Study The Adsorption of Thymol Blue Dye on Plant Allium Sativum

Zahraa A. Mahmood
Department of Chemistry, College of Science for Woman, University of Baghdad, Baghdad-Iraq.
Corresponding Author email: lnm14@yahoo.com.

Abstract

The adsorption of thymol blue anionic color by allium sativum store was right off the bat considered in a cluster framework at different color fixations. The adsorption was considered as an element of adsorbent measurements, contact time, pH, temperature and ionic quality under group adsorption strategy. The balance information fit with Freundlich and Tekmin equations of adsorption and the straight relapse factors R2 was utilized to clarify the best fitting isotherm demonstrate. Diverse thermodynamic factors, similar to ΔG^o vitality, ΔH^o and ΔS^o of the on-going adsorption operation have additionally been assessed. The thermodynamic examinations of the color adsorption on allium sativum store demonstrated that the framework was endothermic in nature. Group adsorption models in light of the presumption of the pseudo first request and pseudo-second request component were connected to inspect the energy of the adsorption. The outcomes demonstrated that dynamic information were taken after more intently the pseudo-second request display than the pseudo-first request. [DOI: 10.22401/JNUS.21.2.06]

Keywords: Adsorption, Thymol blue, Tekmin model, Thermodynamic and Allium sativum.

Introduction

Color toxins radiated from the color assembling material and cowhide ventures, cause genuine ecological issues. Shading materials in wastewater are tastefully disappointing as well as hurtful for amphibian widely varied vegetation. The vast majority of these colors are ineffectively biodegradable. The material business keeps on hunting down a prudent answer for decolorize the almost 200 billion liters of shaded profluent created yearly [1]. Corrosive colors are the most risky because of their brilliant shading, acidic and water solvent responsive qualities. A few investigations have been executed on adsorption of essential colors by mud minerals [2]. Numerous treatment strategies have been utilized to expel the colors from wastewater. Among the different strategies adsorption is a different procedure which is currently perceived as a compelling and temperate strategy for the expulsion of both natural and inorganic poisons from wastewater [3]. Adsorption was observed to be better than different systems for water re-use as far as straightforwardness of configuration, simplicity of operation and lack of care to poisonous substances [4]. Today, scientists have turned out with think about that has been centered around the ease adsorbents that are chiefly gotten from farming waste and mechanical side-effect since they required small handling and plentiful in nature. Plant squanders are modest as they have no or low financial value[5]. Some minimal effort plant squander had specifically been utilized as adsorbent for color adsorption from wastewater treatment. Nonetheless, the utilization of untreated plant squander adsorbent can likewise bring a few issues, for example, bring down adsorption limit, higher synthetic oxygen request and natural substance request and also add up to natural carbon due to the discharged of solvent natural compound contained in the plant material [6]. A few plants were utilized as adsorbent surfaces to expel a few colors, for example, anovel horticultural [7], malvaparviflora[8] and different plants.

This work contemplates the likelihood of utilizing a plant allium sativum, as a reasonable sorbent for the expulsion of thymol blue from watery arrangements utilized isotherm are Freundlich isotherm and Temkin isotherm. Thermodynamic and pH ponders for the evacuation of the color onto allium sativum deposet have been examined.

Practical Part

Absorbed Substance

The thymol blue stock arrangement was set up by dissolving precisely weighted color in

refined water to the centralization of 100 ppm, was utilized without assist cleansing, λmax (436 nm).The exploratory arrangements were gotten by weakening the color stock arrangement in precise extents to various beginning focuses from (10-50) ppm. The structure, physical and chemical properties of dye explained in figure and Table (1).

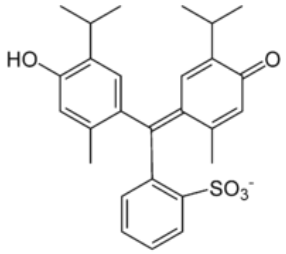


Fig.(1): Structure of thymol blue.

Table (1)
Characteristics of thymol blue dye.

Chemical formula	$C_{27}H_{30}O_5S$
Molar mass	$466.59 g \cdot mol^{-1}$
Appearance	Brownish-green crystal powder
Solubility in water	Insoluble
Melting point	221–224°C (430–435°F; 494–497K) decomposes

The adsorbent

Dry the pieces of allium sativum and then grind then grinded into particle size (75 µ).

Batch adsorption experiment

Group tests were done to decide the impacts of pH, contact time, beginning color focus and adsorbent dosage by differing the factors under examination and saving different factors steady. The feed arrangement was set up by dissolving a precisely measured amount (0.1)g of strong color in 1L of water. The exploratory arrangement of wanted focus was acquired by progressive weakening of stock arrangement. The pH of every one of these arrangements was kept up by including 0.1 N hydrochloric acid or 0.1 N sodium hydroxide. The adsorption was observed by deciding the convergence of thymol blue in arrangement utilizing twofold bar UV-Visible spectrophotometer ,at λmax 436 nm. Percentage of color expulsion and amount of thymol blue adsorbed on adsorbent at the season of harmony quantity of dye adsorbed was figured utilizing condition 1 [9**]:**

$$Qe = (C_o - Ce)\ V / W \quad \text{.....(1)}$$

where C_o and Ce are the primary and the equanimity concentrations (mg/L) of dye, respectively. Qe is quantity of dye adsorbed on the adsorbent at the time of equanimity (mg/g), V is volume (L) of solution and W is the mass of adsorbent (g).

Impact of variable factors

Dosage of adsorbent

Initial of adsorbent dose 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 g. Contact time 60 min, agitation speed 200 rpm, concentration 50 ppm and temperature 25°C.

Contact time

Adsorption equilibrium studies are performed with an adsorbent quantity of 0.2 g by 75 ml of dye and concentration 50 ppm with deferent time 10, 20, 30, 40, 50 and 60 min at 25 °C .

pH

Adsorption tests were done at pH 3, 5, 7 and 9 at 25°C with 75 mL of color focus 50 ppm. The acidic and basic pH of the media was kept up by including the wanted measures of weaken HCl corrosive and NaOH arrangements.

Temperature

The adsorption tests were performed where is the four temperatures 25, 35,and 45°C in an indoor regulator joined with a shaker. The examinations were done by taking 75 mL of thymol blue arrangement with various beginning convergences of colors ranging 10, 20, 30, 40 and 50 ppm.

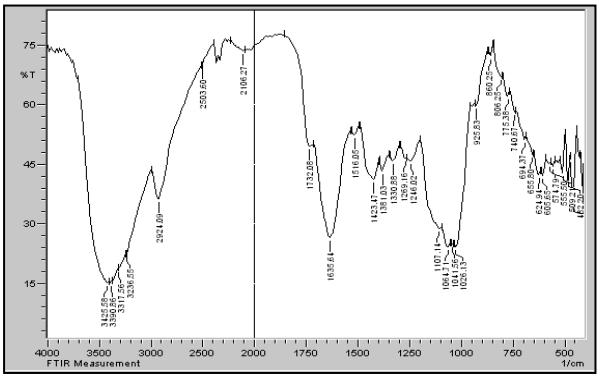
Ionic strength

Adsorption tests were conveyed different concentration of KCl (0. 0 1, 0.0 01 and 0.0001) M at 25°C with 75 mL of dye concentration 50 ppm.

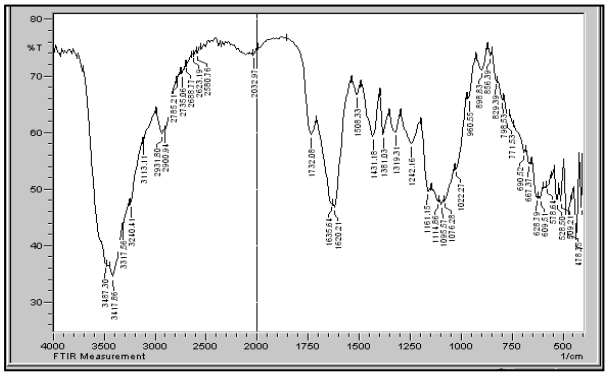
Results and Discussion

Surface characterizations (FTIR)

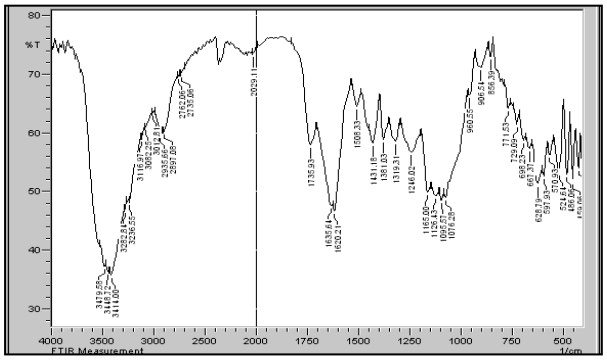
Change Infrared spectroscopy (FTIR) investigations of allium sativum store the adsorbent were completed and the spectra taken before (1 a) and after (1 b) of concentration 10 ppm thymol blue and c of concentration 40 ppm thymol blue adsorption were shown in Fig.(1).



(a)



(b)



(c)

Fig.(1): FTIR spectrum of allium sativum deposit before (a) and after (b) of thymol blue concentration 10 ppm and (c) of thymol blue concentration 40 ppm).

From the range of FTIR we watch the nearness of ingestion packages inside the range (3429.43-3417.86 cm^{-1}) from the OH-hydroxyl gatherings, and the rise of assimilation packs at (3082.25-3074.53 cm^{-1}) after adsorption comes back to the sweet-smelling CH bunches in the color, The retention inside the range (2924.04-2920.23cm^{-1}) is expected to the CH-bunches on the surface of the allium sativum powder, and also the dynamic gathering H-C = O inside the range (1732.08-1728.22 cm^{-1}) and the C-S-aggregate inside the range (1041.56-1026.13cm^{-1}). These gatherings speak to powerful locales where the procedure of adsorption to the possibility of happens in light of the fact, that they can shape compound bonds or physical bonds to contain a couple electronic or electrostatic change as conceivable to be engaged with the arrangement of the physical connections or concoction bonds [18].

Equanimity Time

The effect of contact time on the amount of thymol blue adsorbed per unit of adsorbent was investigated under 25°C at constant concentration. Fig.(2) show the results of equilibrium time for thymol blue allium sativum on for 50 ppm.

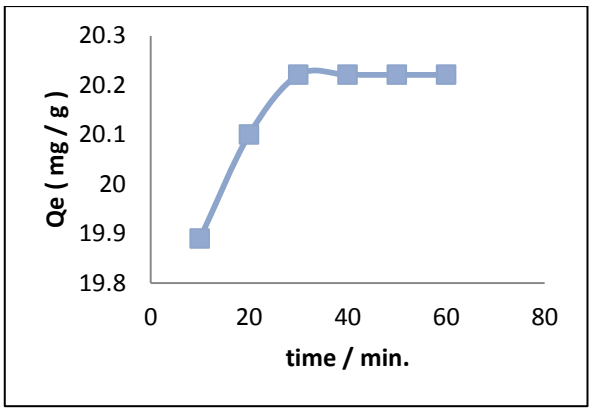


Fig.(2): The empact of contact time on the adsorption of thymol bul.

Show that the adsorption process exhibit an immediate rapid adsorption and reaches equilibrium within a short period of 30 min [10].

Adsorbent Dosage

The adsorption dosage is an imperative parameter in adsorption thinks about in light of the fact that it decides the limit of adsorbent for a given initial centralization of color dye solution. Fig.(3) shows impact of dosage on the adsorption capacity of thymol blue onto allium sativum.

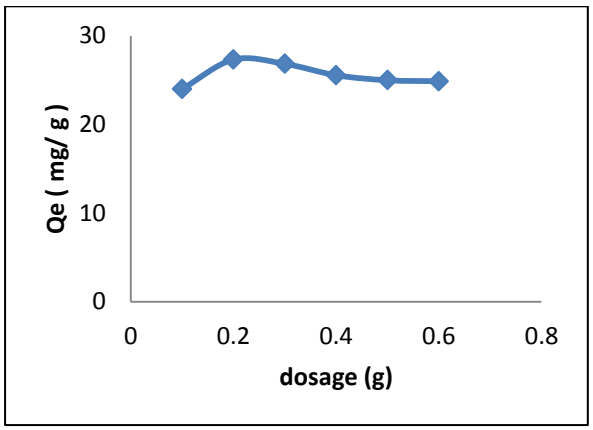


Fig.(3): Impact of adsorbent dosage.

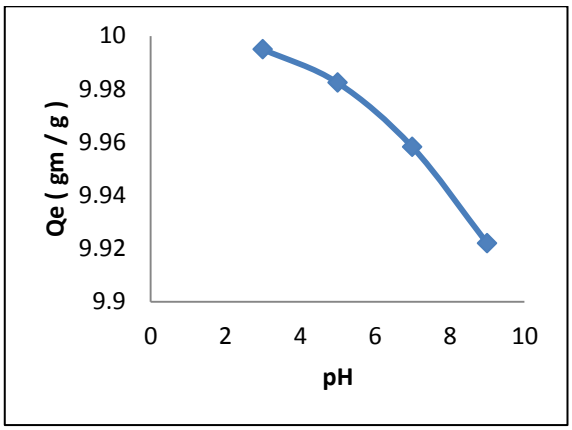


Fig.(4): Effect of pH on removal of thymol blue.

It is clear that the Qe of the color increments with the expansion in adsorbent measurements, however past an estimation of 0.2 g the rate evacuation comes to right around a greatest esteem. This is most likely because of the more prominent accessibility of the replaceable destinations or the expanded surface territory where the adsorption happens [11].

Impact of pH

Demonstrate that, the take-up of thymol blue expanded with diminishing starting pH and was the best at pH 3. At low pH esteems the practical gatherings of allium sativum would be protonated and result in a more grounded fascination for adversely charged particles in the adsorption medium. The pH basically influences the level of ionization of the thymol blue and the surface properties of allium sativum. As the pH expanded the general surface charge of the allium sativum wound up plainly negative and adsorption decreased [12]. Thymol blue being feebly acidic would be mostly ionized in arrangement. These particles will be adversely charged and will be straightforwardly pulled in, because of, electrostatic powers by the protonated amino gatherings of the allium sativum.

As appeared in Fig.(4) the amount of thymol blue adsorbed diminished with an expanding pH. The impact of pH on the adsorption procedure is conceivably related with associations between the color anions in the arrangement and adsorbent surface charge contaminants, the adsorbent surface has more negative charge and hence color anion adsorption is diminished. Corrosive colors are known to ionize to some degree in watery answers for frame hued anions, which could then trade with the hydrogen particles of the biomass. Amid the adsorption analyzes, the arrangement pH somewhat expanded, potentially due to the exchange of OH from the adsorbent's surface into the arrangement.

Additionally, the H^+ and OH particles can impact adsorption limit [12].

Thermodynamic parameters

The thermodynamics factors identified with the adsorption of color. For example, enthalpy change, entropy change and Gibbs free vitality change ΔG°. ΔH° has been computed for all adsorption forms, as indicated by Van't Hoff condition (3) by means of plotting logarithmic estimation of the adsorption balance consistent (K_{eq}) as (ln Qe/Ce) against the temperature as (1/T) [13]. The outcomes are recorded in Table (2) and Fig.(5).

$$G^\circ = - RT \ln K_{eq} \quad \text{.....(2)}\Delta$$

$$\ln K_{eq} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad \text{.....(3)}$$

Where K_{eq} is adsorption equilibrium constant, R is the gas constant.

Table (2)
Thermodynamic parameters of tymol blue adsorption on allium sativum.

T (K)	ΔH(KJ. mol^{-1})	ΔG(KJ. mol^{-1})	ΔS(J. mol^{-1}.K)
298	0.5956	6.146	-0.1862
308		4.676	-0.0132
318		3.952	-0.0105

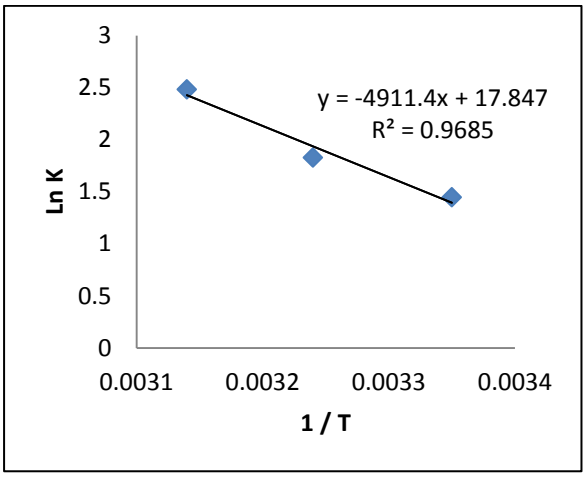


Fig.(5): Van't Hoff plot of thymol blue adsorption.

The adsorption of color increments quickly with an expansion in temperature. The expansion in adsorption limit of allium sativum was credited to the development of pore size and initiation of the sorbent surface with temperature.

Additionally ascend in temperature builds the versatility of the vast color particles and decreases the swelling impact in this manner empowering the substantial color atom to enter encourage [13]. The outcomes likewise demonstrated that the adsorption of thymol blue is an endothermic procedure.

The positive estimation of ΔH shows that the adsorption of thymol blue onto allium sativum is an endothermic response. Which show the perfect and the greatest estimation of a physic-sorption process. All estimations of ΔG were certain these qualities demonstrate that the adsorption procedure went with the procedure of assimilation. As the spreading atoms adsorbed inside the pores of the allium sativum and expands speed of organization with expanding temperature this conduct is inferable from extra assimilation.

The negative values of ΔS indicate the regularity of the dye particles on the surface more than they are in the solution.

Adsorption Isotherms

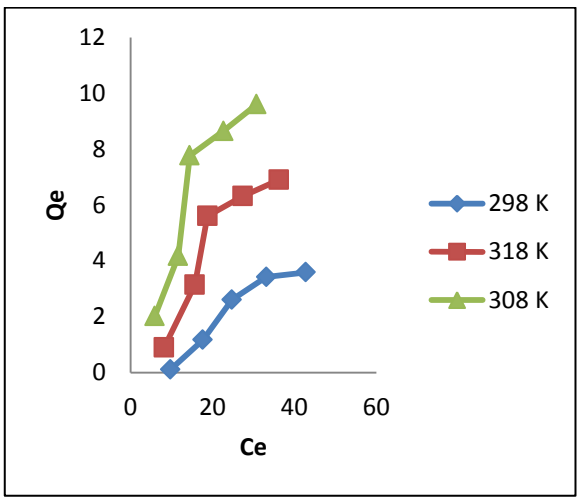
Adsorption properties and balance parameters, normally known as adsorption isotherms, portray how the adsorbate interfaces with adsorbents, and complete comprehension of the idea of cooperation.

Foure famous isotherm conditions, the Freundlich and Temkin. The Freundlich condition [14].

Was utilized for the adsorption of thymol blue on the adsorbent. The Freundlich isotherm was spoken to by condition (4):

$$\log Q_e = \log K_f + 1/n \log C_e \quad \text{.....(4)}$$

where Q_e is the measure of tymol blue color adsorbed (mg/g), C_e is the balance grouping of color in arrangement (mg/L), Kf and 1/n are constants fusing the elements influencing the adsorption limit and force of adsorption, separately



Fig,(6): Adsorption isotherms of thymol blue on allium sativum.

Fig.(6) demonstrated the adsorption isotherm of S-type, showing that the adsorbent is potentially mesoporous or isn't permeable, and has a high vitality of adsorption [15]. Likewise, this showing a vertical or level introduction of adsorbate , and the adsorbate is mono practical.

Temkin and Pyzhev considered the impacts of some circuitous sorbate/adsorbate cooperations on adsorption isotherms and proposed that in view of these connections the

warmth of adsorption of the considerable number of particles in the layer would diminish directly with scope. The Temkin isotherm has been utilized as a part of the accompanying following form [16]:

$$Qe = B_T \ln K_T + B_T \ln Ce \quad \text{..... (3)}$$

Where K_T and B_T is the equilibrium binding constant (L /g).

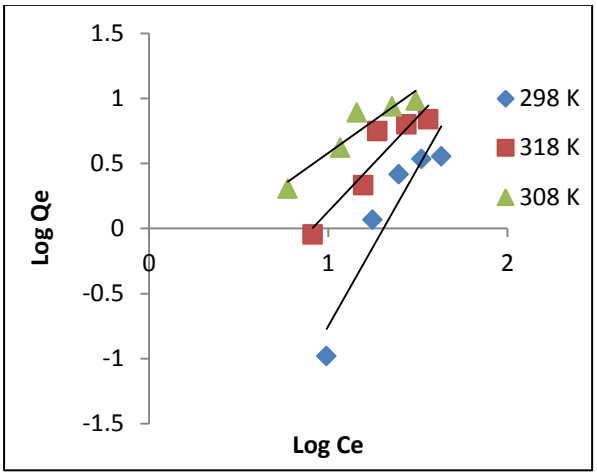


Fig.(7): The linear plot of Freundlich isotherm.

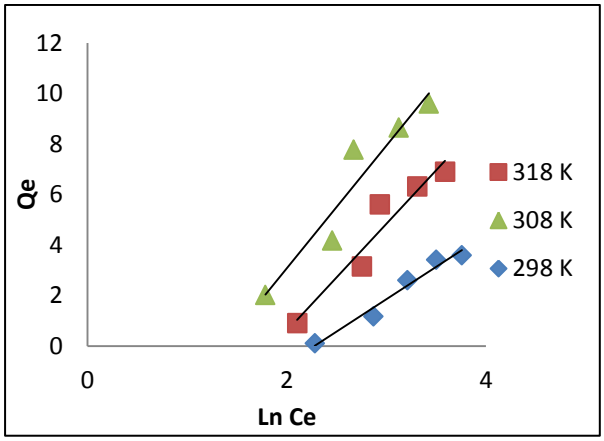


Fig.(8): The linear plot of Temkin Isotherm.

Table (3)
The factors of Freundlich and Temkin condition for the adsorption of thymol bue.

Freundlich factors				Temkin factors		
T	R2	n	Kf	R2	K_T	B_T
298	0.887	0.4113	6.5917	0.9664	5.8378	2.5645
318	0.88	0.6858	0.472	0.9296	7.9071	4.2469
308	0.897	1.0214	0.4008	0.9152	6.6317	4.8555

As appeared in Table (3) the estimations of direct R2 coefficient were high 0.9 for Temkin isotherm showing the helpful estimations of its constants. The adsorption isotherm for the present framework is clarified better by Tmken isotherm demonstrate.

Effect of Ionic strength

Fig.(9) demonstrates the expanded evacuation of Thymol blue color on the allium sativum surface when KCl is included. Discovered that the measure of sabstance on entire surfaces reduces with assembles centralization of potassium chloride plan , keeping in mind the end goal to the way that the extra gathering of potassium chloride courses of action reason a development in competition between particles of the thymol blue and electrolyte particles on the expulsion goals at first look [17].

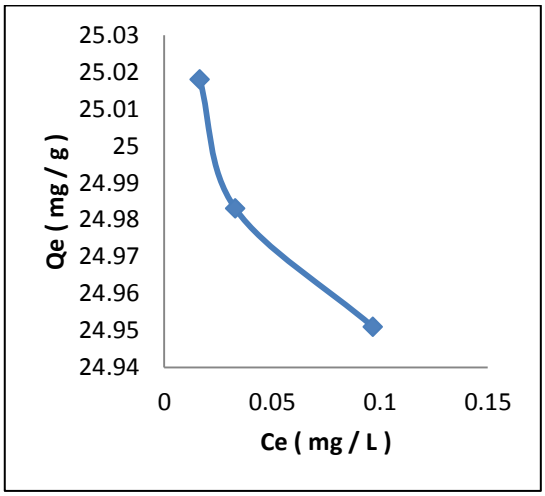


Fig.(9): Effect of ionic strength on removal of thymol blue.

Kinetic studies

Adsorption dynamic is vital from the perspective to control the procedure proficiency. Different dynamic models have been utilized by different scientists, where the pseudo-first-request and pseudo-second-order models were examined. The component of adsorption relies upon the physical and additionally compound characterstics of the adsorbent and in addition on the mass exchange process. The energy of adsorption is imperative from the perspective that it controls the procedure proficiency. Different analysts has been a few energy models, where the adsorption is dealt with as a pseudo initially request and pseudo second request process. The pseudo-first-order rate condition of Lagergren is by and large portrayed by the accompanying condition [12]:

$$\text{Ln } (q_e - q_t) = \text{Ln } q_e - K_{ads}.\ t \quad \ldots\ldots\ldots\ldots (4)$$

Where qt and qe are the measure of thymol blue adsorbed at time (min.), and at, and Kads. /min.$^{-1}$ is the rate steady.

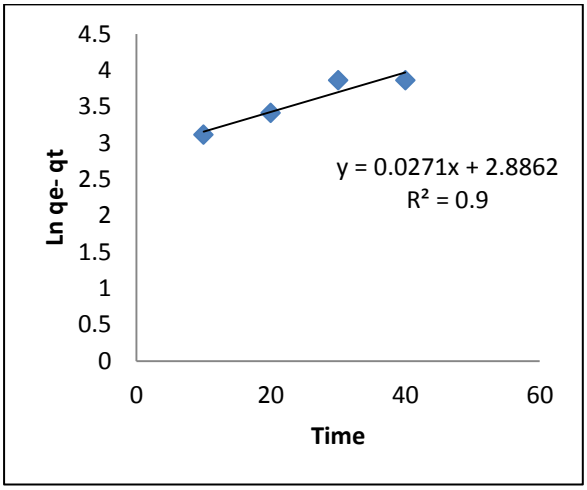


Fig.(10): pseudo-first order plot for adsorption of thymol blue dye.

The pseudo-second - order dynamic model is communicated as takes after [12]:

$$t/\ q = 1\ /\ k_2\ q_e^{\ 2} \ +\ t/\ q_{e\text{---}} \quad \ldots\ldots\ldots\ldots\ldots (5)$$

Where k_2 is the second-order rate consistent (g/mg min), by plotting of t/q versus t is a straight relationship. Estimations of k_2 and q_e . Were ascertained from the block and incline of the plots of t/q versus t.

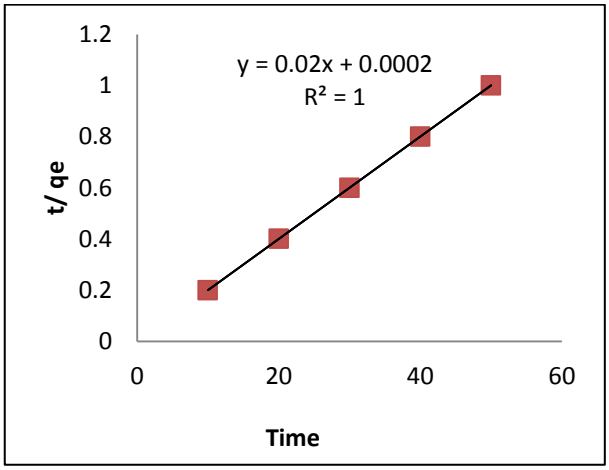


Fig.(11): pseudo- second order plot for adsorption of thymol blue dye.

In the present examinatin the adsorption of thymol blue by allium sativum has been described by the pseudo-second order demonstrate. The correlation coefficients of the second-order kinetic model were greater than the first-order kinetic model.

Conclusions

The after effects of introduced this examination demonstrate that, Can allium sativum has an appropriate adsorption limit with regards to the expulsion of thymol blue from fluid arrangements. The harmony adsorption is for all intents and purposes accomplished in 30 min. The amount of thymol blue adsorbed decreased with an increasing pH. The test comes about were broke down by utilizing Freundlich and Tempkin isotherm models, The adsorption isotherm for the present framework is clarified better by Tmken isotherm display. The thermodynamic investigations of the color adsorption on allium sativum store showed that the framework was endothermic in nature. The information demonstrate that the adsorption energy take after the pseudo-second request rate

Reference

[1] Rita K., "Textile dyeing industry an environmental hazard", Natural Science, 4 (1), 22- 26, 2012.

[2] Ghosh D. and Bhattacharyya K. G., "Adsorption of methylene blue on kaolinite", Appl Clay Sci., 20 (6), 295-300, 2002.

[3] Ramesh K., Rajappa A. and Nandhakumar V., "Kinetic of adsorption of methylene blue onto microwave assisted zinc chloride activated carbon prepared from delonix regia pods", IJCPS, 2(8), 878- 885, 2014.

[4] Abd El-Latif M. M, Ibrahim A. M, El-Kady M F., "Adsorption Equilibrium, kinetics and thermodynamics of methylene blue from aqueous solutions using biopolymer oak sawdust Composite", J. of American Sci., 6(6), 267- 283, 2010.

[5] Nasuha N., Zurainan H.Z., Maarof H.I., Zubir N.A. and Amri N., "Effect of cationic and anionic dye adsorption from aqueous solution by using chemically modified papaya seed", IPCBEE, 8, 50-54, 2011.

[6] Wan Ngah W.S. and Hanafiah M.A.K.M., "Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review", Bioresour. Technol., .99 (10), 3935–48, 2008.

[7] Hameed B. H, Krishni R. R and Sata S. A., "Anovel agricultural waste adsorbent for the removal f cationic dye from aqueous solution", J. of Hazardous Materials, 162 (1), 305- 311, 2009.
[8] Farhan A. M, Abed Jassim R. and Kadhim N. J., "The removal of zinc from aqueous solution using malvaparviflora", J. of Baghdad Sci., 13 (3), 482- 488, 2016.
[9] Aljeboree A. M., Alshirifi A. N. and Alkaim A. F., "Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon", Arabian J. of Chemistry, 10, S3381–S3393, 2017.
[10] Hamaza M. O. and Kareem S. H., "Adsorption of direct yellow 4 dye on the silica prepared from locally available available sodium silicate", Eng. And Tech. Journal, 30 (15), 2609- 2625, 2012.
[11] Fatiha M. and Belkacem B., "Adsorption of methylene blue from aqueous solutions using natural clay", J. Mater. Environ. Sci., 7 (1), 285-292, 2016.
[12] Muthamilselvi P., Balamurugan P. and Karthikeyan Dr. R., "Adsorption of Phenol From Aqueous Solution By Allium Sativum Linn Peel", (IJERA), 2 (5), 727-731, 2012.
[13] Pathania D., Sharma S. and Singh P., "Removal of methylene blue by adsorption onto activated carbon developed from Ficus carica bast", Arabian J. of Chem., 10, S1445–S1451, 2017.
[14] Baskaran, P. K. Venkaramen, B. R. and Arivoli S., "Adsorption of malachite green dye and by acid activated carbon, kinetic thermodynamic and equilibrium studies", J. of Chem., 8 (1), 9- 18, 2011.
[15] Cutcheon M.. Detergents and Emulsifiers, Allied Publishing Co., New Jersey, 2002.
[16] Huarg R. W., BoYang B., Zheng D. and Zhang Z., "Equilibrium, Kinetic and thermodynamic studies of adsorption of Cd (II) from aqueous solution onto HACC-bentonite", Desalination, 280, 297-304, 2011.
[17] Mahmood Z. A., "Adsorption Study for Trifluralin on Iraqi Zeolite", J. of Al-Nahrain University, 15 (4), 31-37, 2012.
[18] Cazetta A.L., Vargas A.M., Nogami E.M., Kunita M.H., Guilherme M.R., Martins A.C., Silva T.L., Moraes J.G. and Almeida V.C., "NaOH-activated carbon of high surface area produced from coconut shell: Kinetics and equilibrium studies from the methylene blue adsorption", Chem. Eng. J. 174 (1) 117–125, 2011.