**International Academy of Science,
Engineering and Technology**
Connecting Researchers; Nurturing Innovations
IASET

REMOVAL OF BASIC BLUE 26 DYE FROM AQUEOUS SOLUTION BY ADSORPTION USING ORGANIC ADSORBENTS

SOWMYA LAKSHMI. K. B, MUNILAKSHMI. N & SAMPATH KUMAR REDDY. V

Department of Civil Engineering, SVUCE, S.V. University, Tirupati, Andhra Pradesh, India

ABSTRACT

The objective of this study was to assess the suitability and efficiency of Gigantia Leaves (GL), Curcuma Longa Leaves (CLL), Morienga Oleifera (MO) and Citrus Sinensis (CS) for the removal of C.I. Basic Blue 26 from aqueous solutions. The effect of different variables in the batch method as a function of solution pH, equilibrium time, optimum dose of adsorbent, adsorption isotherms, kinetic studies, desorption studies and interruption studies.. The corresponding results showed that excellent colour removal of Basic Blue 26 can be achieved with adsorbents at optimum pH of 7. The maximum colour of Gigantia Leaves, Curcuma Longa Leaves, Morienga Oleifera and Citrus Sinensis was 94.66%, 92.55%, 87.77% and 82.44% respectively. The isothermal equilibrium sorption data was well fitted into the Freundlich Isotherm. Kinetic studies which implies that chemisorption is the rate limiting step. Desorption studies, it states that physisorption plays a significant role in the colour removal of dyes. Pore diffusion seems to be the rate controlling in the sorption process as indicated by interruption studies.

KEYWORDS: Adsorption, C.I. Basic Blue 26, Curcuma Longa Leaves, Citrus Sinensis, Gigantia Leaves, Moringa Oleifera

INTRODUCTION

Annually, over seven million tons of dyes are produced in the world and widely utilized in different industries, including paper, plastics, leather, pharmaceutical, food, cosmetics, dyestuffs, and textiles industries[1]. Basic dyes have high brilliance and intensity of colour which create problem in colour removal. Basic dyes are the most resitant to degradation due to their fused aromatic structures and therefore remain coloured for a longer period of time in waste water. Considerable amount of dye-contaminated wastewater discharge in these industries resulted in a potential risk to human health and ecosystem, since coloured dye effluents would interfere with light penetration in the receiving water bodies and the degraded by-products had toxic effects on mammals and aquatic organisms[2]. Therefore, efficient and effective treatment approaches are necessary to overcome these problems.

At present, many treatment technologies, such as adsorption, flocculation, super filter film, oxidation and electrolysis, have been employed for dye removal from wastewaters. Among these methods, adsorption process provides an attractive alternative for the treatment of dye wastewater, especially the inexpensive adsorbent[3]. Activated carbon, the prevalent adsorbent, is effective for dye removal. However, because of its high price and hard regeneration the wide applications of activated carbon were limited[4]. Thus, more economic, efficient and practical adsorbents are necessary for the dye removal.

Recently, numerous approaches have been studied for the development of cheaper and effective adsorbents. Many

non-conventional low-cost adsorbents, including natural materials, bio sorbents and waste materials from industry and agriculture, where these materials could be used as adsorbents for the colour removal of dyes from aqueous solution. Some of the adsorbents include clay materials (bentonite, kaolinite), zeolites, siliceous material (silica beads, alunite, perlite), agricultural wastes (bagasse pith, maize cob, rice husk, coconut shell), industrial waste products (waste carbon slurries, metal hydroxide sludge), biosorbents (chitosan, peat, biomass) and others (starch, cyclodextrin, cotton).

The present investigation was conducted to remove C.I. Basic Blue 26 dye colour employing Gigantia Leaves, Curcuma Longa Leaves, Morienga Oleifera and Citrus Sinensis. Scope of the study includes kinetics and isothermal equilibrium studies, effect of adsorption process parameters such as pH, contact time and adsorbent dose on colour removal. Desorption studies and Interruption studies were also carried in order to know the sorption mechanism involved in the adsorption process.

MATERIALS AND METHODS

Adsorbent

Adsorbents like Gigantia Leaves, Curcuma Longa Leaves, Morienga Oleifera and Citrus Sinensis collected from the local areas are used in the present study. The four organic adsorbents were washed with distilled water to remove dirt and other particulate matter. The washed peels and leaves are dried at low temperature (<105°C) to remove moisture content. After drying process, peels and leaves were grounded to fine powder and sieved through 75µ size. Adsorbents size of 75µ is used in the study.

Adsorb Ate

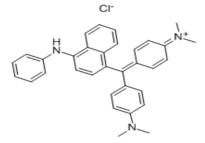C.I. Basic Blue 26 was used as adsorb ate. Chemical structure of the dye:

Figure 1: Chemical Structure of C.I. Basic Blue 26

Analysis and Characterization

The maximum wavelength of C.I. Basic Blue 26 (620 nm) was observed using Thermo make UV VIS Spectrophotometer of Evolution 201 Model. All the analyses were done in accordance with standard methods[5].

Batch Adsorption Experiment

Experiments were conducted for dye solution of pH from 2 to 12. The adsorbent dose and pH at which maximum colour removal of dye were determined, which was adopted as favourable dose and favourable pH. Agitated, non-flow batch sorption studies were conducted by bottle point method using reagent bottles of 250 mL capacity. To a 100 mL of test dye solution (optimum pH) of 50 mg/L concentration taken in the reagent bottle, premeasured quantity of adsorbent was added and the resultant mixture was agitated in a horizontal shaker at a rate of 125 rpm for varying time intervals of 1, 3, 5, 7, 9, 12, 15, 30, 45 and 60 minutes. The bottles were withdrawn from the shaker at designated time intervals and the

reagent bottles were kept undisturbed for 4 hours for sedimentation, at the end of which, samples were withdrawn by carefully pipetting out 10 ml portion and are analyzed for colour content remaining in the test dye solution. The time at which maximum removal of colour takes place and no further significant difference in colour removal occurs from that time, was taken as the equilibrium contact time and used in all further studies. Equilibrium Isothermal studies were conducted by adding varying doses of adsorbents such as 50, 100, 150, 200, 250, and 300 mg/L to the test dye solution and contacted for equilibrium time. The residual colour was analyzed with a Spectrophotometer by measuring OD/%T at respective maximum wavelength (620 nm) of dye solution and computing concentrations from the calibration curve.

RESULTS AND DISCUSSIONS

Effect of Ph

The effect of initial pH on adsorption of dye was studied from pH 2 to 12, at dye concentration of 50 mg/L, contact time 30 min and 300 mg/L dosage. The percentage of colour removal of dye at different pH is as shown in Figure 2.
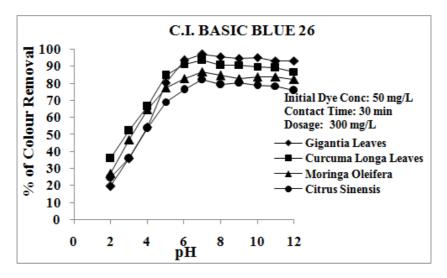

Figure 2: Response of C.I. Basic Blue 26 onto Adsorbents at Different Ph

From Figure 2, it was observed that maximum colour removal of C.I. Basic Blue 26 with all adsorbents was obtained at pH of 7. Hence favourable pH of 7 was considered to the dye C.I. Basic Blue 26.

Effect of Adsorbent Dosage

Equilibrium isothermal adsorption studies were conducted by varying the amount of adsorbent dose from 50 to 300 mg/L and the results are presented graphically as % colour removal at different doses for C.I. Basic Blue 26, at pH=7 as shown in Figure 3
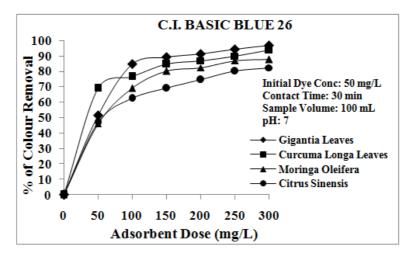
Figure 3: Response of C.I. Basic Blue 26 to Adsorbents at Different Dosages (Ph=7)

From Figure 3, C.I. Basic Blue 26 responded favourably to all adsorbents, exhibited Excellent colour removal of 94.66% with Gigantia Leaves and 92.55% with Curcuma Longa Leaves, 87.77% with Moringa Oleifera and removal of 82.44% with Citrus Sinensis at pH of 7.

Effect of Contact Time

The influences of contact time vis-à-vis kinetics of colour removal by adsorbents are presented in Figure 4. It may be observed from figures that the rate of colour removal was rapid initially. The rate leveled off gradually and then attained a more or less constant value (equilibrium) beyond which there was no significant increase in colour removal. The time required to attain equilibrium was 30 minutes.
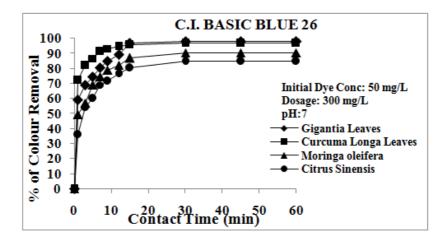

Figure 4: Kinetics of Sorption of C.I. Basic Blue 26 onto Adsorbents at Different Contact Times (Ph=7)

It follows from the experimental results that percentage removal of colour increased with an increase in mixing time; however, the difference is not much beyond a mixing time of 30 min. Therefore, an equilibrium mixing time of 30 min was adopted in all subsequent experiments.

Equilibrium Study

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the homogeneity/ heterogeneity of

adsorbents, the type of coverage and possibility of interaction between the adsorbate species. Adsorption data are usually described by adsorption isotherms, such as Langmuir, Freundlich isotherms. These isotherms relate dye uptake per unit mass of adsorbent, q_e, to the equilibrium adsorbate concentration in the bulk fluid phase C_e.

The Langmuir Isotherm

The **Langmuir model (1918)** is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane.

The linear form of Langmuir isotherm is given as;

$$1/q_e = 1/q_m + 1/(q_m K_L) 1/C_e$$

Where K_L is the energy constant of the sorption, q_m is the maximum value of sorption capacity (mg/g)**,** C_e is the equilibrium conc. of sorbate in solution after adsorption (mg/L), q_e is the mass of sorbate adsorbed per unit mass of sorbent (mg/g).The plot between $1/q_e$ and $1/C_e$ is as shown in the Figure 5.
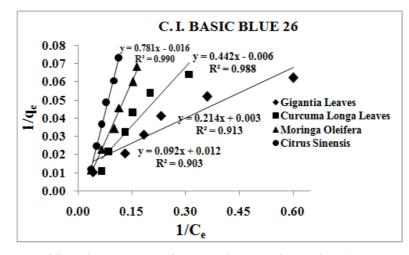

Figure 5: Linearised Plot of Sorption Isotherm of Langmuir Model for Various Adsorbents (C.I. Basic Blue 26)

The Freundlich Isotherm

Freundlich isotherm mode (1906) is applicable for non-ideal sorption on heterogeneous surfaces and multilayer sorption.

The nonlinear and linearised forms of the equation are as follows:

$$\log q_e = \log(K_F + 1/n \log C_e)$$

where C_e is the equilibrium conc. of sorbate in solution after adsorption (mg/L), q_e is the mass of sorbate adsorbed per unit mass of sorbent (mg/g).The constants in the Freundlich isotherms can be determined by plotting $\log q_e$ versus $\log C_e$ which gives a straight line with slope of 1/n and a intercept equal to the value of log K_F, where K_F (L/g) is the Freundlich constant related to the adsorption capacity and *n* is the constant for intensity. Plot between log C_e and log q_e was drawn to generate the intercept value of K_F and the slope of n as shown in the Fig.6. The values of n<1 indicate a favourable adsorption comparable with other researches. It is observed that all the adsorbents satisfy the condition of heterogeneity.
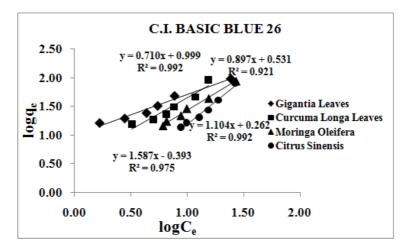
Figure 6: Linearised Plot of Sorption Isotherm of Freundlich Model for Various Adsorbents (C.I. Basic Blue 26)

The isothermal equilibrium sorption data were fitted into linearised Freundlich equation and the values of sorption capacities and coefficient of correlation are presented in Table.1.

Table 1: Isotherm Model Constants and Correlation Coefficients for Adsorption of Dye from Aqueous Solution

Adsorbents	Langmuir Coefficients			Freundlich Coefficients		
	R^2	Q_m (Mg/G)	K_L (L/Mg)	R^2	N	K_F (Mg/G)
Gigantia Leaves	0.90	833.33	0.13	0.975	1.408	2.71
Curcuma Longa Leaves	0.91	333.33	0.01	0.92	1.01	1.70
Morienga Olefiera	0.98	166.66	0.013	0.99	0.90	1.29
Citrus Sinensis	0.99	62.5	0.02	0.99	0.89	1.48

From Table 1, the value of coefficient of correlation (R^2) obtained was nearly equal to one for all adsorbents giving a best fit for Freundlich equation compared to Langmuir Isotherm. It follows from the data that equilibrium adsorption of colour on to all adsorbents follows Freundlich isotherm model, which implies multilayer sorption, with lateral interactions between the adsorbed molecules or ions in the case of Freundlich models; the energetic distribution of sites is heterogeneous due to the diversity of sorption sites.

Kinetic Study

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second-order equations are applied to model the kinetics of dye adsorption on to the ado sorbents.

The **Pseudo-First-Order (1898)** rate equation is given as:

$$\log(q_e - q_t) = \log q_e - (K_1/2.303)$$

Where q_e is the amount of adsorbed adsorb ate on the adsorbent at equilibrium (mg adsorb ate/g adsorbent), q_t is the amount of adsorbed adsorb ate on the adsorbent at time t, K_1 is the adsorption rate constant for pseudo first-order. To determine the correlation coefficients, graph was drawn between $\log(q_e - q_t)$ and time as shown in the Figure 7.
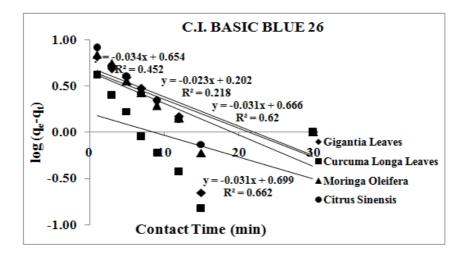
Figure 7: Pseudo-First–Order Plot for C.I. Basic Blue 26 Adsorbed Onto Different Adsorbents

Calculated values of K_1 and q_e along with correlation coefficient (R^2) are summarized in Table 2. The pseudo first-order kinetic model of Lagergren was not fitted well with the experimental data of q_e.

Table 2: Comparison between the Adsorption Rate Constants, q_e, and Correlation Co-Efficient Associated with Pseudo-First Order and Pseudo-Second Order Equations

Adsorbents	Pseudo-First-Order Equation				Pseudo–Second-Order Equation				
	R^2	Q$_e$ Cal (Mg/G)	Q$_e$ Exp (Mg/G)	K_1 (L/Mg)	R^2	Q$_e$ Cal (Mg/G)	Q$_e$ Exp (Mg/G)	H	K_2 (Mg/G)
Gigantia Leaves	0.45	4.50	16.33	0.07	0.99	17.24	16.33	30.53	0.03
Curcuma Longa Leaves	0.21	1.59	16.11	0.05	0.99	16.66	16.11	9.31	0.03
Morienga Olefiera	0.62	4.63	15.07	0.07	0.99	15.87	15.07	8.91	0.03
Citrus Sinensis	0.66	5	14.11	0.07	0.99	14.11	9.67	7.80	0.11

The **Pseudo-Second Order ((Ho, 1995)** kinetics is expressed as:

$t/q_t = 1/h + t/q_e$

The initial adsorption rate, h, (mg/g min) is expressed as h $=k_2q^2_e$, Where k_2 is the rate constant of Pseudo-second-order adsorption (min^{-1}) and q_e is the equilibrium adsorption capacity (mg/g). The graph between t/q$_t$ versus t was drawn as shown in the Figure 8, to determine the values of qe, k and h from the slope and intercept of the plot.
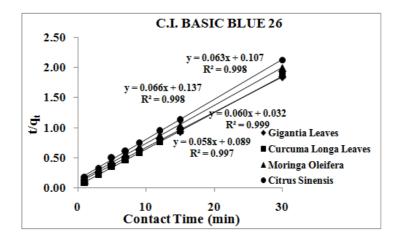

Figure 8: Pseudo-Second-Order Plot for C.I. Basic Blue 26 Adsorbed Onto Different Adsorbents

From Table 2, it was observed that R^2 is equal to 1.0 with respect to pseudo-second-order, moreover the experimental values of q_e is nearer to the values obtained in pseudo-second -order, indicating that pseudo-second-order model is well fitted to the data than pseudo – first-order model, which implies that chemisorptions is the rate limiting step.

Desorption Studies

Desorption studies are useful in the elucidation of the mechanism of adsorption reaction and also to assess the regeneration capacity of the sorbent for reuse in a more economic manner. The amount of desorption provides an insight into the nature of sorbent-sorbate bonding.

Desorption is generally studied by employing a solvent (dispersion media) like Distilled water, 0.1N NaOH and 0.1N HCL. If the dye bound to the sorbent is desorbed by distilled water, then it may be deduced that the dye molecule is attached to sorbent surface by weak bonds and that sorption can be said to be of physical in nature. If the inorganic solvents are required to desorb, then the adsorption is attribute to be the type of ion-exchange.

In the present study, desorption studies were conducted for C.I. Basic Blue 26 and sorbents by dispersing the (adsorbed) loaded sorbent in distilled water and inorganic solvents like 0.1N NaOH, 0.1N HCL and agitated for a period of 30min.

Tables 3. represents the percentage of desorption of dye C.I. Basic Blue 26 from GL, CLL, MO, and CS with distilled Water, 0.1N NaOH and 0.1N HCL.

Table 3: Desorption Data of Four Adorbents by Various Inorganic Solvents

Adsorbents	Percentage of Desorption		
	Distilled Water	0.1N Hcl	0.1N Naoh
Gigantia Leaves	60	5	20
Curcuma Longa Leaves	50	4	27
Morienga Olefiera	40	6	15
Citrus Sinensis	70	8	27

From the above Table 3, the percentage of C.I. Basic Blue 26 dye adsorbed on to adsorbents was easily desorbed in distilled water. Desorption was significant (40-70%) with the distilled water indicating that the dye molecules in its original form are desorbing into solution. This type of dye-adsobent interaction may be attributed to a physisorption type reaction in which dye molecules are bound to the surface by some type of weak bonding perhaps due to hydrogen bonding.

Interruption Studies

In order to probe into the nature of the sorptive uptake of dye colour by the adsorbents, interruption studies were conducted by interrupting the ongoing process of adsorption for 30min in a batch system. For film diffusion controlled process, the interruption does not affect the rate of uptake, since there is no increase in concentration gradient on the sorbent after the interruption (Helffirich 1962).

However, in the case of pore diffusion to be rate controlling step, the concentration gradient increases immediately after interruption compared to that of before interruption and this may result in a higher uptake. Result of interruption tests are presented in Figure 9, for various dyes using different adsorbents.
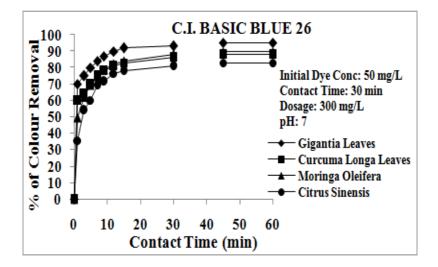
Figure 9: Interruption Kinetic Plot of C.I. Basic Blue 26

It is evident from the Figure 9, that there is slight increase in the slope of the concentration gradient curve after interruption and hence it indicates the possibility of pore diffusion to be the rate controlling in the sorption process.

CONCLUSIONS

Adsorption studies have been conducted for the different organic adsorbents to assess their capability to remove C.I. Basic Blue 26 in the aqueous phase. Excellent colour removal can be achieved with adsorbent of Gigantia Leaves, Curcuma Longa Leaves, Moringa Oleifera and Citrus Sinensis at pH of 7. The data fitted well to Freundlich model, which implies that the possibility of multilayer adsorption with a heterogeneous energy distribution of the active sites, accompanied by interaction between the adsorbed molecules. Kinetic studies data of all the sorbents are fitted well to pseudo-second-order, which implies that chemisorption is the rate limiting step. Attempts to desorb the sorbed dye molecules with distilled water preclude the possibility of physisorption playing significant role in the colour removal of dye. Further Interruption Studies implies that pore diffusion to be the rate controlling one in the adsorption process.

ACKNOWLEDGEMENTS

REFERENCES

1. Afkhami, A., Moosavi, R., 2010. Adsorptive removal of Congo red, a carcinogenic textile dye, from aqueous solutions by maghemite nanoparticles. J. Hazard. Mater. 174, 398–403. Van der Zee, F.P., Lettinga, G., Field, J.A., 2001. Azo dye decolourisation by anaerobic granular sludge. Chemosphere 44, 1169–1176.

2. Guo, J.Z., Chen, S.W, Liu, L, Li, B, Yang, P, Zhang, L.J, Feng, Y.L., 2012. Adsorption of dye from wastewater using chitosan-CTAB modified bentonites. J. Colloid nterface Sci. 382, 61–66.

3. Sureshkumar, M.V, Namasivayam, C, 2008. Adsorption behavior of Direct Red 12B and Rhodamine B from water onto surfactant-modified coconut coir pith. Colloids Surf. A 317, 277–283.

4. Xia, C.L., Jing, Y., Jia, Y.Z., Yue, D.Y., Ma, J., Yin, X.J., 2012. Adsorption properties of congo red from aqueous solution on modified hectorite: kinetic and thermodynamic studies. Desalination 265, 81–87.

5. Clescerl L.S, A.E. Greenberg, A.D. Eaton (1998), APHA, Standard Methods for the Examination of Water and Wastewater. 20th ed, American Public Health Association/American water works Association/Water Environment Federation,Washington, DC.