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ADSORPTION OF METHYLENE BLUE IN AQUEOUS SOLUTION BY RED MUD AS ADSORBENTS

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The use of reasonable and eco friendly adsorbent studied as an alternative substitution of activated carbon for removal of dyes from wastewater. Adsorbents prepared from activated red mud, which is a residue generated in Bayer process of extraction of alumina from bauxite, prosperously used to remove the Methylene Blue from aqueous solution in a batch wise column. This study explores the potential use of red mud for the removal of Methylene Blue at changing dye concentration, adsorbent dosage, pH and contact time. The sorption data were then correlated with the Freundlich and the Langmuir adsorption isotherm models. In both isotherms exhibited a maximum K value in which indicates that the red mud has greater affinity for Methylene Blue.

KEYWORDS: red mud, Methylene Blue, Freundlich's, Langmuir's isotherms.

Introduction

Dyes, nowadays plays an important role in industries ranging from clothes to paper, plastic to metals etc. Basically every industry uses dyes for one purpose or other, as a result the effluents discharged from these industries generally contains these dyes making it colored and hazardous, making it an environmental problem affecting every living organism. The major being the rising toxicity of water making it unfit for use.

There is a need to identify an inexpensive and effective dye removal method. There exist various methods based on chemical, physical or biological treatment process [1]. Among the various chemical, physical or biological treatment processes, such as Trickling fitter, activated sludge chemical coagulation and flocculation, oxidation or ozonation, membrane separation, Photo degradation and adsorption process [2-4], physical adsorption has been most popular as a potent technique for dye removal, due to its cost effectiveness and unpretentious operation [5-6].

Literature show us that various adsorbents have been tried for the same, such as as activated carbon [7-8], clay [9], silica [5, 10], metal hydroxide [11], polymers [12], carbonic matter from agricultural waste [13-15], alumina [16] and zeolite bed [17], however red mud has attracted more attention and success. It is is a residue generated in Bayer process of extraction of alumina from bauxite.

MATERIALS AND METHODS

DYE AS AN ADSORBATE: Methylene blue (MB) (fig. 1) is a heterocyclic aromatic chemical compound with the molecular formula $C_{16}H_{18}N_3SCl$ .Methylene blue (3,7-bis (Dimethylamino)-phenothiazin-5-ium chloride) was first prepared in 1876 by German chemist Heinrich Caro (1834-1910).

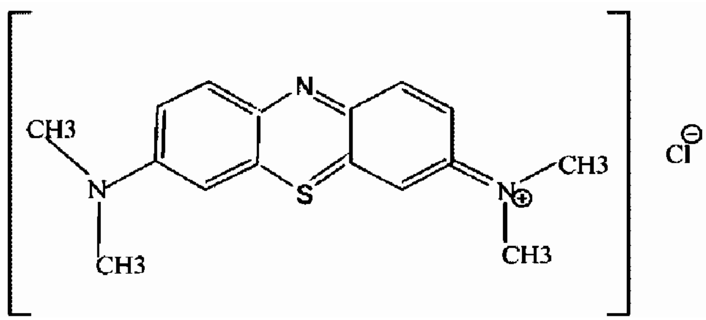

Fig. 1. Structure of Methylene blue

The Methylene blue is dark green crystals or crystalline powder, having a bronze-like luster. Solutions in water or alcohol have a deep blue color.

ESTIMATION OF DYES

The dye Methylene blue was estimated spectrophotometrically. Absorbance of the dye was noted at various wavelengths and its λ_{max} was determined as 665 nm. It is the wavelength at which the dye solution shows the maximum absorbance of light at a fixed temperature and pH. The aqueous solutions of the dye were prepared in distilled water.

RED MUD AS AN ADSORBENT:-

Red mud was obtained from Hindustan Aluminum Company (HINDALCO) Renukoot, India. It was in the form of a clay type -waste residue composed of a fine fraction (mud) and a relatively coarse fraction (sand) with small granules. Red mud varies in physical, chemical, and mineralogical properties due to differing bauxite ore sources and refining processes employed. The general consensus of the composition of red mud has been found to be largely composed of iron oxides, primarily hematite (Fe_2O_3), and goethite (FeOOH), boehmite (AlOOH), quartz(SiO_2), other aluminium hydroxides [gibbsite $Al(OH)_3$], calcium oxides, titanium oxides (anatase and rutile), and aluminosilicate minerals; sodalite ($Na_4Al_3Si_3O_{12}Cl$) [18].

The chemical composition [19] of supplied red mud mentioned by HINDALCO, Renukoot is given in table-1.

Table 1.

Al_2O_3 (%)	Fe_2O_3 (%)	SiO_2 (%)	TiO_2 (%)	Na_2O (%)	CaO (%)	LOI * (%)
17.5-19.0	35.5-36.2	7.0-8.5	16.3-4.5	5.0-6.0	3.2-4.5	10.7-12.0

*LOI-Loss On Ignition

ACTIVATION OF RED MUD

A method for activating the red mud formed in the Bayer alumina producing process for allowing its use as adsorbent, catalyst, ion-exchanging substance and clarifying substance, comprising a digesting red mud and dispersing the metal oxide compound particles in the compound of metal hydroxides and silica gel.

The obtained material in the crude form showed poor adsorption properties. Therefore, the material was first treated with hydrogen peroxide at room temperature for 24 h to oxidize adhering organic matter and washed repeatedly with doubly distilled water. The resulting material was dried at 100°C [20]. Further the dried raw red mud was treated with hydrochloric acid. The 2-1 treatment solution was refluxed for 2 h. The weight of added hydrochloric acid ranged from 5 to 30 % of red mud. The treated mud was separated from the acid solution and washed with distilled water for removal of residual acid and soluble compounds, then it was dried at 105^o C, ground in a mortar, sieved through steel sieve. The resulting product exhibited an optimum surface area with the best adsorption capacity. The product obtained at higher temperatures had a poor adsorption capacity probably because of the collapse of surface functional groups on the adsorbent. Therefore, the optimization of activation conditions was carried out very carefully [21].

PARTICLE SIZING OF ADSORBENT

The activated red mud was crushed into smaller particles and was passed through sieves of different mesh size. The sieved fractions corresponding to B.S.S mesh sizes 100-150 (particle radius 0.0075 to 0.0059cm), 150-200 (particle radius 0.0059 to 0.0037cm), and 200-250 (0.0037 to 0.0021cm) was separated and collected. The average value of the sieve openings in cm, as mentioned in the 'Conversion table for U.S. Standard screen series' [22] was taken as particle radius. Finally, the product was stored in a vacuum desiccators until required for use.

BATCH METHOD

The batch technique (finite bath method) because of its relative simplicity is commonly used. Other advantages of this technique are its freedom from complex hydraulic parameters indigenous to flow-through systems, its adaptability to small volume work, ease of investigation in various conditions and general facility of operation.

A series of 50 ml Erlenmeyer flasks were used for adsorption studies. 10 ml of aqueous solutions of varying concentrations of dye was added to each flask and maintained at the desired temperature in a thermostatic shaker water bath. A known amount of fly ash was added to each flask. The flasks were shaken for 2-3 minutes and equilibrated for eight hours.

The supernatant liquid was centrifuged and analyzed for the residual dye concentration. The concentration of the residual dye in the dilute solution was estimated from the calibration curves drawn for this purpose. The amounts sorbed were determined by difference between initial and final concentrations expressed as mg of dye/g of adsorbent. Knowing the dilution made, the concentration of the residual dye in the undiluted solution was estimated by using the following equation given below

$$q_e = \frac{\left(C_0 - C_e\right)V}{W}$$

where C_0 and C_e are the initial and equilibrium concentrations of the dye in the solution (mg/l), V is the volume of dye solution (l), W is the weight of the adsorbents (g) and qe is the amount of adsorbate per mass of the adsorbent (mg/g).

One gram of red mud was maintained in contact with 50 mL dye solution (initial concentration; 5, 10, 20 mg L^{-1}) in an Erlenmeyer flask and was shaken in a thermostatic water bath (120 cycle/min). After the different contact times, the solution was filtered by filter membrane. The residual dye concentration in each solution was measured spectrophotometrically at the corresponding λ_{max} (665 nm for Methylene blue). Sorption rate is determined by measuring the uptake of adsorbate in solution. Thus, a number of experiments are carried out and the uptake of the adsorbate, as a function of time, is determined. The change in the concentration of the solution is estimated by analysis of aliquots withdrawn at various intervals of time.

INSTRUMENTATION

Measurements for pH determinations were made with Century CK 710 Water Analyzer kit. Absorbance measurements were studied with a Shimadzu UV-VIS Spectrophotometer 2100S (Japan) at corresponding wavelength for maximum absorbance (λ_{max}) 665 nm for Methylene blue. The surface micro-morphology of materials was investigated using a high resolution scanning electron microscope JEOL JSM 840.

RESULTS AND DISCUSSIONS

EFFECT OF CONTACT TIME.

The effect of contact time on the adsorptions of methylene blue was studied for particle size 150-200 BSS mesh, and the result is given in table-2 and shown in Figure 2.

Table-2 Effect of contact time on the adsorption of methylene blue (pH 8) on red mud, particle size 150-200 mesh.

Time(min)	
40	Amount of dye adsorbed (M) x10^{-4}
80	2.516
120	3.249
180	3.598
240	3.849
300	4.082
360	4.124
420	4.248
480	4.276

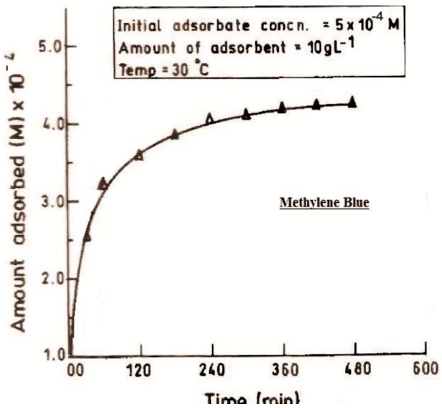

Fig. 2 Effect of contact time on the adsorption of methylene blue (pH 8) on red mud, particle size 150-200 mesh.

The results indicate that equilibrium was achieved in 8 h for methylene blue. Further, the results show that the rates of uptake of the dye is rapid in the beginning and that 50% of the ultimate adsorption occurs within the first hour of contact.

EFFECT OF TEMPERATURE.

To determine the effect of temperature, adsorption studies of rhodamine B and methylene blue were performed at three different temperatures, i.e., 30, 40, and 50°C, and the results are given in table-3 and shown in Figure 3.

Table-3 Effect of temperature on the adsorption of methylene blue (pH 8) on red mud.

Time (min)	30°C	40°C	50°C
	Amount of Dye Adsorbed (M) $\times 10^{-4}$		
40	2.499	1.643	1.228
80	3.035	2.214	1.428
120	3.428	2.571	1.857
180	3.714	2.928	1.928
240	3.885	3.035	1.989
300	3.857	3.214	2.357
360	4.071	3.785	2.571
420	4.143	3.821	2.643
480	4.152	3.857	2.714

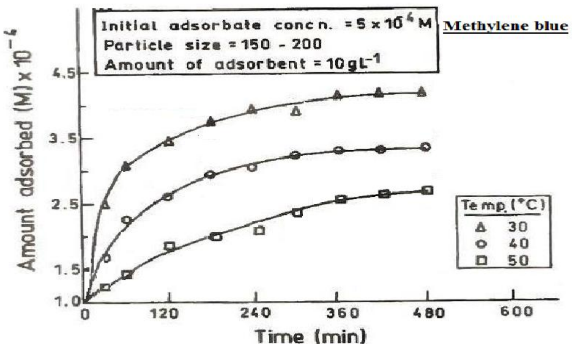

Fig. 3 Effect of temperature on the adsorption of methylene blue (pH 8) on red mud.

Fig. 3 indicates that the adsorption decreases with increasing temperature. The decrease in adsorption with increasing temperature indicates that the process of removal of the dye on red mud is exothermic in nature.

ADSORPTION MODELS.

To determine the mechanistic parameters associated with Methylene blue adsorption, the results of the adsorption experiments were analyzed according to the well-known models of Langmuir and Freundlich.

LANGMUIR ISOTHERM

The Langmuir isotherm has been used by various researchers to study the sorption of a variety of compounds. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The linear form of the Langmuir isotherm equation [23] can be written as follows

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_oC_e}$$

where q_e is the amount adsorbed (mg/g); C_e is the equilibrium concentration of the adsorbate (mg/L); and Q_0 and b are Langmuir constants related to the maximum adsorption capacity and energy of adsorption, respectively. When $1/q_e$ is plotted against $1/C_e$, for Methylene blue, straight line (correlation coefficients ranging from 0.9534 to 0.9918) with slopes of $1/bQ_o$, are obtained, which shows that the adsorption of both the dye follows the Langmuir isotherm.

Table 3. Langmuir Constants for the Removal of Methylene Blue*

	Q_o (mol/g)			B (L/mol)			R_L
Dye	**30°C**	**40°C**	**50°C**	**30°C**	**40°C**	**50°C**	
Methylene Blue	5.23×10^{-5}	4.81×10^{-5}	4.35×10^{-5}	1.79×10^{2}	1.28×10^{2}	0.84×10^{2}	0.89

* Adsorbent dose = 10 g/L; particle size = 150-200 mesh; pH 8.0 for methylene blue.

The Langmuir constants b and Q_o were evaluated, and the values of these at the three different temperatures studied, *i.e*., 30, 40, and 50°C, are reported in Table 3. For Methylene blue dye, the Langmuir constants b and Q_o decreased with increasing temperature, indicating the exothermic nature of the adsorption process. The influence of the shape of the isotherm on the feasibility of the process, *i.e*., whether the sorption is favorable or unfavorable, has been considered by Weber and Chakravorti [24] in terms of a dimensionless constant separation factor *(R_L)*. The calculated values of the dimensionless factor *RL* for Methylene blue are included in Table 3. The magnitude of the R_L values, i.e., ($0 < RL < 1$) indicates the favorable adsorption of Methylene under consideration. [25]

FREUNDLICH ISOTHERM

The adsorption data for Methylene blue was also analyzed by Freundlich model. The logarithmic form of Freundlich model is given by

$$\log q_e = \log K_F + (Un) \log C_e$$

where q_e is the amount adsorbed (mg/g); C_{e1} is the equilibrium concentration of the adsorbate (mg/L); and K_F and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. When log q_e is plotted against log C_e for Methylene blue, straight line (correlation coefficients ranging from 0.9135 to 0.9673) with slope $1/n$ is obtained, which shows that the adsorption of the dye follows the Freundlich isotherm. However, the Langmuir model fits slightly better with better correlation coefficients compared to Freundlich isotherm, indicating the process to correspond to mono-layer adsorption. The Freundlich constants K_F and n were evaluated, and their values at the three different temperatures considered, i.e., 30, 40, and 50°C, are reported in Table 4. From Table 4, it is clear that the values of K_F is highest for the Methylene blue.

Table-4 Freundlich Constants for the Removal of Methylene Blue*

	Q_o (mol/g)			B (L/mol)		
Dye	**30°C**	**40°C**	**50°C**	**30°C**	**40°C**	**50°C**
Methylene Blue	0.24	0.27	0.57	4.57×10^{-5}	3.55×10^{-5}	2.82×10^{-5}

* Adsorbent dose = 10 g/L; particle size = 150-200 mesh; pH 8.0 for methylene blue.

CONCLUSIONS

Red mud is available in abundance as it is a byproduct of the aluminium industry. The present paper demonstrates a very useful and effective removal process of methylene blue from polluted effluents either domestic or industrial. The study was able to conclude that the maximum adsorption of the Methylene Blue was obtained at 5.0 mg/L, 100 minutes, 1.0 g/L, 7.5, 150-200 mesh and 30°C initial concentartion, contact time, dose, pH, particle size and temperature respectively. The adsorption data was analysed by Langmuir and Freundlich models. The red mud adsorbent is able to adsorb the dye with high affinity and capacity making it a low cost viable adsorbent.

REFERENCES

1. Barragan, B.E., Costa, C. and Marquez, M.C., Biodegradation of azo dyes by bacteria inoculated on solid media, *Dyes and Pigments,* **75**, 73-81 (2007).
2. Yasin, Y., Hussein, M. Z. and Ahmad, F.H., Adsorption of methylene blue onto treated activated carbon, *The Malaysian J. Analytical Sci.,* **11**, 400-406 (2007).
3. Srinivasan, S.V., Rema, T., Chitra, K., Sri Balakameswari, K., Suthanthararajan, R., Uma Maheswari, B., Ravindranath, E. and Rajamani, S., Decolourisation of leather dye by ozonation, *Desalination,* **235**, 88-92 (2009).
4. Khadhraoui, M., Trabelsi, H., Ksibi, M., Bouguerraand, S., Elleuch, B., Discoloration and detoxicification of a Congo red dye solution by means of zone treatment for a possible water reuse, *J. Hazardous Materials*, **161**, 974-981 (2009).

5. Zhao, M., Tang, Z. and Liu, P., Removal of methylene blue from aqueous solution with silica nano-sheets derived from vermiculate, *J. Hazardous Materials*, **158**, 43-51 (2008).
6. Bestani, B., Benderdouche, N., Benstaali, B., Belhakem, M. and Addou, A., Methylene blue and iodine adsorption onto an activated desert plant, *Bioresource Technol.,* **99**, 8441-8444 (2008).
7. Wang, S., Zhu, Z. H., Coomes, A., Haghseresht, F., Lu, G.Q., The physical and surface chemical characteristics of activated carbons and the adsorption of methylene blue from wastewater, *J. Colloid and Interface Sci*., **284**, 440-446 (2005).
8. Santos, V.P., Pereira, M. F. R., Faria, P. C. C. and Orfao, J. J. M., Decolourisation of dye solutions by oxidation with H_2O_2 in the presence of modified activated carbons, *J. Hazardous Materials,* **162**, 736-742 (2009).
9. Gürses, A., Karaca, S., Dogar, C., Bayrak, R., Cikyildiz, M. and Yalcin, M., Determination of adsorptive properties of clay/water system: methylene blue sorption*. J. Colloid and Interface Sci.,* **269**, 310-314 (2004).
10. Yan, Z., Li, G. T., Mu, L. and Tao, S. Y., Pyridine-functionalized mesoporous silica as an efficient adsorbent for the removal of acid dyestuffs, *J. Material Chemistry*, **16**, 1717-1725 (2006).
11. Pereira, M.F.R., Soares, S. F., Orfao, J. J. M. and Fiqueiredo, J.L., Adsorption of dyes on activated carbons: influence of surface chemical groups, *Carbon*, **41**, 811-821 (2003).
12. Maffei, A.V., Budd, P. M. and McKeown, N.B., Adsorption studies of a microporous phthalocyanine network polymer, *Langmuir*, **22**, 4225-4229 (2006).
13. Filhoa, N.C., Venancioa, E. C., Barriquelloa, M. F., Hechenleitnerb, A. A. W. and Pinedab, E. A. G., Methylene blue adsorption onto modified lignin from sugar cane bagasse, *Ecletica*, **32**, 63-70 (2007).
14. Hameed, B.H., Ahmad, A. L. and Latiff, K. N. A., Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust, *Dyes and Pigments*, **75**, 143-149 (2007).
15. Karagoz, S., Tay, T., Ucar, S. and Erdem, M., Activated carbon from waste biomass by sulfuric acid activation and their use on methylene blue adsorption, *Bioresource Technol.,* **99**, 6214-6222 (2008).
16. Asok, A., Bandyopadhyay, M. and Pal, A., Removal of 2 crystal violet dye from wastewater by surfactant-modified alumina, *Separation and Purification Technol*., **44**, 139-144 (2005).
17. Jin, X., Jiang, M., Shan, X., Pei, Z. and Chen, Z., Adsorption of methylene blue and orange onto unmodified and surfactant-modified zeolite, *J. Colloid and Interface Sci.,* **328**, 243-247 (2008).
18. Chvedov, D., Ostap, S., Le, T., Colloids and Surfaces A : Physicochemical and Engineering Aspects, **182**, 131-141 (2001).
19. Chaddha, M. J., Rai, S. B., Goyal, R. N., *National Seminar on Environmental Concern and Remedies in Alumina Industry at NALCO*, Damanjodi, India, 27-28th Jan. (2007). Characteristics of red mud of Indian Alumina Plants and their possible utilization, *ENVICON*, 41-44 (2007).
20. Singh, A.P., Srivastava, K.K. and Shekhar, H., *Journal of Scientific & Industrial Research*, Vol. **66**, 952-956, Nov. (2007).
21. Shiao, S.J., Akash, K., Phosphate Removal from aqueous solution from activated red mud, JSTOR : *Journal (water pollution control federation)*, Vol. **49 (2)**, 28 (1977).
22. Melfferich Friedrich. "*Ion exchange*", MacGraw Hil, New York, 573 (1962).
23. Yang, Jun and Wang, Yunxiu, "Study on Activated Carbon in Chromium Containing Waste water Treatment by XPS", *J. Environ. Sci*., **6**, 173 (1994).
24. Weber, T. W., Chakravorti, R. K., Pore and solid diffusion models for fixed bed adsorbers, *J. Am. Inst. Chem. Eng.*, **20**, 228 (1974).
25. Liu, Y., Naidu, R. and Ming, H., "Red mud as an amendment for pollutants in solid and liquid phases", *J. ELSEVIER, Geoderma*, Vol. **136**, 1-2 (2011).

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