Bulgarian Chemical Communications, Volume 49, Special Issue J, (pp. 222 – 228) 2017

Synthesis of new adsorbent based on graphene oxide with n-(3nitrobenzylidene)-4-chlorobenzen amine and removing methyl violet

S.J. Hoseyni*, M. Daghighi Asli, M. Manoochehri

Departman of Chemistry, Central Tehran Branch, Islamic Azad University, Tehran-Iran

Received June 26, 2015, Revised September 10, 2015

Water is the source of life and no living creature can survive without water. Water health is an important issue in public health and health management. The majority of plants' tissues and animals' body is composed of water. Water plays a key role in delivering nutrients to the tissues, cells and detoxifies the body. It also delivers the absorbed nutrients by plants' roots to other organs. On the earth, water has variety of uses, such as drinking usage, processing crops, wheeling industries, power generation and cultivating marine organisms, most of which have nutritional value to humans. Pollutants in drinking water causing illness or death contain organic and inorganic compounds and different kinds of microorganisms. Chemical dyes are considered as the most dangerous groups of chemical compounds found in industrial waste water, which are due to some reasons such as reducing light penetration, followed by disrupting the ability of photosynthesis in water resources has been of great significance. These compounds authentically leave negative impacts on the quality of water to drink and other consumptions. They also bring about allergy, skin irritations, cancer and genetic mutations in humans. Textile and industrial wastewater due to the use of different colors in different processes, is intensely mixed with chemical dyes which is to be purified before entering into environment. Therefore, the aim of the present study was to investigate the effectiveness of graphene oxide and magnetic graphene oxide in removal of methyl violet ionic colors from aqueous solutions. The study was conducted in laboratory scale. First, the absorbents were prepared and they were confirmed according to the pattern of the infrared spectrum of the functional groups in the absorbents. Then, the effects of different parameters like initial dye concentration, absorption dosage, contact time, temperature and PH on removal efficiency and also kinetics and absorption isotherm were studied. The results of the calculations showed that the absorption process follows the second stage kinetics and Freunflich absorption isotherms of the same temperature. According to obtained results, it is possible to use synthesized absorbent to remove the environmental pollutants, particularly toxic compounds, from environmental solutions.

Keywords: Dye Adsorption, Methyl Violet, Adsorption Kinetics, Adsorption Isotherm

INTRODUCTION

Dyed waste water produced by textile and color production industries has toxic effects on aquatic ecosystems [1]. The presence of aromatic rings in the structure of azo dyes toxifies them and makes them non-decomposable [2].

Methyl violet, as a cationic azo dye with molecular formula of C24H28CIN2 and molecular mass of 393.96 is widely used in dyeing of wool, cotton and so on. This color can cause harmful effects like dyspnea, skin irritation, heart palpitations and seizure on humans. Therefore, it is essential to remove the existing industrial waste water. Violet methyl's structure is shown in Fig 1.

Adsorption is one of the most widely used techniques for the removal of dyes, especially for non-decomposable dyes [3]. Color adsorption depends on its chemical properties and adsorbent's chemical level. Nano-adsorbents with a large specific surface and a very high absorption power produce less waste. On the other hand, they are not only highly capable of absorbing the materials through adsorption processes, but also can be refined and reused.

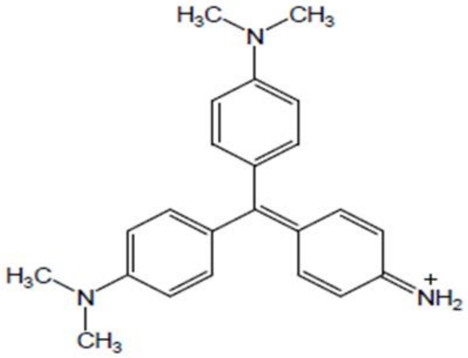


Fig 1. Chemical structure of violet methyl

Graphene oxide due to having different oxygen functional groups and unfixed negative charge on its surface is highly capable of removing cationic compounds. In graphene oxide magnetic due to the presence of iron in the surface and existence of empty orbitals there is an increase in tendency towards removing the cationic materials. In addition, graphene oxide magnetic separation is

---

To whom all correspondence should be sent:
E-mail: Sjalal135mm@gmail.com

easily done by magnetic field which requires less time and energy than graphene oxide.

The aim of the present study was to investigate the performance of synthesized absorbent in removing the cationic dyes such as methyl violet from aqueous solutions. Methyl violet adsorption was investigated in various conditions such as contact time, adsorbent dosage, PH and initial concentration.

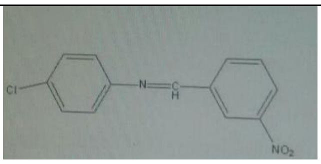
MATERIALS AND METHOD

Analysis devices and chemical materials

To prepare and analyze the sample, magnetic stirrer was used. To determine the concentration Shimadzu UV-visible 1650 PC was used. And to get the infrared spectrums Jasco 4200 FT-IR in potassium bromide tablet was used. To investigate samples' behavior in different pHs, pH meter device (Company AZ) was used. To separate the absorbent after adsorption process centrifuges device PLCseties 307548 and magnetic field were used.

Chemicals used in the present study are listed in Table 1.

Table 1 Chemicals

Chemical characteristics	Chemical	Row
NH_3 ,MW=17/03 g/mol,1L=0.91Kg, (Merck)	Ammonia	1
Graphite Fine powder , (Merck)	Graphite powder	2
H_2SO_4 , 98.08 g/mol , %98, 1.8 g/ml (at 20°) , (Merck)	Sulfuric acid	3
$KMnO_4$, M.W: 158.04g/mol , (Merck)	Potassium permanganate	4
$NaNO_3$, M.W=84.99 g/mol , (Lobachemie, India)	Sodium nitrate	5
$FeCl_2.4H_2O$, M.W : 198.75g/mol, a: 98% (Merck) $FeCl_3.6H_2O$, M.W : 270.30g/mol (Merck)	Iron chloride	6
H_2O_2, M.W: 34.01g/mol, a: 30% (Lobachemie, India)	Hydrogen Peroxide	7
HCl ,MW=36.46g/mol ,1L=0.79 Kg (Merck)	Hydro chloric acid	8
NaOH, MW=39.99g/mol ,1Cm2=2.13g (Merck)	Sodium hydroxide	9
H_2O, MW=18g/mol	Double distilled water	10
 MW=277g/mol	N(3nitrobenzylidene)-4- chlorobenzen amine	

Absorbent synthesis

In the present study Hummer method was used to prepare graphene oxide [4]. Graphite stage oxidation in presence of strong oxidizers is the basic element of the method. Graphite, sodium nitrate and sulfuric acid were poured in a round-button balloon and placed in an ice bath. After an hour, potassium permanganate was added and removed from water bath and was stirred for two hours at room temperature. Then distilled water was added slowly and it was reflux in oil bath for 30 minutes at a temperature of 98 ° C. Finally, distilled water and hydrogen peroxide were added. Graphene oxide was separated in open temperature, and it was washed three times with 5% hydrochloric acid and it was again washed with distilled water to extract remaining acids. Sediment of graphene oxide was placed in a vaccum oven at 50 ° C for 72 hours to dry.

To prepare graphene oxide magnetic, the graphene oxide produced from the previous stage was exposed to ultrasound waves along with water. Iron chloride (II) and Iron chloride (III) were added into three spans balloon after homogenization and reflux system was closed at 70°C, under nitrogen atmosphere. Then, ammonia was added drop by drop. After 45 minutes, the balloon was taken out from bath and after reaching environment temperature- as it is a magnetic absorbent- using a magnetic field, the absorbent was separated and washed with distilled water for three times. Sediment of graphene oxide magnetic was placed in a vaccum oven at 50 ° C for 24 hours to dry completely [4].

To prepare absorbent under investigation in the present experiment, the prepared graphene oxide magnetic in the previous stage was placed under ultrasound waves along with ethanol. Then, after homogenization, tetra ethoxy silane and ammonia were added to the solution. The cap of the container was closed and it was left for 4 hours to fulfill the reaction. Finally, the absorbent's cap was removed and it was washed with distilled water for three times and placed in a vaccum oven at 60 ° C for 24 hours to dry completely.

Absorption tests

All adsorption tests were conducted in a batch system. Maxλ amount of methyl violet by UV-vis was 574nm.

Before optimizing the factors, it is desirable to make sure of the initial quality of the synthesized absorbent. Therefore, 0.05 gram of synthesized absorbent, graphene oxide, graphene oxide magnetic and ligand were added to 30mg/l methyl violet dye solution separately and all were stirred. If the quality of synthesized absorbent is acceptable, it should absorb the existing dye to a great deal. Accordingly, after smoothing the solution, UV-vis spectrum of the solutions were checked. As it is shown in Fig. 2, the UV-vis absorption of the synthesized solution was more than that of the graphene oxide, graphene oxide magnetic and ligand. The distinctive difference of UV-vis absorption by the synthesized solution indicates that the solution is of high quality and it paves the way to continue the experiment with more certainty.

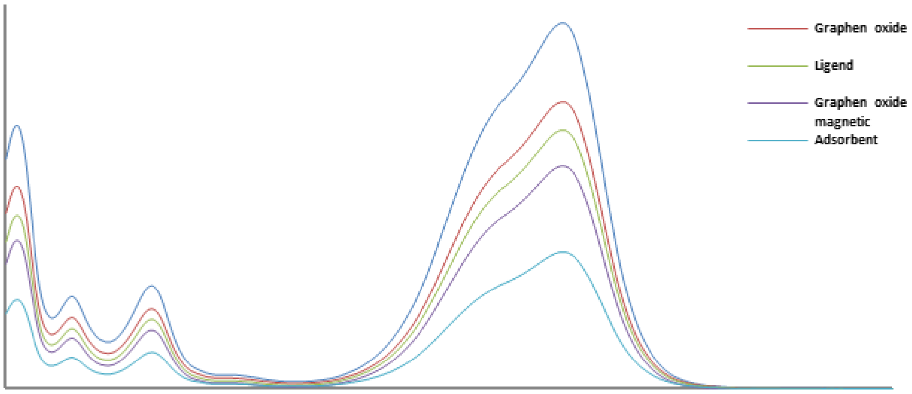


Fig 2 Absorption tests results

Different conditions and environmental factors effecting adsorption process were investigated.

60 minutes) and the amount of the absorbent (0.005 to 0.03g). It is important to mention that all tests were conducted in a volume of 50 ml of the dyed solution and at 25 ° C.

They were initial concentration of dye (10 to 100 mg/l), pH (2 to 10), contact time (1 to

In each test, dye removal rate (%) and the amount of absorption (mg/l) were calculated using the following formulas:

$$q_e = \frac{C_0 - C_e}{W} \times V$$

$$R\% = \frac{C_0 - C_e}{C_0} \times 100$$

C_0 represents the initial concentration, C_e dye balance dosage in equilibrium point (mg/l), W weight of the absorbent (g), V volume of the solution (L) and q_e the amount of absorbed material (mg/l).

Kinetics and Isotherm models

Adsorption kinetics using pseudo-first order and pseudo-second order equations and Ellovich was investigated by linear analysis method.

Pseudo-first order equation is expressed as follows [5]:

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

In this equation, *qe* and qt respectively represents adsorption capacity on the equilibrium point and time (mg/l). By drawing the log (*qe-qt*) chart, according to *t* it is possible to determine k_f and q_e through slope and intercept charts.

Pseudo-second order kinetics is expressed as follows [5]:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}$$

K_2 is pseudo-second constant (g/mg.min), q_e the amount of absorbed item in the balance point (mg/g) and q_t is the amount of absorbed item in t. now it is possible to determine k_2 and q_e.

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

By drawing q_t in front of *In(t),* if the Ellovich equation is applicable, the relationship between q_t and *In(t)* will be direct and linear.

Adsorption isotherm was investigated by Freundlich and Langmuir models.

Langmuir isotherm is expressed as follows [5]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_l q_e}$$

In this equation q_e represents equilibrium adsorption capacity (mg/g), C_e represents dye concentration at equilibrium time (mg/l) and q_m represents maximum adsorption capacity (mg/g). To investigate the adherence of the adsorption amount of this law, C_e/q_e chart was drawn according to C_e. Then k_l and q_m were calculated using slope and intercept.

Ellovich kinetics is expressed as follows [5]:

Freundlich isotherm is expressed as follows [5]:

$$\log q_e = \log k_f + \frac{1}{n}\log C_e$$

In this equation q_e represents equilibrium adsorption capacity (mg/g), C_e represents dye concentration at equilibrium time (mg/l). *kf* and n are Freundlich constants and by drawing log q_e chart according to log C_e, slope and intercept were calculated.

DISCUSSION AND CONCLUSION

Absorbent properties

FT-IR method is used to identify and study the existing groups in compounds

In Fig 3, FT-IR spectrum of graphene oxide, graphene oxide magnetic, ligand and synthesized absorbent are shown.

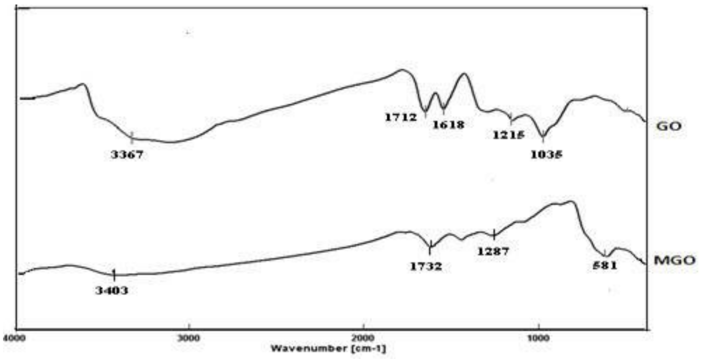


Fig. 3. Graphene oxide and graphene oxide magnetic spectrum pattern.
GO:(1035C-O,1215R-O,1618C=C,1712C=O,3376 OH)

Effect of absorbent's amount

To investigate the effect of the amount of the absorbent, different amounts of the absorbent (0.005 to 0.03g) were studies at environmental temperature (25 ° C), the initial concentration of 50 mg/l, pH 7 and contact time of 10 minutes. With the increasing amount of absorbent from 0.005 to 0.2 g the amount of methyl violet (%) loss rate increases intensely (as shown in Fig 3) and there is no visible change with the increase of the absorbent. This increase is due to increased active sites and the availability of more absorbing locations.

The optimum value was determined to be 0.2 g according to Fig 4.

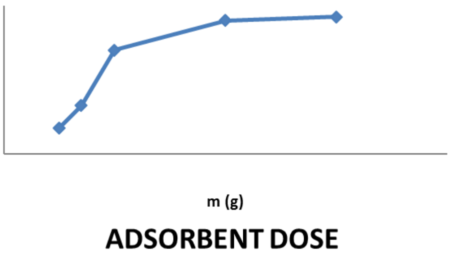


Fig. 4. The effect of absorbent amount to the amount of methyl violet loss.

Investigating adsorption kinetics

Contact time is another important parameter in the adsorption studies. Results of the effects of time on dye dosage are shown in Fig 5. Dye adsorption is clearly understood from the slope of the curve in Fig 5. Adsorption pace is high at the beginning of the process, and it slows down as the time goes by and it reaches a fixed amount. This is due to the existence of many empty holes at the beginning of the process which helps the pace of the adsorption. The extraction pace is in a high level. But, after 30 minutes, the empty holes are filled and adsorption process reaches an equilibrium state. There seems to be no change after this stage. That is why 30 minutes time was selected as optimum time.

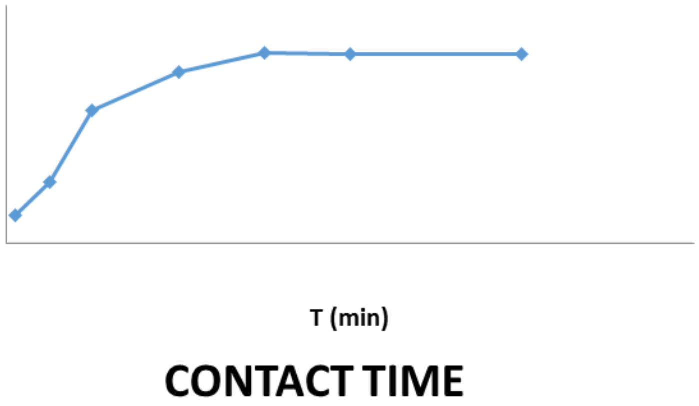


Fig. 5. Adsorption percent according to time

To study the adsorption kinetics of methyl violet, contact times of 1 to 60 minutes at environmental temperature (25 ° C), adsorption amount (0.2 g), initial concentration 50 mg/l and pH of 7 were investigated.

Results show the suitable adsorption speed of methyl violet in the surface of absorbents. The kinetic results were studied by models, pseudo-first order and pseudo-second order. According to Fig 6, due to higher correlation coefficient, pseudo-second order kinetics is better matched with experimental data. Therefore, methyl violet adsorption follows pseudo-second order and according to the thesis' hypothesis, adsorption nature is of chemical reaction and ion exchange [6].

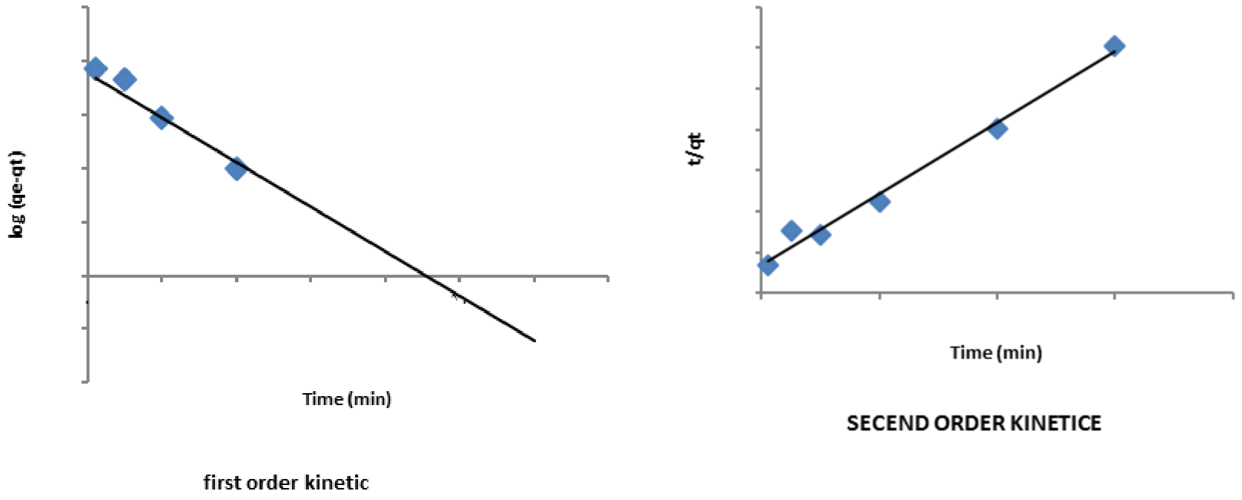


Fig 6 Kinetic study of dye adsorption

pH effect

The amount of adsorption depends on the surface load-absorbing surface of the absorbent [7]. pH parameter, by effecting the surface charge of the absorbent, ionizing the existing materials in solution and decomposing the functional active groups of the absorbent, plays a dominant role in adsorption process [8].

The effect of pH on the adsorption process at (2 to 10 minutes) at environment temperature (25 ° C), 0.2 g of absorbent and initial concentration of 50 mg/l was studied. To adjust the dye solution pH, hydrochloric acid and sodium hydroxide were used.

Results show the higher loss of methyl violet in pH 8, Fig 7

At acidic pH, due to the high level of H+ concentration in the environment and the competition between H+ and cationic molecules and also because of protonation of oxygenated functional groups on absorbent's surface (hydroxyl and carboxyl) adsorption rate was low [9].

In alkaline environments, due to deprotonated carboxyl and hydroxyl groups and changing into –COO and –O ions, there is a high level of adsorption between cationic molecules of methyl violet and the absorbent. As a result, adsorption rate increases. As the pH increases, environment ionic power and the competition between +Na and dye cationic molecule to occupy the adsorbing locations decreases [10].

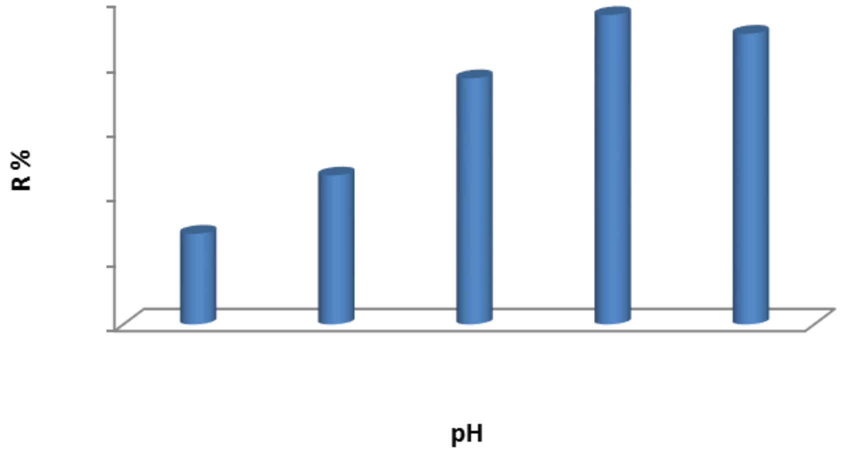


Fig. 7. The effect of pH on the amount of methyl violet dye.

Methyl violet concentration effect and adsorption isotherm

To study the effect of methyl violet, different concentrations of methyl violet 910 to 100 mg/l) at environment temperature (25 ° C), 0.2 g of the absorbent and pH of 8 were used. Langmuir and Freundlich adsorption isotherm were investigated too. According to Fig 8, the less the amount of the dye concentration, the more the amount of adsorption. This is because, there are more empty holes in the absorbent and it is more capable of absorbing the dye. It means that as the dye concentration decreases, the amount of the adsorption increases.

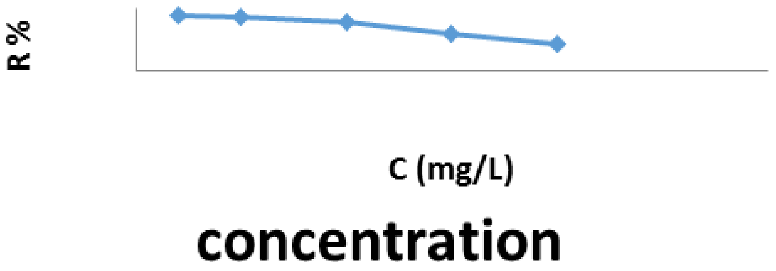


Fig. 8. Adsorption chart based on concentration amount.

Adsorption isotherm is really important and it is used to describe how the interaction between absorbed and absorbent at constant and fixed temperature [5].

Tests results show a suitable speed of methyl violet adsorption on the surface of absorbents. Results of adsorption isotherm were investigated by both Langmuir and Freundlich models. According to Fig 9, due to higher level of correlation coefficient, Freundlich adsorption isotherm shows better match with experimental data. According to theory's hypothesis, dye has been adsorbed in a single layer by the absorbent [6].

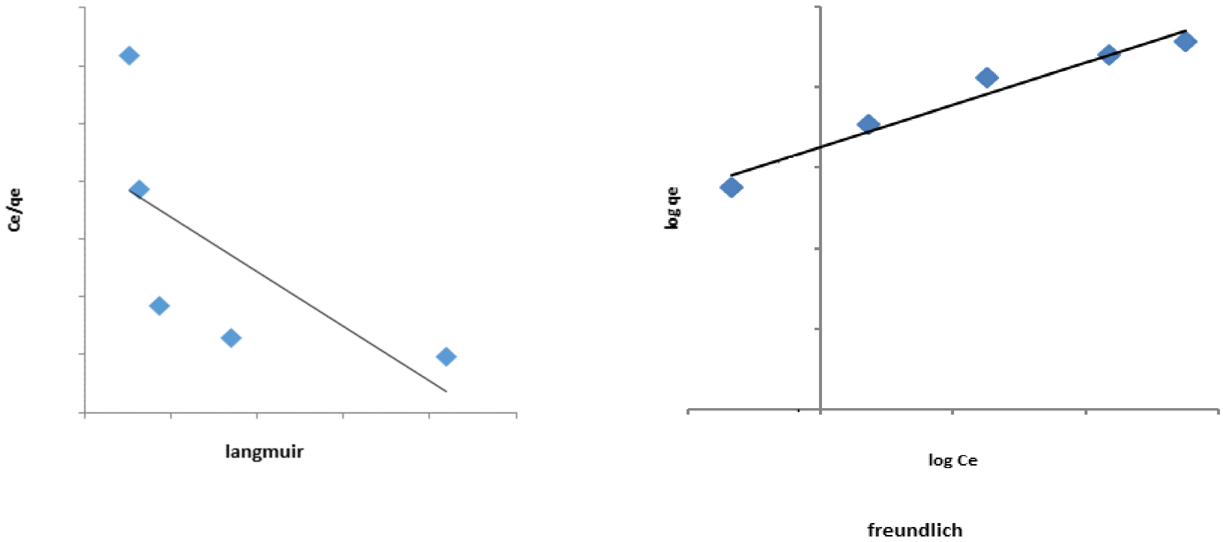


Fig. 9. Investigating the adsorption isotherm.

CONCLUSION

In the present study, the efficiency of methyl violet on the surface of the synthesized absorbent was investigated. The obtained results showed high level of adsorption of methyl violet. In addition, it was construed that N-(3nitrobenzylidene)-4-chlorobenzene amine existing in the structure, shows more tendency to adsorb cationic dye of methyl violet. At environmental temperature (25°C), initial concentration of 50 mg/l, 0.2 g of absorbent, pH of 8 and 50 ml the adsorption was 95.54%. Results also showed that, the adsorption process follows pseudo-second order kinetic and Freundlich isotherms. As a result, both synthesized absorbents are highly useful in adsorption of cationic dyes.

REFERENCES

1. V. Mane, I.D. Mall, V.C. Srivastava, *Dyes & Pigments*, **73,** 278 (2007).
2. X. Xiao, Physica E: L-Dim. Sys. *Nanostructures*, **65**, 12(2015).
3. A. Donia, M. Doni, X. Chen, *J. Haz. Mat.*, **161,** 1550 (2009).
4. J. Deng, X. Zhang, G. Zeng, *Chem. Eng. J.*, **226,** 200 (2013).
5. A. Khaled, S. Salimi, R. Ranzi, *J. Haz. Mat.*, **165,** 110 (2009).
6. H. Boparai, M. Joseph, D. O'Carroll, *J. Haz. Mat.*, **186**, 458 (2011).
7. A. Ofomaja, *Chem. Eng. J.*, **143,** 85 (2008).
8. S. Chowdhury, *Desalination*, **265,** 168 (2011).
9. D. Dreyer, S. Park, C. Bielawski, *J. Chem. Soc. Rev.*, **39**, 240 (2010).
10. C. Cheng, J. Deng, B. Lei, *J. Haz. Mat.*, **263,** 478(2013).