Kinetic and equilibrium studies of Methylene blue adsorption on *Alstonia Scholaris* Plant leaf powder

GAURI D. DARUNTE [1]. AISHWARYA P. MORE [1]. SAKSHI V. SHINGARE [1]. HARSHADA D. MAHALE[1]. JAYANT. P. SONAR [1]. S. N. THORE[1]. SANDEEP. D. PARDESHI [1*]

[1] Department of Chemistry, Vinayakrao Patil Mahavidyalaya, Vaijapur, Maharashtra 423 701, India.

[*]Email: sandeeppardeshi007@gmail.com [*] Orcid ID orcid.org/0000-0001-8794-5629

Abstract

In the present study the adsorption of methylene blue on leaf powder of Alstonia Scholaris was investigated. Pseudo first order, second order and Elovic model was applied, it has been observed that the adsorption follows second order kinetic model. The isotherm study was done by using Temkin isotherm, Langmuir isotherm and Freundlich isotherm, the Freundlich isotherm was best suited for present study.

Keywords: bioadsorbent, removal, saptaparni, dye, isotherm

---

1. Introduction

Dyes are extensively used as coloring materials in various industries like paper, pulp, textile, leather etc. [1]. The industrial wastewater containing residual dye content causes serious damage [2]. Cationic dye, methylene blue is mostly used to color cotton, silk, paper etc. [3]. It causes some serious health issues to human as well as animals [4]. There are various methods available for removal of dye from effluent water but adsorption is the most simple and economic method [5]. The most commonly used adsorbent is activated charcoal which is expensive, some paper report the use of activated charcoal prepared from various waste material like bamboo [6], Jute Fiber [7] etc. Safe, efficient, economic and environment friendly adsorbent is a need, some of the adsorbent derived from waste materials such as cellulosic olive stone [8], spent coffee ground [9, 10], Coffee husk [11], neem leaf powder [12], agro industrial waste [13], Vilayati tulsi [14] etc. In the present study the adsorption of methylene blue on the Alstonia Scholaris leaf powder was investigated. Alstonia Scholaris is also known as saptaparni.

2. Experimental

2.1 Preparation of Adsorbent

Leaves of Alstonia Scholaris Plant were collected and dried under shade. The dried leaves were grinded in domestic grinder to get powder. The powder was washed with distilled water for two times followed by washing with 0.01 M NaOH. The excess of alkali was removed by washing with distilled water. The leaf powder was dried at 80^0C in hot air oven, placed in air tight container for further use.

2.2 Preparation of dye solution

Methylene Blue (CI-52015) supplied by Loba Chem Pvt. LTD was used. The maximum absorbance was observed at 665 nm. A stock solution of 1000 mg/L was prepared in double distilled water, by dilution, desired experimental solutions were prepared.

2.3 Adsorption Studies

Standard curve was prepared at 665 nm using 1 to 10 mg/L solution (Elico double beam spectrophotometer SL-210). The batch adsorption studies were performed by taking 50 mL dye solution of desired concentration and pH in 250 mL stopper flask. 0.1g of leaf powder was added and the mixture was stirred at 1000rpm. The absorbance of supernatant liquid was measured to determine the concentration. The pH was adjusted by using 0.5 M HCl and 0.5 M NaOH. The effect of adsorbent dose, dye concentration and pH was studied. The solid phase dye concentration at a particular time was determined using following equation [15]

$$q_t = \frac{(C_0 - C_t)V}{W} \qquad (1)$$

Where q_t is adsorption amount at time t, C_o and C_t are dye concentration initial and at time t in mg L^{-1} respectively, V is volume of solution in L and W is weight of adsorbent in g. Langmuir and Freundlich isotherm was used to determine the adsorption capacity of adsorbent

3 Results and Discussion

3.1 Effect of pH

The effect of pH was studied by stirring 50mL dye solution of concentration 40mg/L with 0.1 g leaf powder for 90 min. Initially with increase in pH, the adsorption of Methylene blue increases up to 7.5, further increase in pH decreases the adsorption.

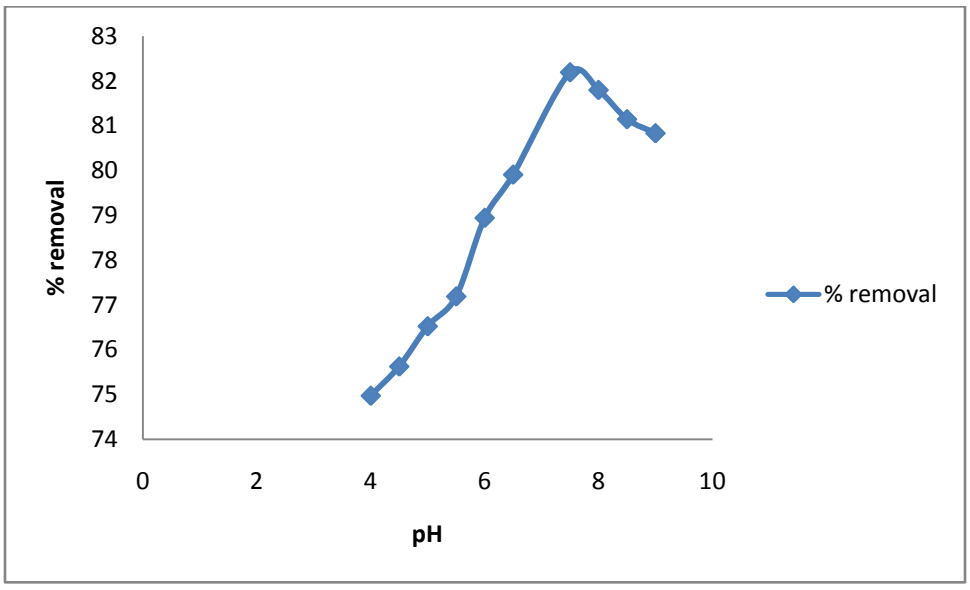

Fig1. Effect of pH on dye removal

3.2 Effect of Adsorbent dose

The effect of adsorbent dose was evaluated by stirring 50 mL 60 mg/L Methylene blue at optimum pH with adsorbent amount (0.05 to 0.3 g) for 60 min. The result was represented in Fig.2. Though the % removal increases with increase in adsorbent dose but the dye adsorbed per gram of adsorbent is decreases as shown in Fig.3

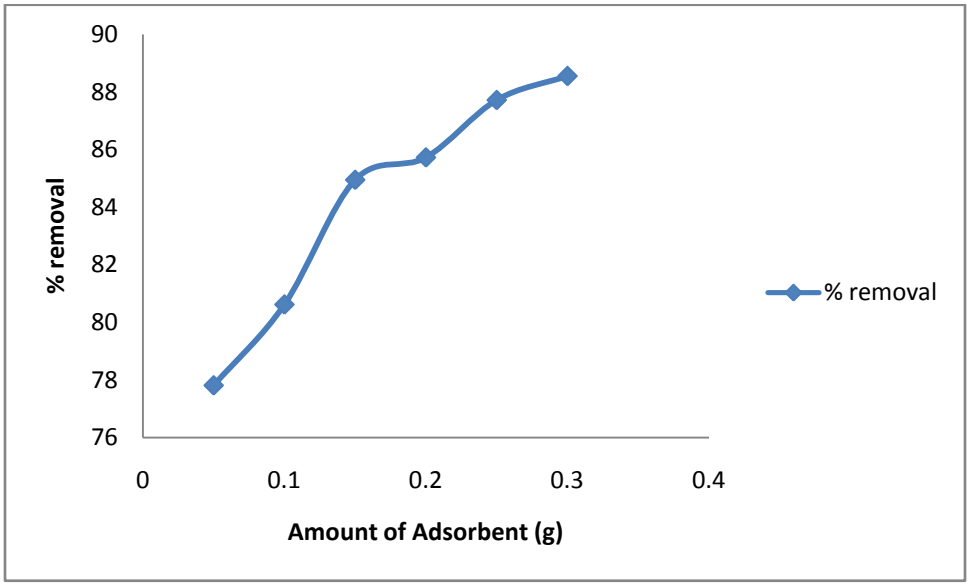

Fig. 2 Effect of Adsorbent dose (% removal)

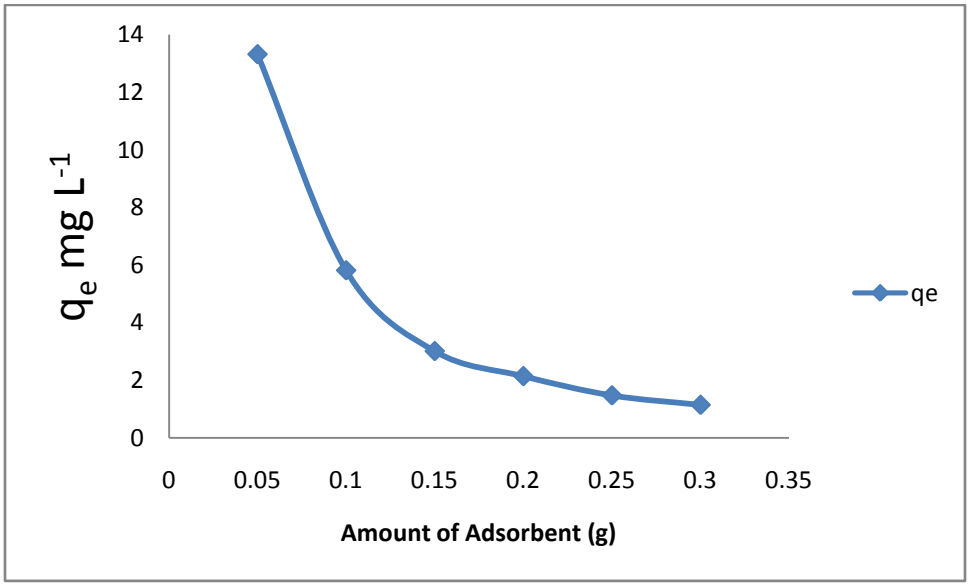

Fig 3 Effect of Adsorbent dose (q_e)

3.3 Effect of dye concentration

The effect of Methylene blue concentration was investigated by stirring 0.1 g adsorbent at optimum pH with 50 mL dye solution (20 mg/L to 100 mg/L).

3.4 Adsorption dynamics

The adsorption dynamics was studied by applying pseudo first order kinetic model, pseudo second order kinetic model and Elovic model.

3.4.1 The pseudo first order kinetic model

Lagergren expression for pseudo first order kinetic model is as follows [16]

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (2)$$

Where q_t dye adsorbed at time t, q_e dye adsorbed at equilibrium and k_1 is the rate constant. The pseudo first order plot is represented by Fig.4. The values of k_1 and q_e are represented in table1. From the values of regression coefficient it has been observed that the present data does not follows the pseudo first order kinetic model.

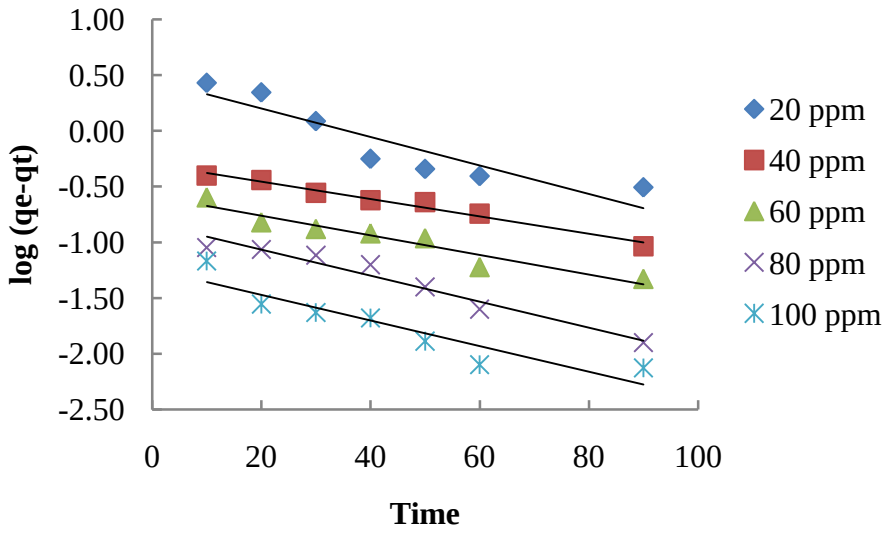

Fig. 4 The pseudo first order kinetic

3.4.2 Elovic model

The Elovic equation represented as follows was used [17]

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \qquad (3)$$

Where β represent the number of available sites for adsorption and α represent the initial adsorption rate, the data represented in table 1 shows that present study does not follow Elovic mode

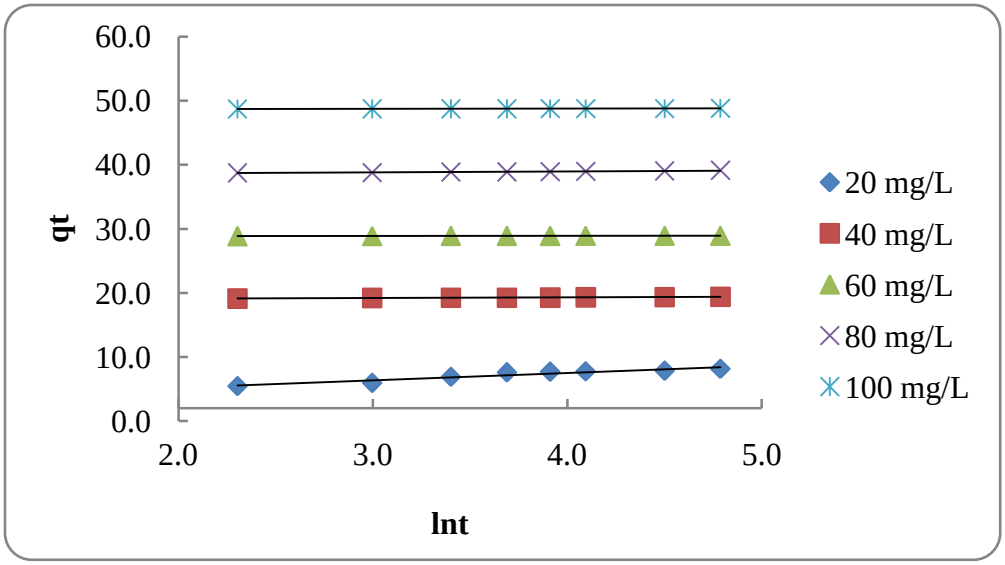

Fig 5 Elovic Model

3.4.3 The second order kinetic model

Lagergren equation for the second order is expressed as follows [18]

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{t}{q_t} \qquad (4)$$

Fig.5 represents the plot of t/q_t versus t. The values of equilibrium adsorption capacity (q_e) and second order rate constant (k_2) were represented in table 1. It can be observed that the pseudo second order kinetic model is followed by present study

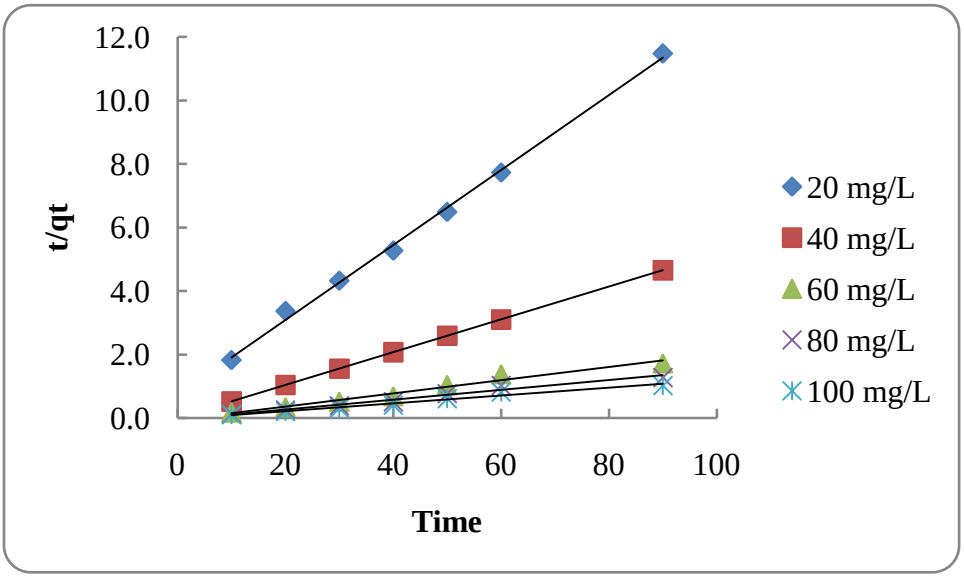

Fig. 6 The pseudo second order kinetic

Table 1 Rate constants for pseudo first-order , pseudo second-order adsorption and Elovic model

Dye Conc.	First order				Second order				Elovich model		
(mg L^{-1})	K_1	$q_{e(exp)}$	$q_{e(cal)}$	R^2	K_2	$q_{e(exp)}$	$q_{e(cal)}$	R^2	β	α	R^2
	(min^{-1})	(mg g^{-1})	(mg g^{-1})		(min^{-1})	(mg g^{-1})	(mg g^{-1})		(mg g^{-1})	(mg g^{-1} min^{-1})	
20	0.0295	8.1549	2.8685	0.8370	0.0190	8.1549	8.4794	0.9948	0.8651	0.4239	0.9082
40	0.0202	19.3895	0.2605	0.9211	0.3166	19.3895	19.3707	1.0000	10.6964	0.0343	0.9610
60	0.0265	28.9380	0.0575	0.8522	2.4204	28.9380	28.9416	1.0000	40.7798	0.0090	0.8788
80	0.0179	39.1550	0.5023	0.9787	0.2232	39.1550	39.1649	1.0000	6.3313	0.0579	0.9344
100	0.0065	48.8309	0.0941	0.9507	0.9687	48.8309	48.8186	1.0000	34.2700	0.0107	0.6982

3.5 Adsorption equilibrium study

Three isotherm, Temkin isotherm, Langmuir isotherm and Freundlich isotherm were applied for present study

Langmuir isotherm is represented by following equation [19, 20]

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \qquad (5)$$

Where q_m is Langmuir constant in mg g^{-1} and b is Langmuir constant in L mg^{-1}, qe is the amount adsorbed at equilibrium in mg g^{-1} and Ce is the equilibrium dye solution concentration in mg L^{-1}. The parameters are represented in the table 2.

Freundlich isotherm is represented by following equation [21, 22]

$$\log q_e = (1/n) log C_e + \log k_f \qquad (6)$$

The Fig 7 represent the plot of log q_e versus log C_e and the parameters are represented in table 2.

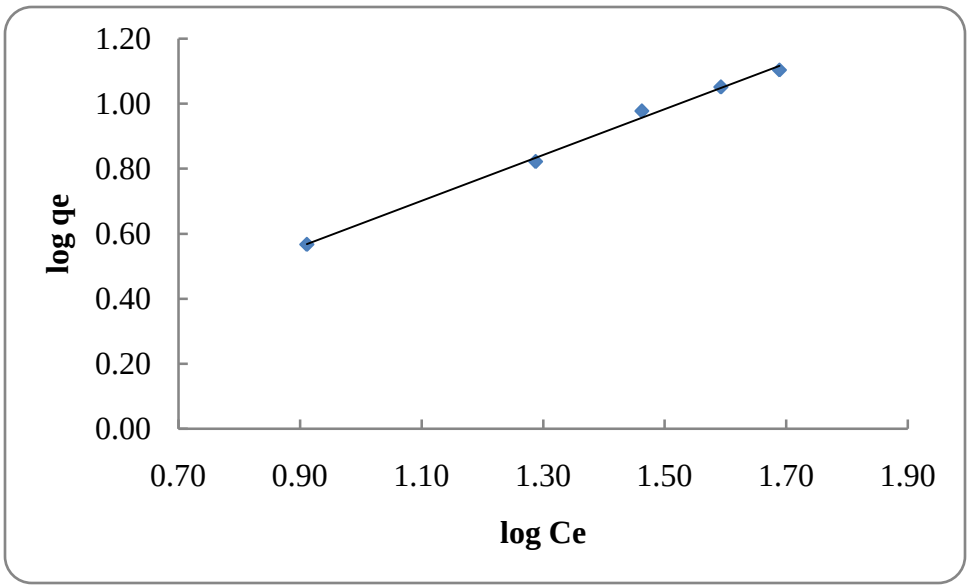

Fig 7 Freundlich isotherm

Temkin isotherm is represented by [23,24]

$$q_{e=BlnA+Bln\,C_e} \qquad (7)$$

Where A and B are constant, values are calculated from plot and represented in table 2.

Table 2 Langmuir , Freundlich and Temkin isotherm parameter

Langmuir Isotherm			Freundlich Isotherm			Temkin Isotherm		
Ka ($L\ mg^{-1}$)	Q_0 ($mg\ g^{-1}$)	R^2	n	K_f($mg\ g^{-1}$)	R^2	A ($L\ mg^{-1}$)	B ($J\ mole^{-1}$)	R^2
-0.0388	-50.9940	0.9281	0.7082	1.2928	0.9961	3.7924	30.7653	0.9191

4 Conclusion

Leaf powder prepared from Alstonia Scholaris Plant was investigated for adsorptive removal of methylene blue. The data shows that the adsorption follows the second order kinetics and Freundlich Isotherm. The maximum adsorption conditions were optimized. The leaf powder can be used as economical adsorbent.

5 Acknowledgements

Authors are thankful the Principal, V. P. Mahavidyalaya, Vaijapur for providing laboratory facilities.

Conflict of interest

The authors declare that they have no conflict of interest

6 References

[1] A. H. Jawad, A. S. Abdulhameed, Mohd S. Mastuli "Acid-factionalized biomass material for methylene blue dye removal: a comprehensive adsorption and mechanism study" Journal of Taibah University for Science, 14:1, 305-313,2020. https://doi.org/10.1080/16583655.2020.1736767

[2] C. Patawat, K. Silakate, S. C. Udom, N. Supanchaiyamat, A. J. Hunt, Y. Nagernyen "Preparation of activated carbon from Dipterocarpus alatus fruit and its application for methylene blue adsorption" RSC Adv, 10, 21082, 2020 https://doi.org/10.1039/d0ra03427d

[3] Z. Li, H. Hanafy, L. Zhang, L. Sellaoui, M. S. Netto, M. L. S. Oliveira, M. K. Seliem, G. L. Dotto, A. B. Petriciolet, Q. Li " Adsorption of congo red and methylene blue on an ashitaba waste and walnut shell based activated carbon from aqueous solution : experiments, characterization and physical interpretation" Chemical Engineering Journal, 388, 124263, 2020. https://doi.org/10.1016/j.cej.2020.124263

[4] M. Rafatullah, O. Suliman, R. Hashim, A. Ahmad "Adsorption of methylene blue on low cost adsorbent: A review" Journal of Hazardous Material, 177, 70, 2010. https://doi.org/10.1016/j.jhazmat.2009.12.047

[5] A. H. Jawad, A. S. Abdulhameed, L. D. Wilson, S. Shatir, S. Hassan, Z. A. Alothman, M. R. Khan " High surface area and mesoporous activated carbon from KOH-activated dragon fruit peels for methylene blue adsorption: optimization and mechanism study" Chinese Jouranl of Chemical Engineering, 32,281,2021 https://doi.org/10.1016/j.cjche.2020.09.070

[6] B. H. Hameed, A. T. M. Din, A. L. Ahmad "Adsorption of methylene blue onto bamboo-based activated carbon : Kinetic and equilibrium studies" Journal of Hazardous Material , 141, 819, 2007.

[7] S. Senthilkumar, P. R. Varadrajan, K. Porkodi, C. V. Subbhuraam " Adsorption of methylene blue onto jute fiber carbon : kinetic and equilibrium studies" J. Colloid Interf Sci, 284, 78, 2005.

[8] M. A. Al-Ghouti, R. S. Al-Absi "Mechanistic understanding of the adsorption and thermodynamic aspects of cationic mehthylene blue dye onto cellulosic olive stones biomass from waste water"Scientific Reports, 2020. https://doi.org/10.1038/s41598-020-72996-3

[9] F. Taleb, M. Ammar, M. B. Mosbah, R. B. Salem, Y. Moussaoui " Chemically modification of lignin derived from spent coffee grounds for methylene blue adsorption" Scientific Reports, 2020 https://doi.org/10.1038/s41598-020-68047-6

[10] A. S. Franca, L. S. Oliveira, M. E. Fereira " Kinetics and equilibrium studies of methylene blue adsorption by spent coffee grounds" Desalination, 249, 267,2009. https://doi.org/10.1016/j.desal.2008.11.017

[11] H. T. Thi, A. L. Hoang, T. P. Huu, T. N. Dinh, S. W. Chang, W. J. Chung, D. D. Nguyen "Adsorption isotherm and kinetic modelling of methylene blue dye onto carbonaceous hydrochar adsorbent derived from coffee husk waste" Science of the Total Environment https://doi.org/10.1016/j.scitotenv.2020.138325

[12] K. G. Bhattacharyya, A. Sharma " Kinetics and thermodynamics of Methylene blue adsorption on neem (Azadirachta indica) leaf powder" Dyes and Pigments, 65, 51, 2005. https://doi.org/10.1016/j.dyepig.2004.06.016

[13] L. Meili, P.V.S. Lins, M.T. Costa, R.L. Almeida, A.K.S. Abud, J.I. Soletti, G.L. Dotto, E.H. Tanabe, L. Sellaoui, S.H.V. Carvalho, A. Erto Adsorption of methylene blue on agroindustrial wastes: Experimental investigation and phenomenological modelling, Progress in Biophysics and Molecular Biology , 2018. https://doi.org/10.1016/j.pbiomolbio.2018.07.011.

[14] S. D. Pardeshi, J. P. Sonar, A. M. Zine, S. N. Thore " Kinetic and thermodynamic study of Adsorption of methylene blue and rhodamine B on adsorbent prepared from Hyptis suaveolens

(Vilayti Tulsi)" Journal of the Iranian Chemical Society, 10,6, 1159, 2013. https://doi.org/10.1007/s13738-013-0256-y

[15] Y. Kuang, X. Zhang, S. Zhou "Adsorption of methylene blue in water onto activated carbon by surface modification" Water, 12, 587, 2020. https://doi.org/10.3390/w12020587

[16] H. K. Yagmur, I. Kaya " Synthesis and characterization of magnetic ZnCl2- activated carbon produced from coconut shell for the adsorption of methylene blue" Journal of Molecular Structure, 1232, 130071, 2021. https://doi.org/10.1016/j.molstruc.2021.130071

[17] A. M. Zine, S. N. Thore, R. P. Pawar, S. D. Pardeshi, N. M. Lingde, J. P. Sonar " Kinetic and isotherm model for the adsorption of acid red from aqueous solution by Parthenium hysterophorus L" Current Pharma Research, 422, 176, 2019.

[18] B. M. Marmat, A. S. Salunke, N. N. Gund, J. P. Sonar, S. A. Dokhe, a. M. Zine, S. N. Thore, S. D. Pardeshi " Adsorptive removal of Malachite green from aqueous solution using low cost adsorbent" International Journal of Chemical and Physical Science, 10, 4, 2021,. https://doi.org/10.30731/ijcps.10.4.2021.1-7

[19] I. Langmuir , Journal of American Chemical Society, 57 (1918) 1361.

[20] N. N. Gund, B. M. Marmat, A. S. Salunke, J. P. Sonar, S. A. Dokhe, a. M. Zine, S. N. Thore, S. D. Pardeshi " Removal of rhodamine 6G from aqueous solution by adsorption on Bioadsorbent prepared from Hyptis Suaveolens (vilayti tulsi): Kinetic, equilibrium and thermodynamic study" International Journal of Chemical and Physical Science, 10, 2, 2021,. https://doi.org/10.30731/ijcps.10.3.2021.1-9

[21] H.Z., Freundlich, J. Phys. Chem, 1906, 57a, 385-470.

[22] A. S. Salunke, N. N. Gund, B. M. Marmat , J. P. Sonar, S. A. Dokhe, a. M. Zine, S. N. Thore, S. D. Pardeshi " Adsorptive removal of Amido black from aqueous solution using economical adsorbent: Kinetic and isotherm study" International Journal of Chemical and Physical Science, 9, 5, 2020,. https://doi.org/10.30731/ijcps.9.5.2020.1-7

[23] M.I. Tempkin, V. Pyzhev, Kinetics of ammonia synthesis on promoted iron catalyst, *Acta Phys. Chim*. USSR **12** (1940), 327–356.

[24] A. M. Zine, S. N. Thore, R. P. Pawar, S. D. Pardeshi, N. M . Ligde, J. P. Sonar "Adsorption studies of acid red 73 on parthenium hysterophorous L" International Journal of Chemical and Physical Science, 7, 4, 2018,. https://doi.org/10.30731/ijcps.7.4.2018.13-22