Available online at **www.joac.info**

ISSN: 2278-1862

Journal of Applicable Chemistry

2018, 7 (5): 1252-1259

(International Peer Reviewed Journal)

Adsorption Study for Removal of Crystal Violet Dye using MMT-MWCNTs Composite from Aqueous Solution

Tarachand Nargawe[1]*, Avinash Kumar Rai[1], Rakshit Ameta[2] and Suresh C. Ameta[1]

1. Department of Chemistry, PAHER University, Udaipur (Raj.), **INDIA**
2. J.R.N. Rajasthan Vidyapeeth (Deemed to be) University, Udaipur (Raj.), **INDIA**

Email: tcnargawe@gmail.com

Accepted on 2nd August, 2018

ABSTRACT

Montmorillonite-MWCNTs composite was synthesized, characterized and used for removal of crystal violet from aqueous solution. Various parameters like pH, dye concentration and amount of composite were studied to obtain its effect on adsorption. The adsorption equilibrium was achieved in180 min and adsorption efficiency was found to be76.02% at optimum conditions. Kinetic studies made using pseudo-first order, pseudo second order and the intraparticle diffusion model, but were it was found that the adsorption data fitted well with pseudo-second order model (R^2=0.967).Langmuir and Freundlich isotherms were applied and thermodynamic parameters were evaluated, which indicated study that this adsorption process was not solely by physisorption but also some chemisorption.

Keywords: Adsorption, Crystal Violet, Montmorillonite, MWCNTs, Adsorption Kinetics, Thermodynamics.

INTRODUCTION

Adsorption processes is considered for removal of organic pollutants from industrial wastewater due to its versatility [1]. Dyes are frequently used in various industries. During its production and application in dyeing, a huge amount of effluent water containing high concentration of organic dyes is generated. Due to high solubility of dyes in water, it is quite difficult to remove these from waste water [2-8]. Many dyes may cause allergy, skin irritation, and various health issues like nausea, vomiting, profuse sweating or some time mutation in human even some of them are carcinogenic [9]. Different techniques like electrochemical reduction method [10], photodegradation [11], adsorption [12], etc. are widely used for removal of organic pollutants. These unwanted hazardous dyes from contaminated effluent water may be removal using various naturally occurring adsorbents like chitosan, zeolites, fly ash, coal, paper mill sludge, etc. [13]. Among these adsorbents, clay and MWCNTs are most promising alternatives due to their availability, feasibility, various applications, highly specific surface area, and cost effectiveness [14-16].Various composite like cellulose-MMT [17], pillared clay [18], doubled layered hydroxide-MMT [19] modified bentonite composite [20], activated palygorskite clay [21], Ni-CNTs [22], and oxidized MWCNTs [23] are used for the removal of various organic pollutants and dye. In the present work multi walled carbon nanotubes and montmorillonite were used for synthesis of composite and for used removal of crystal violet.

MATERIALS AND METHODS

Materials: Montmorillonite nanoclay was procured from Ultrananotech Ltd. It is in powder form and its particle size is about < 80 nm, with more than 99% purity. Multiwalled carbon nanotubes were from Ad Nano Technologies Pvt. Ltd. with purity higher than 99% and average diameter 10-15 nm. Crystal violet was purchased from Himedia lab.

Synthesis of Composite: 110 g of montmorillonitenanoclay was taken, washed with distilled water and filtered. Filtered clay was dried at 80°C in oven for 24 hr. 5.5 g of MWCNTs was taken and mixed with the help of magnetic stirrer to obtain 5% MWCNTs per 100 g montmorillonite. Distilled water was added to mixture and it was stirred at room temperature until the mixture becomes viscous, mixture was filtered and dried in an oven at 120°C for 12 h. Mixture was allowed to cool at room temperature and calcination was done at 650°C for an hour to obtain (MWCNTs-MMT) composite.

Experimental: The stock dye solution was prepared by dissolving 0.0408 g of crystal violet dye dissolved in100 mL double distilled water. Working solutions were prepared from stock solution for further experiments. The 0.10 g of MWCNTs-MMT composite was added in 50.0 mL solution of dye and magnetically stirred. The absorbance of solution was determined with the help of a spectrophotometer at λmax 588 nm on a fixed time interval. The absorbance of the solution was found to decrease as compared to its initial value with increase in time.

A plot of 1 + log A against time was found to be linear and rate constant for this reaction was measured with the help of expression

$$k = 2.303 \times \text{slope} \quad \ldots (1)$$

The efficiency of % removal of crystal violet was calculated by the expression

$$\text{Removal efficiency (\%)} = C_o - C_t / C_o \times 100 \quad \ldots (2)$$

The amount of adsorption at equilibrium, q_e was evaluated as.

$$q_e = (C_o - C_t)\, V / M \quad \ldots (3)$$

where, q_e is amount of dye adsorbed at equilibrium, C_o and C_t are initial and concentrations at fix time interval of dye, V represents amount of solution taken for experiment and M represents amount of composite.

RESULTS AND DISCUSSION

Effect of pH: The adsorption of crystal violet was studied in the pH range from 5.0-9.0. The rate of reaction was found to increase up to almost neutral pH and then it shows a decreasing behaviour. pH 7.5 was taken as optimum value for adsorption(Fig. 1)

Effect of Concentration: The effect of concentration of dye on its removal by composite (MWCNTs-MMT) was also studied. The rate of reaction was found to increase up to 2.0 x 10^{-5} M, but after that, it was found to decrease with an increase in dye concentration (Fig. 2).

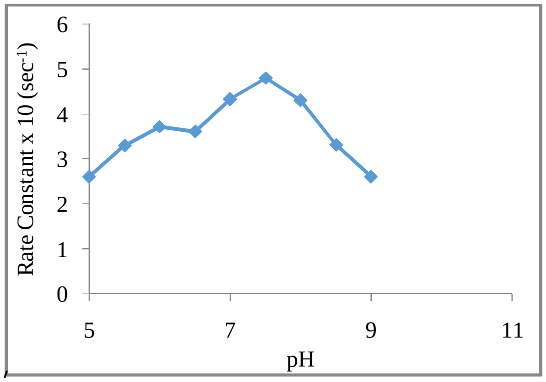

Figure 1. Effect of pH.

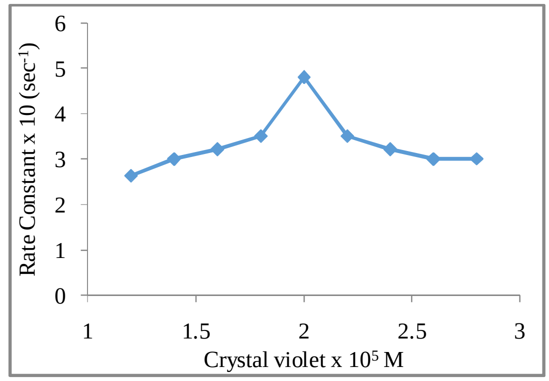

Figure 2. Effect of Concentration.

Effect of Composite doses: The effect of dose of composite on the dye removal was also studied. It was observed that rate of dye removal increases significantly as adsorbent dose was increased upto a certain amount after that the rate of reaction decreases. The results of dose of adsorbent on the removal of crystal violet are given in fig. 3. Highest rate of reaction was observed at 0.12 g, and hence, taken as optimum value for further studies.

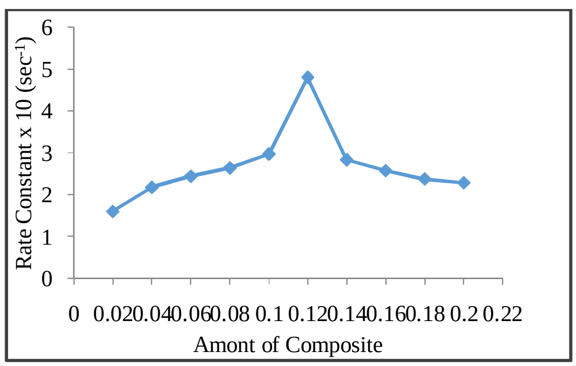

Figure 3. Effect of Composite doses.

Effect of Contact Time and Maximum Adsorption: Effect of contact time on the removal of crystal violet from the aqueous solution was studied. It was observed that 58% removal efficiency was achieved in just 60 min, but after that the rate of adsorption is slow with further increase in time. The equilibrium condition was found at about 180 min, where the maximum adsorption capacity was found to be 21.58 mg g^{-1}.

Isotherm Studies: The parameters obtained from the different models provide some important information on the adsorption mechanism as well as affinity of the adsorbent. Linear regression is frequently used to determine the best fitting isotherm by judging its correlation coefficient.

The equation for Langmuir isotherm is

$$1/q_e = 1/q_m \text{ x } K_L \text{ x } C_e + 1/q_m \qquad \ldots(4)$$

where q_e is amount of dye adsorbed per unit weight of adsorbate, C_e is remaining dye concentration at equilibrium, q_m is maximum adsorption capacity and K_L is theLangmuir constant. A linear plot (Fig.4) of $1/q_e$ v/s $1/C_e$ suggests the applicability of Langmuir isotherm.The R^2 value of linear correlation plot of $1/q_e$ v/s $1/C_e$ is 1.0, which suggests that the Langmuir isotherm provides a good model for this adsorption system.

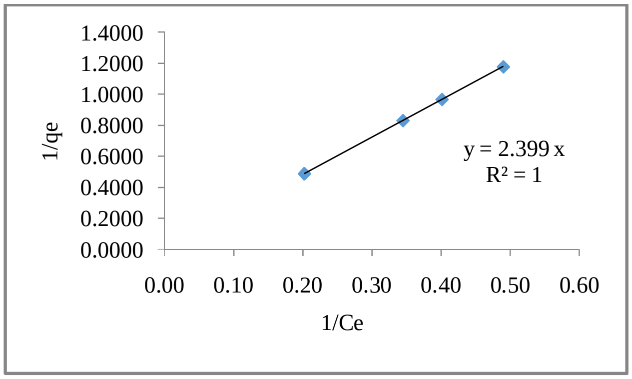

Figure 4. plot of Langmuir isotherm.

Kinetic Studies: The kinetics can be described by pseudo-first order and pseudo-second order model. The linear form of pseudo-second order is expressed as–

$$t/q_t = 1/k_2 / q_e^2 + 1/q_e \text{ x } t \qquad \ldots(5)$$

Where, k_2 is pseudo-second order constant. A plot of t/q_t against t gives a linear relationship (Fig.5)q_e and k_2 can be determined from the slope and intercept of this plot.

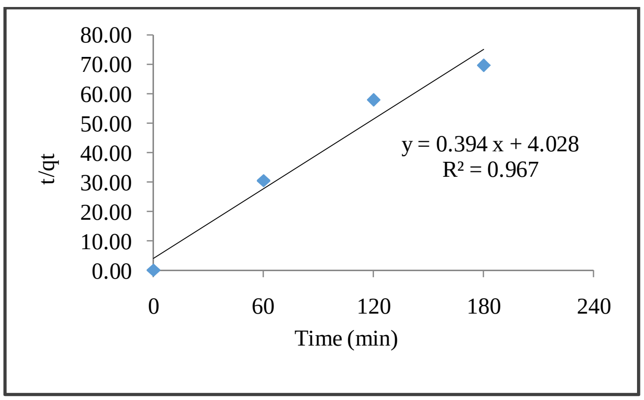

Figure 5. plot of Kinetic Studies.

The value of R^2 in plots is 0.967 for pseudo-second order, which indicates that pseudo-second order model was suitable this adsorption process as compared to pseudo-first order model.

Intra-particle diffusion model is given by equation-

$$q_t = K_d \text{ x } t^{1/2} + C \qquad \ldots (6)$$

where C is mg g^{-1} (intercept) and K_d is intra-particle diffusion rate constant.

A linear plot was observed between q_t v/s $\sqrt{}_t$ (Fig. 6). Intercept C provides information about the thickness of the boundary layer. Rate constant K_d was evaluated from slope of the regression line. The linearly of the plot demonstrated that intra-particle diffusion played a significant role in the uptake of the adsorbate by adsorbent.

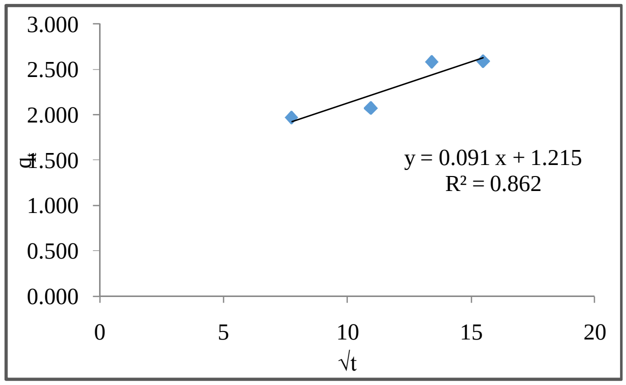

Figure 6. plot of intra-particle diffusion.

Thermodynamic Parameters: Effect of different temperatures on adsorption of crystal violet over composite (MWCNT-MMT) was studied using different temperatures. Feasibility, spontaneity, and exothermic/endothermic nature of process can be determined by thermodynamics parameters. Activation energy was determined for the adsorption of crystal violet by carrying out experiment at three different temperatures (318, 328 and 338 K).

The linear from of the Arrhenius equation is –

$$- Ea = slope \times 2.303 \times R \qquad \dots (7)$$

where, k = Rate constant at given temperature, Ea = Activation energy, R = Gas constant, (8.314 J mol^{-1}), T = Temperature (Kelvin) and A = Frequency factor or Arrhenius constant. A plot of log k v/s 1/T was found to be linear (Fig.7). The energy of activation was found to be 5.073 J mol^{-1}. It was observed that reaction rate decreases on increasing the temperature, which means that adsorption of crystal violet is an exothermic process. As the activation energy is relatively low and therefore, the reaction rate can be controlled by intra-particle diffusion mechanism.

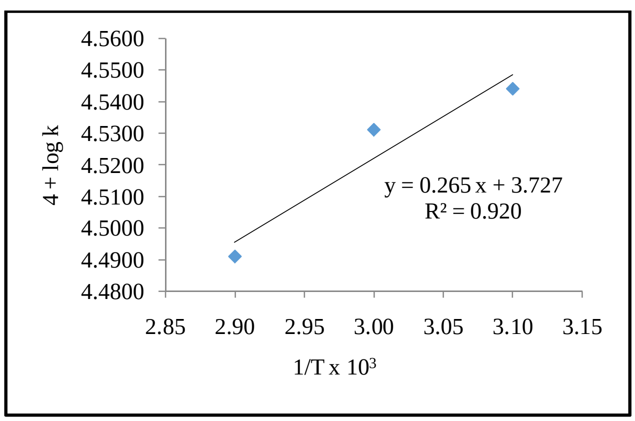

Figure 7. Plot of log k v/s 1/T.

The value of Gibbs free energy is determined by studying the adsorption at 318 K. The change in Gibbs free energy was calculated from the equation

$$\Delta G° = - RT \log K \qquad \dots (8)$$

Where, ΔG° = Gibbs free energy (kJ mol^{-1}), R = Gas constant, T = Temperature and, K_c = Langmuir constant obtained from fig. 8. The value of K_c may be calculated from intercept of plot, log q_e/C_e v/s q_e by extrapolating the line, where q_e tends to zero. It was found to be 0.619. Hence, the value of ΔG° is -2.09 $kJmol^{-1}$. Negative value of ΔG° indicates that this adsorption process is feasible and spontaneous in nature.

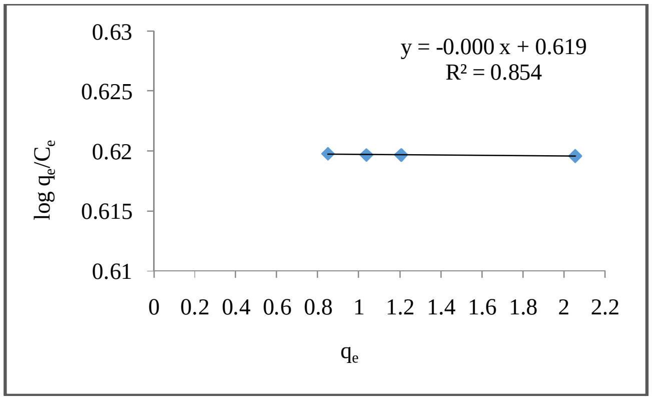

Figure 8. Plot of log qe/Ce v/s qe.

The enthalpy was evaluated from Langmuir isotherm plot $1/q_e$ v/s $1/C_e$ (Fig. 9, 10) at two different temperatures (328 and 338 K) using the following equation.

$$\Delta H° = R\ (T_2\ x\ T_1\ /\ T_2 - T_1)\ \log\ (K_2\ /\ K_1) \qquad ....(9)$$

Where, K_1= Equilibrium constant at temperature 328 K (T_1) K_2 = Equilibrium constant at temperature 338 K (T_2)and R = Gas constant. The value of enthalpy was determined by equation and it was found to be 106.91 kJ mol^{-1}. This much change in enthalpy during adsorption of crystal violet (106.91 kJ mol^{-1}; ΔH > 40 kJ mol^{-1}), indicates that the binding occur through physisorption. It was concluded that the reaction is not driven solely through physisorption but some chemisorptions also.

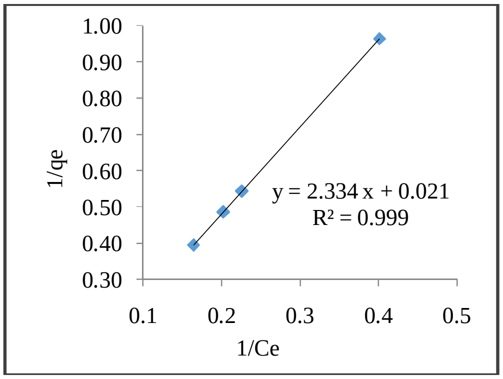

Figure 9. Plot at 328 K

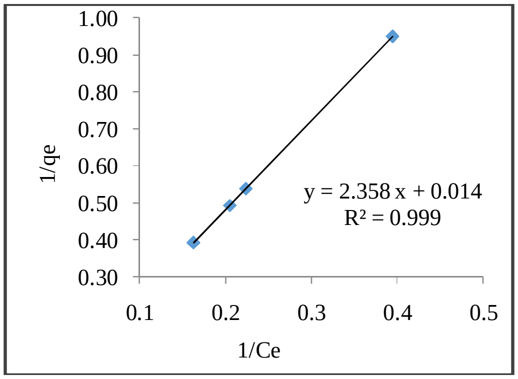

Figure 10. Plot at 338 K

The value of entropy change was also calculated by using the values of ΔG° and ΔH° by equation:

$$\Delta S° = \Delta H° - \Delta G°/T \qquad ...(10)$$

It was determined as 0.342 kJ mol^{-1} K^{-1}, which is very small. A very low value of entropy suggests that there is less randomness of crystal violet molecules on the surface of MWCNT-MMT composite as compared to bulk of the solution.

APPLICATION

CNTs demonstrate the considerable potential for the elimination of dyes and could be utilized for commercial purpose

CONCLUSIONS

Crystal violet can be effectively used for removal by using MWCNT-MMT composite by adsorption process, which is spontaneous and exothermic in nature. Langmuir isotherm and pseudo-second order model described the experimental data very well.

REFERENCES

[1]. Z. Al-Qodah, Adsorption of dyes using shale oil ash, *Water Res.* **2000**, 34 ,17, 4295.

[2]. H. Zollinger, Colour Chemistry-Synthesis, Properties and Application of Organic Dyes and Pigments, VCH, New York, **1987**.

[3]. E.A. Clarke, R. Anliker, Organic dye and pigments Handbook of Environmental Chemistry, Anthropogenic Compounds, Part A, vol. 3, Springer, New York, **1980**.

[4]. A. F. Halbus, Photocatalytic degradation of cobalamin, M.Sc. Thesis, College of Sciences, University of Babylon, Iraq, **2012**.

[5]. Y.M. Slokar, A.M. Le Marechal, Methods of decolouration of textile wastewaters *Dyes Pigment.***1997**, 37, 335-356.

[6]. V. Vadivelan, K. V. Kumar, Equilibrium, kinetics, mechanism and process design for the sorption of methylene blue onto rice husk, *J. Colloid Interface Sci.*, **2005**, 286, 90-100.

[7]. B. H. Hameed, M. I. El-Khaiary, Removal of basic dye from aqueous medium using a novel agricultural waste material: pumpkin seed hull, *J. Hazard. Mater*., **2008**, 155, 601-609.

[8]. M. L. Richarson, Adsorption of disperses blue dye on iraqi date palm seeds activated carbon, *J. Soc. Dyers Colour*, **1983**, 99, 198-200.

[9]. D. Ghosh, K.G. Bhattacharyya, Adsorption of methylene blue on kaolinite, *Appl. Clay Sci.* **2002**, 20, 295-300.

[10]. H. P. Sachin, B. M. Praveen, Treatment of industrial azo dye effluents by electrochemical technique and its COD measurement, *J. Applicable Chem*., **2017**, 6, 1149-1157.

[11]. A. Paliwal, R. Banu, R. Ameta, S. C. Ameta, Photocatalytic degradation of methylene blue using undoped and Co-doped bismuth ferrite, J. *Applicable Chem*., **2017**, 6, 967-975.

[12]. R. Dandge, M. Ubale, S. Rathod, Adsorption of crystal violet dye from aqueous solution onto the surface of Green Peas Shell (GPS), *J. Applicable Chem.*, **2016**, 5, 792-801.

[13]. A. Gücek, S. Şener, S. Bilgen, Adsorption and kinetic studies of cationic and anionic dyes on pyrophyllite from aqueous solutions, *J. Colloid Interface Sci.*, **2005**, 286, 53-60.

[14]. M. Stydini, I. K. Dimitris, X. E .Verykios, *Appl. Catal B Environ.*, **2004**, 47, 189-193.

[15]. M. Doğan, Y. Özdemir, Adsorption kinetics and mechanism of cationic methyl violet and methylene blue dyes onto sepiolite, M. Alkan, *Dyes Pigment.*, **2007**, 75, 701-713.

[16]. B. Bestani, N. Benderdouche, B. Benstaali, M. Belhakem, Methylene blue and iodine adsorption onto an activated desert plant, A. Addou, *Bioresour. Technol.*, **2008**, 99, 8441-8444.

[17]. A. S. K. Kumar, S. Kalidhasan, V. Rajesh, N. Rajesh, Application of cellulose-clay composite biosorbent toward the effective adsorption and removal of chromium from industrial wastewater, *Ind. Eng. Chem. Res.*, **2012**, 51(1), 58-69.

[18]. K. O. Martinez, P. Reddy, W. A. Cabrera-Lafaurie, F. R. Roman, A. J. Hernandez-Maldonado, Single and multi-component adsorptive removal of bisphenol A and 2,4-dichlorophenol from aqueous solutions with transition metal modified inorganic–organic pillared clay composites: Effect of pH and presence of humic acid, *J. Hazard.Mater.*, **2016**, 312, 262-271.

[19]. K. Zhou, Q. Zhang, B. Wang, J. Liu, P. Wen, Z. Gui, Y. Hu, The integrated utilization of typical clays in removal of organic dyes and polymer nanocomposites, *J. Clean. Prod.*, **2014**, 81, 281-289.

[20]. T. S. Anirudhan, P. S. Suchithra, Heavy metals uptake from aqueous solutions and industrial wastewaters by humic acid-immobilized polymer/bentonite composite: Kinetics and equilibrium modelling, *Chem. Eng. J.*, **2010**, 156(1), 146-156.

[21]. H. Chen, J. Zhao, A. Zhong, and Y. Jin, Removal capacity and adsorption mechanism of heat-treated palygorskite clay for methylene blue,*Chem. Eng. J.*, **2011**, 174(1), 143-150.

[22]. Y. B. Onundi, A. A. Mamun M. F. Al Khati, M. A. Al Saadi, A. M. Suleyman, Heavy metals removal from synthetic wastewater by a novel nano-size composite adsorbent, *Int. J. Environ.* Sci. *Technol.*, **2011**, 8(4) 799-806.

[23]. M. Ghaedi, S. N. Kokhdan, Oxidized multiwalled carbon nanotubes for the removal of methyl red (MR): Kinetics and equilibrium study, *J. Desalin. Water Treat.* , **2012**, 49(1), 317-325.