKE, Fisons Ltd, Germany). After a definite interval of time each bottle was withdrawn from the shaker. The supernatant of the bottle was transferred and centrifuged repeatedly until a clear liquid was obtained. The absorbance of the clear solution was measured spectrophotometrically at λ_{max} 663.0 nm. The adsorption experiments were carried out to investigate the effect of pH on adsorption at solution pH 3.0, 7.0 and 11.0 keeping other parameters constant. In all cases, the pH of the solution was adjusted by using acid or alkali without affecting the volume of the solution.

To investigate the effect of temperature on adsorption, adsorption experiments were carried out with different initial concentrations of MB from 3.0 to 30.0 mg/L at pH 7.0. The experiments and the analysis were performed as described earlier. The equilibrium concentration and amount adsorbed for different initial concentrations were calculated at different temperatures and adsorption isotherms were constructed.

To determine the effect of adsorbent dose on adsorption isotherms, adsorption experiments were performed at pH 7.0 and temperature 30°C using 0.1, 0.2 and 0.3 g of silt following the same procedure as mentioned earlier.

A small portion of fractionated silt were separately taken in a SEM sample holder and made it platinum coated using a Pt-coated auto system (JFC-1600, JEOL, Japan). Platinum coated silt was placed in the SEM sample chamber and SEM picture was taken at 20 kV with 2,000 and 30,000 magnification. Again this procedure was carried out for the sample collected after adsorption of MB on silt with 30,000 and 60,000 magnifications.

Results and Discussion

Characterization of Adsorbent: Silt was characterized by LIBS, FT-IR, SEM, XRD and pH_{zpc} and results have been discussed in the earlier study[24].

Estimation of Equilibrium: Equilibrium time for adsorption of MB on silt water interface was estimated as 90 minutes beyond which no change of amount adsorbed was found.

Effect of pH on Adsorption: Figure-2 shows that the adsorption of MB on silt increases with the increase of pH indicating favorable adsorption at alkaline medium which can be explained from the pH_{zpc} value of silt. The pH_{zpc} value of silt is 6.39±0.02[24]. When the pH of solution is higher than the pH_{zpc}, the surface becomes negatively charged. MB is a cationic dye. Due to electrostatic force of attraction molecules of MB are adsorbed on the surface of silt. Similar trends were observed in the literature[25].

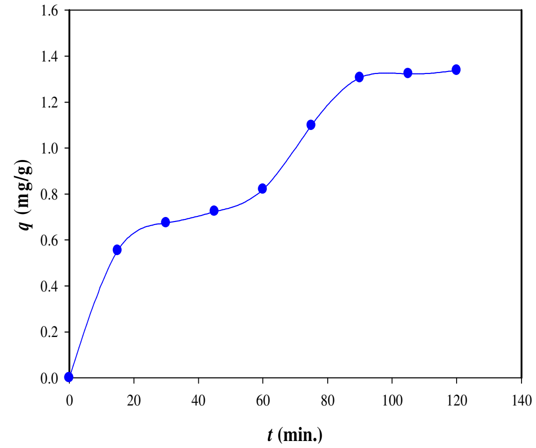

Figure-1
Equilibrium time of the adsorption of MB on silt at pH 7.0

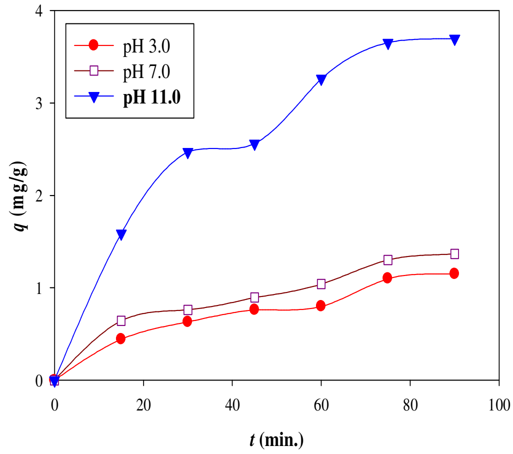

Figure-2
Change of surface coverage of silt at different pHs of MB solution

Adsorption Isotherms at Different Temperatures: Adsorption isotherms of MB on silt were determined at different temperatures as shown in figure-3. In all cases, the nature of isotherms is almost same suggesting the possible formation of bi-layers. Figure-3 shows the amount of MB adsorbed on silt increases with increasing concentration non-uniformly and amount adsorbed increases with increasing temperature indicating endothermic process. Similar trend was observed during the investigation of the adsorption of Brilliant Red on activated charcoal over the temperature range from 5°C to 55°C[26]. But both exothermic and endothermic effect of temperature on the adsorption of methylene blue onto clay was also observed[25]. Exothermic effect was observed over the range of 20ºC to 40ºC. But above 40ºC, endothermic effect was found. High temperature favors the diffusion of dye molecules in the internal porous structure of surface. Figures-4 and 5 show the application of Langmuir and Freundlich models to the adsorption equilibrium separately.

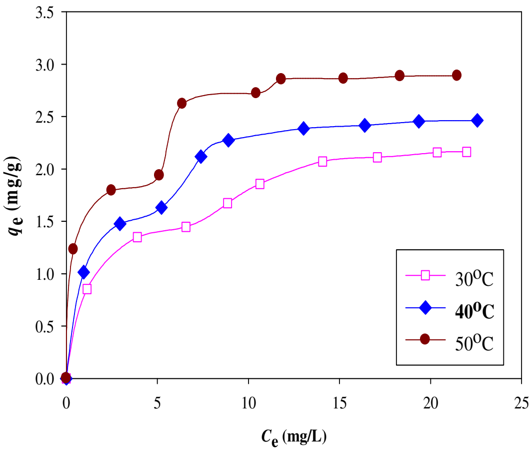

Figure-3
Adsorption isotherms of MB adsorption onto silt at different temperatures

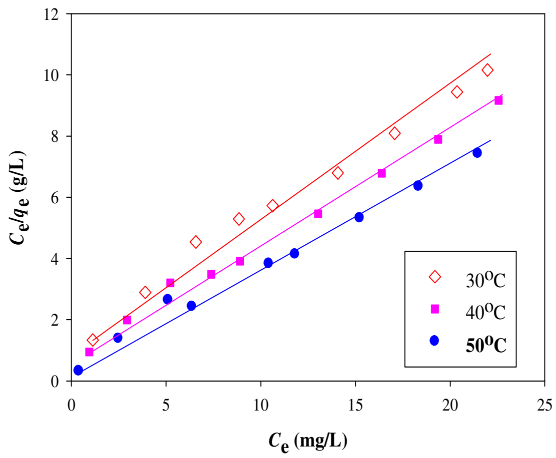

Figure-4
Langmuir plots for MB adsorption onto silt at different temperatures

From Langmuir plots (figure-4) amount adsorbed for monolayer formation (q_m), Langmuir adsorption-desorption equilibrium constant (K_l) and regression constant (R^2) were determined and values are shown in table-1. From Freundlich plots (Figure-5), Freundlich adsorption-desorption equilibrium constant (K_f) and regression constant (R^2) and n were estimated and are shown in table-2. Values of R^2 as shown in table-1 and table-2 suggest that the equilibrium data fit better in Langmuir isotherm than Freundlich isotherm over the temperature range of 30 to 50ºC.

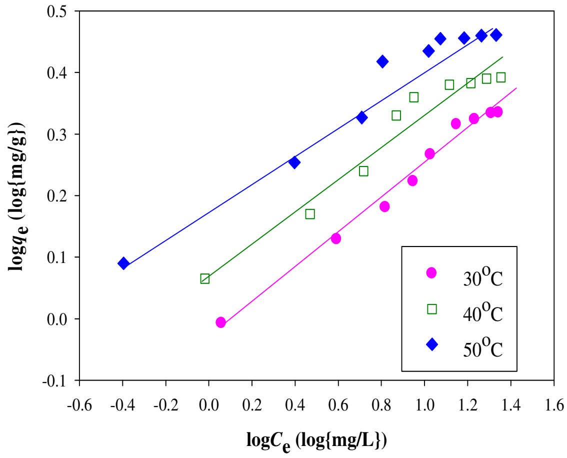

Figure-5
Freundlich plots for MB adsorption onto silt at different temperatures

Table-1
Langmuir parameters for the adsorption of MB on silt

T (K)	q_m (mg/g)	K_l (L/mg)	R^2
303	2.505	0.287	0.989
313	2.737	0.439	0.995
323	3.120	0.641	0.991

Table-2
Freundlich parameters for the adsorption of MB on silt

T (K)	n	R^2	K_f (mg/g)
303	3.554	0.987	0.930
313	3.865	0.952	1.181
323	4.329	0.961	1.525

Adsorption Isobar: The isobar in figure-6 shows positive temperature coefficient. This may be due to the activated adsorption. An increase in temperature leads to an increase in kinetic energy of adsorbate molecules. This favors the molecules to move from single adsorption site to the cavities and pores to form higher order aggregates depending on concentration and other interactions like adsorbed- adsorbed MB molecules, adsorbed- unadsorbed molecules and adsorbed molecule-surface etc. The formation of dimer of MB is also very likely. The adsorption of MB from aqueous solution onto kaolinite and four soil samples to determine the effect of MB dimerization on the measured surface area have been reported[27]. The visible spectra of adsorbed molecules indicated that MB was present at the surface as a mixture of monomeric and dimeric species. The results also suggest that dimmers are formed in the contact region between two aggregating particles.

Adsorption Isoster: From figure-3, adsorption isosters were drawn as shown in figure-7. Differential molar isosteric heats of adsorption (ΔH) were estimated at different values of amount of MB adsorbed by silt as shown in table-3. In figure-8, heat of adsorption is plotted as a function of MB adsorbed.

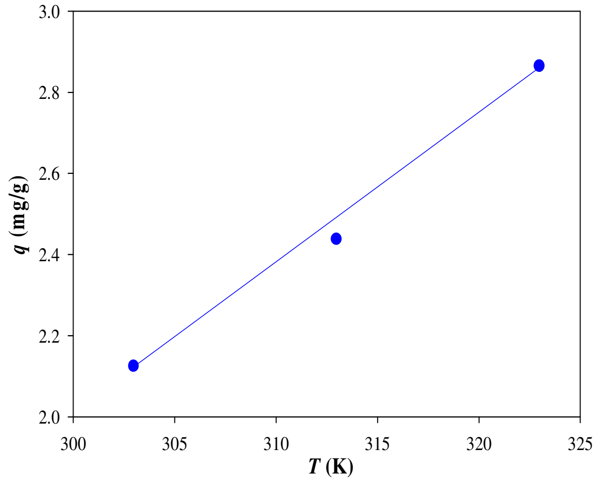

Figure-6
Adsorption isobar of MB on silt

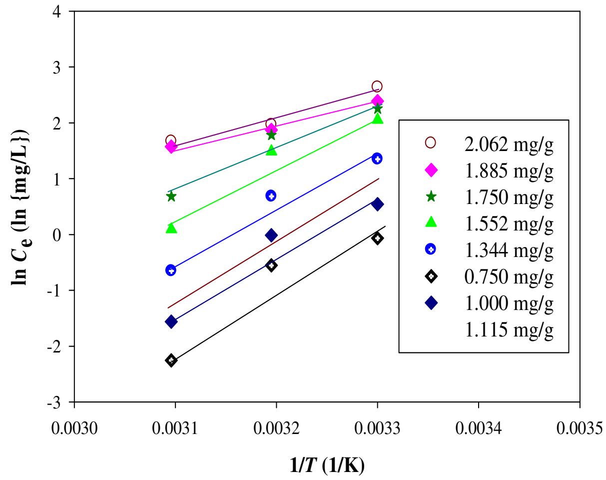

Figure-7
Adsorption isosters of MB on silt for different initial concentrations

Table-3
Heat of adsorption of MB on silt for different amount adsorbed

q (mg/g)	C_e (mg/L)	lnC_e (ln{mg/L})	T (K)	$1/T \times 10^3$ (K)	Differential heat of adsorption, ΔH (kJ/mol)
0.750	0.935	-0.067	303	3.300	88.627
	0.575	-0.553	313	3.194	
	0.105	-2.254	323	3.096	
1.000	1.720	0.542	303	3.300	85.302
	0.990	-0.010	313	3.194	
	0.210	-1.561	323	3.096	
1.115	2.290	0.829	303	3.300	88.295
	1.250	0.223	313	3.194	
	0.260	-1.347	323	3.096	
1.344	3.855	1.349	303	3.300	81.353
	1.980	0.683	313	3.194	
	0.520	-0.654	323	3.096	
1.552	7.810	2.055	303	3.300	79.715
	4.425	1.487	313	3.194	
	1.095	0.091	323	3.096	
1.750	9.530	2.254	303	3.300	63.768
	5.935	1.781	313	3.194	
	1.980	0.683	323	3.096	
1.885	10.935	2.392	303	3.300	33.256
	6.510	1.873	313	3.194	
	4.845	1.578	323	3.096	
2.062	14.010	2.639	303	3.300	39.683
	7.135	1.965	313	3.194	
	5.310	1.669	323	3.096	

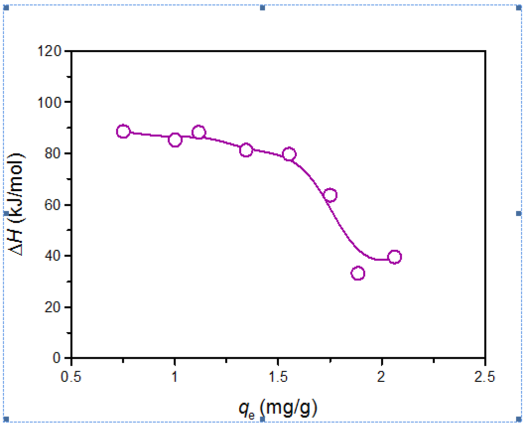

Figure-8
Variation of differential isosteric heat of adsorption with amount of MB adsorbed on silt

The values of Δ*H* increased with the increase of surface coverage showing a maximum value. This might be due to the occurrence of structural rearrangement in the adsorbate molecules as suggested by Fomkin[28] who studied the adsorption of gases, vapors and liquids by micro porous adsorbents. Adsorption interaction between adsorbate molecules and solid surface generally modifies the state of solid and the magnitude of this modification depends on the high energy adsorption sites capable of specific interactions[29]. Adsorption on micro porous adsorbents involves the adsorbent and adsorbate as equal partners of the adsorption process[30].

Effect of adsorbent dose: Figure-9, demonstrates effect of adsorbent dose on amount adsorbed for MB on silt-water interface. Figure shows the increase of amount adsorbed with increasing adsorbent dose suggesting that to obtain maximum removal of dye within reasonable time dose of adsorbent is an important factor as earlier investigation[26].

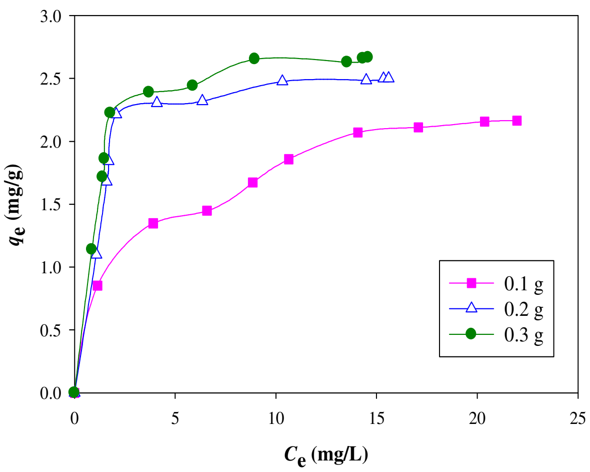

Figure-9
Variation of amount adsorbed of MB on silt with adsorbent dose

SEM Characterization of Silt Surface: The surface of silt was analyzed by Scanning Electron Microscopy (SEM) before and after adsorption of MB molecules from aqueous solution. Figure-10 shows the SEM micrograph of silt in two different magnifications 2000 and 30,000 before adsorption and figure-11 shows the SEM micrograph of silt surface after adsorption of MB in two different magnifications 30,000 and 60,000.

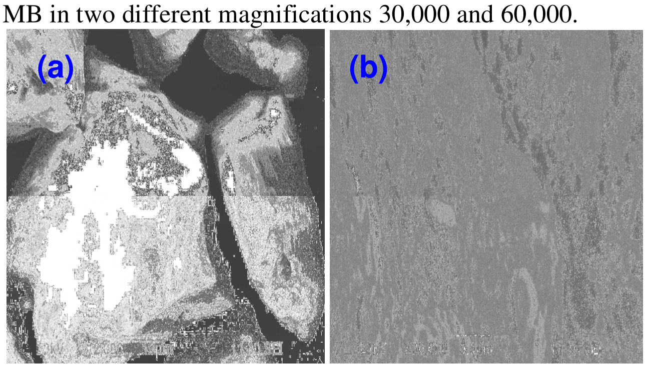

Figure-10
SEM micrograph of silt before adsorption in (a) 2,000 and (b) 30,000 magnifications

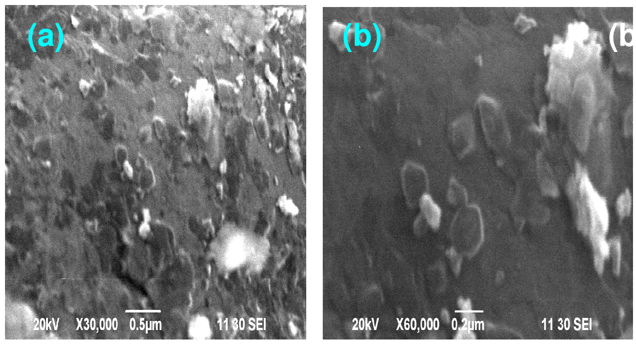

Figure-11
SEM micrograph of MB adsorbed silt in (a) 30,000 and (b) 60,000 magnifications

SEM images show different structural features with uneven surface (figure-10). After adsorption, the adsorbed molecules remain as aggregates on the silt surface as shown in figure-11.

Conclusion

The present study shows that about 1.3 mg of MB adsorbed per g of silt in 90 minutes at 30ºC and pH 7. The adsorption isotherms follow Langmuir models over the temperature range of 30 to 50ºC. Increase in temperature increased adsorption suggesting the possible formation of dimer of MB molecules. SEM micrographs show the energetically different active sites on the surface like pores and cavities, and formation of aggregates after adsorption. At high surface coverage the differential molar isosteric heat of adsorption shows a maximum value which may be due to the structural rearrangement in the adsorbate molecules.

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