International Journal of Engineering Research-Online
A Peer Reviewed International Journal
Articles available online http://www.ijoer.in

Vol.1., Issue.4, 2013

RESEARCH ARTICLE

ISSN:2321-7758

METHYLENE BLUE ADSORPTION STUDIES ON SYNTHESIZED Ni-Li-Al SPINEL NANO FERRITES

MMVY SWAMY
Lecturer in Chemistry, K.V.R. College, Nandigama, Krishna District, Andhra Pradesh, India

Article Received: 12/09/2013 | Article Revised: 19/11/2013 | Article Accepted: 11/12/2013

ABSTRACT

The main objective of this research work is to study the adsorption of methylene blue (MB) dye solution using $Ni_{0.5}Li_{0.5}Al_{0.5}Fe_2O_4$ (NLAF) nanoferrites synthesized by sol-gel method. Batch adsorption studies were carried out and the effect of experimental parameters like dye solution pH, initial concentration of MB, and contact time were studied. Adsorption isotherms and kinetic studies also conducted which shows that the adsorption follows pseudo second order mechanism. The experimental data fitted well with the Freundlich isotherm (R^2 = 0.974), yielding a maximum adsorption capacity of 45.6mg/g. The optimum adsorbent dose was found to be 4 g/L and stirring experiment reveals that 94% of decolourisation was observed for 40 minutes of stirring at 9.5 pH, which is much more efficient than those reported in literature.

Keywords: Methylene Blue, nanoferrites, Adsorption, Isotherm study, Kinetics, sol-gel method,

Introduction

Contamination of environment with a wide array of organic and inorganic pollutants is a serious health concern. Effluents from the dyeing and finishing processes in the textile industry are known to contain colour, high amounts of surfactants, dissolved solids and possibly heavy metals[1]. The effluents from the dyestuff manufacturing and some similar industries are also generally highly coloured with a large amount of suspended organic solids and hence are the important sources of water pollution. From an environmental point of view, the removal of synthetic dyes is of great concern, since some dyes and their degradation products may be carcinogens and toxic and, consequently, their treatment cannot depend on bio-degradation alone[2]. Hence, decolourisation of dye house effluent via the removal of dyes has become an important aspect of textile wastewater treatment. Many studies have been conducted on the toxicity of dyes and their impact on the ecosystem[3], as well as the environmental issues associated with the manufacture and subsequent usage of dyes[4]. The removal of organic pollutants and dyes from industries remain as a challenge as these dye molecules are difficult to decompose. Varieties of organic and heavy metal pollutants were removed by nano adsorbents by various research groups. Various methods have been devised for the degradation of dyes in aqueous solution. These include adsorption, biological treatment, advanced oxidation process, electrochemical deposition and photocatalysis[5]. All the above said methods are successful to certain extent. Spinels are the class of compounds of the type $M^{2+} M_2^{3+}O_4$, which has attracted researches because of its versatile properties and applications in various fields[6]. When M^{3+}= Fe, we get spinel ferrites with the general formula MFe_2O_4 and the transition metal spinel ferrites are obtained when M = Cu, Fe, Mn, Ni, Zn etc. These spinel ferrites are studied more due to their magnetic property and semiconducting property. Among physical methods, adsorption is very often employed for effective treatment of wastewater. The adsorption consists in attaching of soluble pollutants on a solid material (organic or inorganic support). Therefore, different sorbents such as activated carbon, coal, fly ash, clays, silica, alumina, and chitosan have been employed in dye adsorption studies[7]. Despite their good adsorption performances, the separation and recovery of these adsorbents from heterogeneous systems still remain a drawback. Recently, the magnetic separation technology has attracted attention as a feasible alternative for traditional separation technologies such as settling, centrifugation, or membrane filtration[8]. In this line, ferrites were proposed as potential adsorbents for dyes removal due to their appropriate physical characteristics and facile separation under external magnetic fields. The objective of the research was to investigate the methylene blue (MB) adsorptive removal efficiency of $Ni_{0.5}Li_{0.5}Al_{0.5}Fe_2O_4$ (NLAF) nanoferrites. The effect of parameters such as pH, contact time, and initial solute concentration (Ci) on MB adsorption were studied to determine the optimum conditions.

2.0 Experimental

2.1 Material and Method

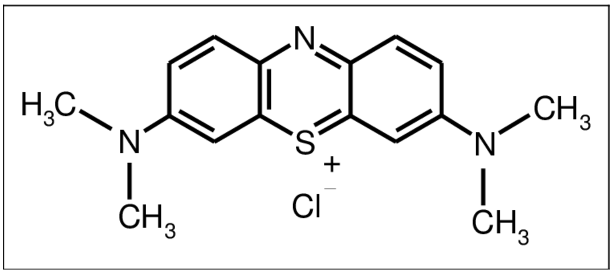
All chemicals and solvents were AR grade or better purchased from Merck Co.Pvt Ltd and Sd. fine chemical used without any further purification. The stoichiometric amounts Citric acid $C_6H_8O_7$, ferric nitrate $Fe(NO_3)_3.9H_2O$ (99%), nickel nitrate $Ni(NO_3)_2.6H_2O$ (99.8%),– Al $(NO_3)_3$ $9H_2O$ (98%) and Lithium nitrate ($LiNO_3$) used as starting materials for the synthesis of NLAF spinel nanoferrites by sol-gel auto combustion technique.

2.2 Synthesis of nanoparticles

Required stoichiometric quantities of metal nitrates were dissolved in a minimum quantity of distilled water and mixed together. Aqueous solution of Citric acid was then added to the mixed metal nitrate solution. Ammonia solution was then added with constant stirring to maintain pH of the solution at 7.0. The resulting solution was continuously heated on the hot plate at 100°C up to dryness with continuous stirring. A viscous gel has resulted, increasing the temperature up to 250°C lead the ignition of gel. The dried gel burnt completely in a self propagating combustion manner to form a loose powder. The burnt powder was ground in Agate Mortar and Pestle to get a fine ferrite powder. Finally the burnt powder was calcinated in air at 750°C temperature for six hours and cooled to room temperature.

Adsorbate

Methylene blue, a cationic dye supplied in powder form by Merck India, was used without further purification for the preparation of synthetic aqueous solution (100 mg/L) using distilled water. Its molecular formula is $C_{16}H_{18}N_3SCl$ and the structure is:



The chemical structure of methylene blue

Adsorption Study:

A stock solution of methylene blue (1000 mg/L) was prepared and suitably diluted to the required initial concentrations. Adsorption experiments were carried out at room temperature (30±1°C) under batch mode. The initial concentrations (Ci) of MB were obtained by measuring O.D. at 663 nm (? max) (Figure 1) using Elico UV–visible spectrophotometer (Model: SLI59). Exactly 50 ml of MB solution of known initial concentration (Ci range: 5 to 100mg/L) was shaken at the constant agitation speed (500 rpm) with a required dose of NLAF (4g/L), for a specific period of contact time (range: 5-45 minutes) in a magnetic shaker, after noting down the initial pH of the solution (pH=7.0). The pH of the solutions were adjusted to the required value (range:3-9.5) by adding either 1 M HCl or 1 M NaOH solution. After equilibration, the final concentrations (Ce) were measured at 663nm by spectrophotometeric method (Elico UV visible spectrophoto meter— Model: SL159). The percentage removal of dye and amount adsorbed (in mg/g) were calculated using the following relationships:

Percentage removal (%R) $= \frac{(Ci - Ce)}{Ci} \times 100$

Amount adsorbed (mg/g) $= \frac{Ci - Ce}{m}$

where Ci and Ce are the initial and final concentrations (in mg/l) of dye, respectively and m is the mass of NLAF (in mg/l). Blanks containing no dye were used for each series of experiments as controls. The average values of duplicate runs were obtained and analysed. Error in data: 1– 2% for percentage removal 0.005–0.01 mg/g for amount adsorbed.

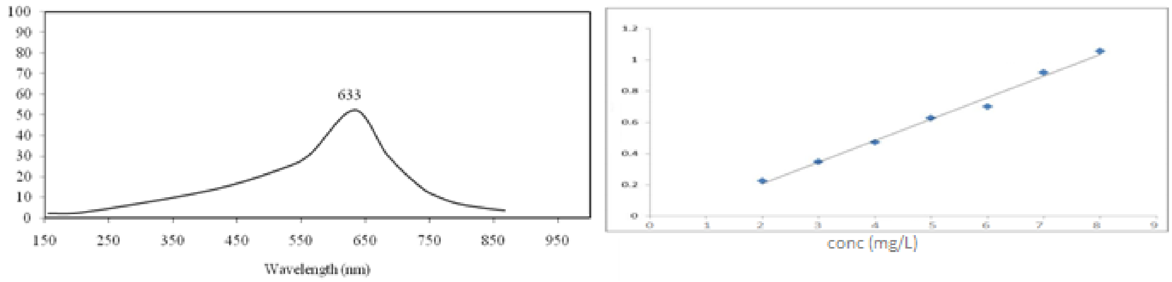


Figure: 1: UV Visible spectra of MB (right) and Calibration curve and wavelength for methylene blue dye adsorption study (left)

RESULTS AND DISCUSSION

Effect of pH

The effect of pH on methylene blue dye (MB) adsorption by NLAF synthesized by sol gel method over a pH range of 3-9.5 at 30±1^{o}C with agitation of 250 rpm is illustrated in Figure 2.

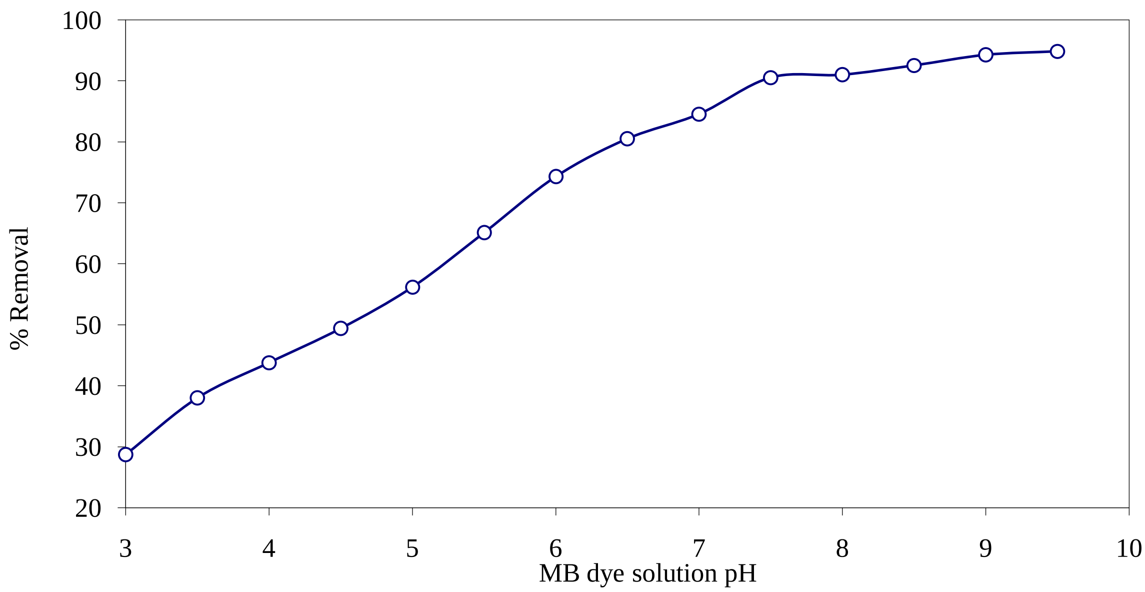


Figure 2: Effect of pH on methylene blue dye adsorption

The results indicated that the adsorption capacity of NLAF for solution of initial concentration 50 mgl/L reached the maximum value at pH 9.5. The increase in initial pH increases the amount of dye adsorbed. The final pH of the solution was found to decrease slightly (by 0.5 pH units) after adsorption of MB as MB+ cationic form with the release of H+ ion from the active site of the adsorbent surface. The results are in harmony with the literature reports[9]. The adsorption of dye increases with increase in pH from 3 to 9.5 (Santhi and Manomani 2009)[10]. Bazrafshan et al (2012)[11] reported that when the pH increased, the adsorbed MB also increased. So, pH 9.5 is selected for future experiments.

Effect of MB initial concentration

The adsorption data for the uptake of MB versus initial dye concentration are presented in figure 3.These results indicate that the amount of dye adsorbed per unit mass of adsorbent increased with increase in MB concentration. This is due to increase in the driving force of concentration gradient, as an increase in the initial dye concentration[12].

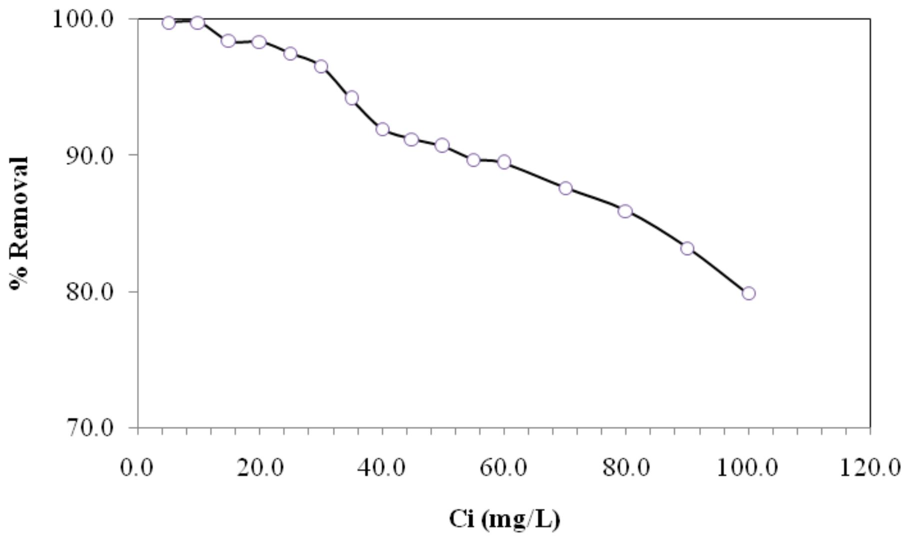


Figure 3: Effect of initial dye concentration of MB on the adsorbent

Removal Efficiency The effect of the initial concentration of the MB dye on the adsorption efficiency of the produced NLAF nanoparticles was evaluated at different concentrations of 5-100 mg/L. As Figure 3 reveals, one of the effective factors in the rate of dye uptake was the initial dye concentration of MB. It should be noted that all the experiments were carried out at pH= 9.5 which was revealed as the most efficient in the test of the best pH. In the present study, with the increase of the initial concentration from 5 mg/L to 55 mg/L, the rate of dye removal was reduced from 100 % to 81.4%. In addition, as the pollutant concentration increased in the aquatic environment, the number of the available sites on the adsorbent surface decreased.[13] In other words, with the decrease of the pollutant concentration in the aquatic environment, molecules of the adsorbate have more chance to react with the available active sites on NLAF nanoparticles and, as a result, the adsorption rate is increased. Hence, one can claim that one method to increase the percentage of dye removal is dilution of wastewater[14].

Adsorption Isotherms study

The adsorption capacity of the adsorbent, the solute-solution interaction and the degree of accumulation of adsorbed materials on the surface of the adsorbent can be explained from adsorption isotherm. Data from a batch adsorption experiment which conducted under constant pH and temperature were collected and analyzed using Langmuir and Freundlich adsorption isotherm.

The following Langmuir isotherm is used to predict the sorption of compound in aqueous solution onto a solid phase at constant temperature[15]:

Langmuir isotherm : $(Ce/qe) = (1/ab) + (Ce/a)$

where qe (mg/g) is the amount of adsorbed materials per unit weight of the adsorbent at equilibrium concentration, Ce (mg/L).The a (mg/g) and b (L/mg) are the Langmuir constants related to the maximum monolayer capacity and energy of adsorption respectively.

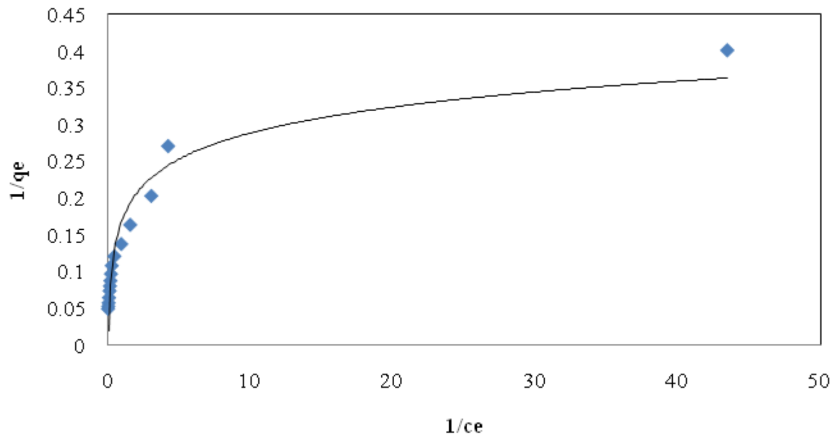


Figure 4: The linear Langmuir adsorption isotherms for MB ion adsorption by the NLAF.

Freundlich isotherm is assuming that the adsorption process takes place on a heterogeneous surface. The linear form is derived by taking the natural log of the term to give Equation.[16]:

Freundlich isotherm : $log\ qe = log\ Kf + (1/n)\ log\ Ce$

K_f (L/mg) value in Equation is an indicator of the adsorption capacity, and 1/n is the adsorption intensity and indicates both the relative distribution of energy and the heterogeneity of the adsorbent sites.

Table 1: Langmuir and Freundlich isotherm constants

Isotherms	Constants/correlation coefficients	Values
Langmuir	R^2	0.950
	q_e	45.24
	K_L	0.171
Freundlich	R^2	0.974
	K_f	45.67
	n	0.357

The values of K_f and 1/n have been obtained from the linear correlations of log Qe against log Ce (Figure 5) and the Langmuir constants have been also determined from the linear correlations of 1/Qe against 1/Ce (Figure 4). As mentioned above, maximum adsorption capacity for the NLAF sample can be obtained using Langmuir equation. In this context, reaction conditions that were applied in this part were as follows: temperature was 25°C, pH 5.5, and the initial concentration of mb was 50 mg/L The amount of the used NLAF sample ranged from 0.05 to 0.20 g with increasing rate of 0.05 g for each dose. The obtained results for the isotherms constants are summarized in Table 1. These results are represented graphically in Figures 4 and 5 as against. These results were more fitted with Freundlich isotherm. This arises from a high value of correlation coefficient for these results.

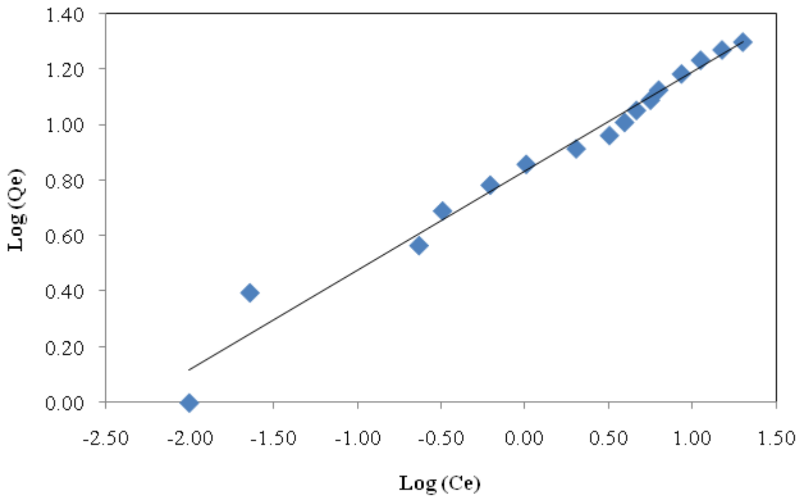


Figure 5: The linear Freundlich adsorption isotherm for MB adsorption by the NLAF

Effect of Contact Time

In adsorption system, the contact time plays a vital role irrespective of the other experimental parameters, affecting the adsorption kinetics. Figure 7 depicts the effect of contact time on the percent removal of MB dye. Solution having MB concentration 50 mg/L and 4g of adsorbent were used for this experiment. To observe the time taken for the maximum adsorption of the dye on NLAF nanoadsorbent, we carried out the experiment at different time intervals by keeping constant weight of 4g/L ferrite nanoparticle and the experiment was carried out by varying time of contact(5 min to 45 min). The maximum removal was achieved in 40 min for all the three adsorbents. The results also showed the amount of MB adsorbed increased with time and reached the saturation after 40 minutes.

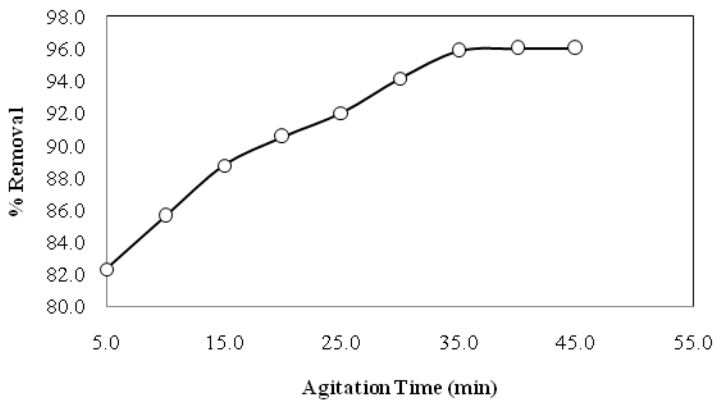


Figure 6: Effect of contact time on methylene blue dye adsorption at room temperature

It can be concluded that adsorption rate of dye Methylene Blue increases sharply at short contact time and slowed gradually as equilibrium was approached. It may be due to the availability of initial large number of vacant surface active sites for adsorption and adsorption rate is very fast. As equilibrium was approached, the filling of vacant sites becomes difficult due to repulsive forces between dye Methylene Blue adsorbed on solid surface and dye Methylene Blue from solution.

In batch type adsorption systems, monolayer of adsorbate is normally formed on the surface of adsorbent and the rate of removal of adsorbate species from aqueous solution is controlled primarily by the rate of transport of the adsorbate species form the exterior/outer sites to the interior sites of the adsorbent particles[17].

Adsorption Kinetic Study

The study of adsorption kinetics describes the solute up take rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface .The kinetics of MB dye adsorption on the NLAF nanoparticles were analyzed using pseudo first-order, pseudo second-order and intra-particle diffusion kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation co- efficient (R^2) and the values are close or equal to 1. A relatively high correlation coefficient value indicates that the pseudo second-order model successfully describes the kinetics of MB dye adsorption.

In order to investigate the mechanism of dye Methylene Blue sorption, three models were used in this study. The linear pseudo-first-order model of Lagergren is given as follows[18]:

$$\ln qe - qt = \ln qe - k_1 \times t$$

Where qe and qt are the amounts of dye Methylene Blue absorbed onto the adsorbent (mg/g) at equilibrium and at t respectively. k_1 is the rate constant of first-order adsorption (min^{-1}). The logarithmic term ln (qe-qt) indicates that qe is given a maximum measured value. From the data plotted in Figure 7, the maximum value is shown by the second last data point measured at 40 min. So for NLAF qe =0.135 mg/g and the data in Figure 7, plotted according to equation (above), is shown in Figure 7. It is clear from the value of R^2 (0.949) that the linear fit is satisfactory.

The pseudo-second-order kinetic model developed by Ho and McKay[19] is based on the experimental information of solid-phase sorption. The linear pseudo-second-order model can be expressed as follows:

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

Where k_2 is the rate constant of second-order adsorption ($g \cdot mg^{-1} \cdot min^{-1}$). If second–order kinetics was applicable, the plot of t/qt versus t should show a linear relationship. There is no need to know any parameter beforehand and qe and k2 can be determined from the slope and intercept of the plot. Also, this procedure is more likely to predict the behavior over the whole range of adsorption. The linear plots of t/qe versus t (fig 8) showed a good agreement towards adsorption process. The correlation coefficient for the second–order kinetic model was greater than 0.999, indicating the applicability of this kinetic equation and the second-order nature of the adsorption process of MB on activated carbon. The kinetic data fitted closely with the pseudo-second order reaction, indicating that MB adsorption onto NLAF is chemisorptions.

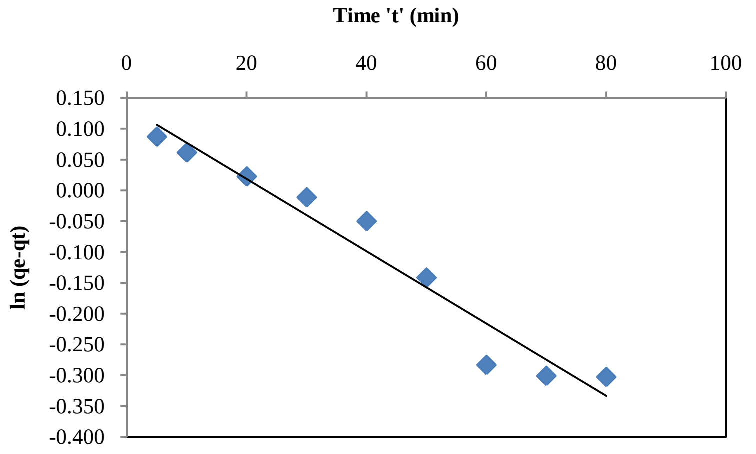


Figure 7: Pseudo first- order kinetic plot for the adsorption of methylene blue onto NLAF

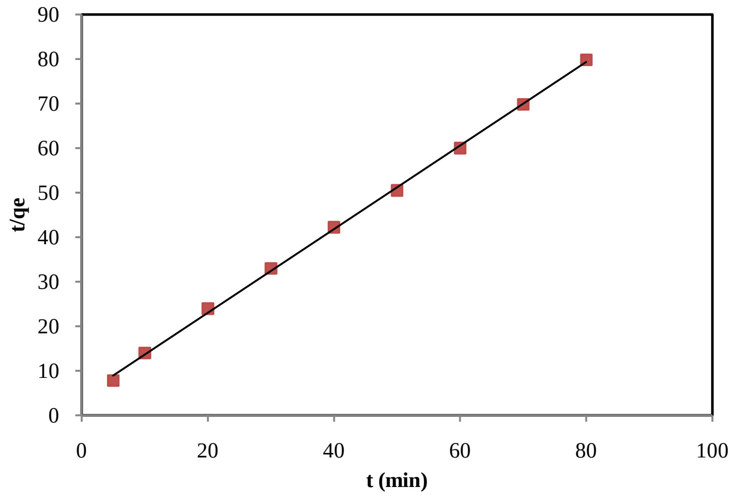


Figure 8: Pseudo second- order kinetic plot for the adsorption of methylene blue onto NLAF

The intra particle diffusion model The intra-particle diffusion model used here refers to the theory proposed by Weber and Morris [23] based on the following equation for the rate constant:

$$q_t = k_{id}\, t^{(1/2)} + C$$

Where kid is the intra-particle diffusion rate constant (mg/g/min) and C is the constant. If the rate limiting step is intra-particle diffusion, then the graph drawn between (qt) (mg/g) verses square root of the contact time ($t^{1/2}$) should yield a straight line passing through the origin. The slope of the will give the value of the intra-particle diffusion coefficient (kid) and correlation coefficient (R^2= 0.937) indicate the fitness of this model. The value of C gives an idea about the thickness of the boundary layer. From these data the intercept value indicate that the line were not passing through origin, there are some other process affect the adsorption. But the correlation coefficient (R^2) value is very high, so that the intra-particle diffusion takes place along with other process that may affect the adsorption.

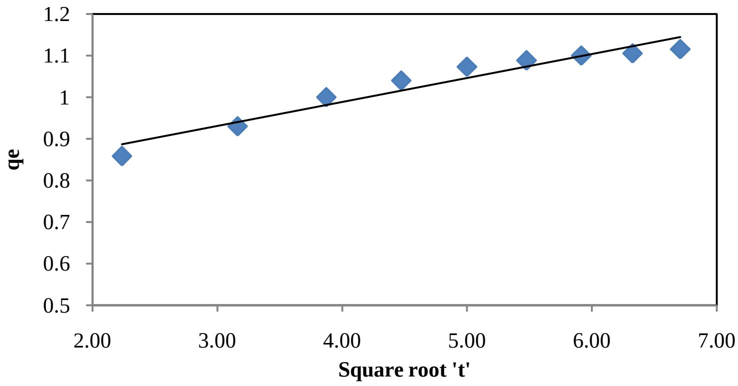


Figure 9: intraparticle diffusion model for adsorption of dye Methylene Blue onto NLAF

Conclusion

Dyes are widely used in the industry such as textile, plastic, paper or cosmetics in order to colour their products. Methylene blue dye (MB) with cationic structure is widely used as a coloring agent and is one of the major causes of pollution in the waste water. It can also have harmful effects on living organisms. It causes nausea, vomiting and difficulty in breathing. Therefore, the necessity of an effective and economically viable waste water treatment method is an important subject of study. Many adsorbents have been studied for the decolorizing of waste water. Many studies have reported the use of different ferrite nanoparticles, synthesized by various methods as adsorbents due to their reduced cost, high surface area and easily recovery. The aim of this work was to study the adsorption of MB on $Ni_{0.5}Li_{0.5}Al_{0.5}Fe_2O_4$ (NLAF) nanoferrites synthesized sol gel method. The present study has shown the effectiveness of using NLAF in the removal of methylene blue dye from aqueous solutions. The adsorption capacity of the contaminant on the surface of the NLAF increases with increasing pH, always when working at acid pH value intervals. Since the MB solution is at basic pH values, the MB adsorption capacity remains constant; the pseudo-second-order model presented the best fit to the data obtained from the adsorption kinetics of MB on the Adsorbent surface; It was shown that the adsorption isotherm studies showed that Freundlich isotherm fits better than the Langmuir isotherm. The pseudo-second order kinetic model better described the sorption data.

References

1 Grau P. Textile industry wastewaters treatment. Water Sci Technol 1991;24:97.

2 Pagga U, Braun D. The degradation of dye stuffs: part II. Behaviour of dyestuffs in aerobic biodegradation tests. Chemosphere 1986;15:479

3 Shenai VA. Azo dyes on textiles vs German ban: an objective assessment. Part III another study. Colourage 1996;XLIII(8):41

4 Saha C. Eco-textile: a novel concept of clearner product. Textile Dyer Printer 1996;XXIX(21):13

5 Ali, I.: New generation adsorbents for water treatment. Chem. Rev. **112**, 5073–5091 (2012)

6 Sugimogo, M.: Past, present & future of ferrites. J. Am. Ceram. Soc **82**, 269–280 (1999)

7 E. Forgacs, T. Cserhati, and G. Oros, “Removal of synthetic dyes ´ from wastewaters: a review,” Environment International, vol. 30, no. 7, pp. 953–971, 2004

8 W. Konicki, D. Sibera, E. Mijowska, Z. Lendzion-Bielun, and ´ U. Narkiewicz, “Equilibrium and kinetic studies on acid dye Acid Red 88 adsorption by magnetic ZnFe2O4 spinel ferrite nanoparticles,” Journal of Colloid and Interface Science, vol. 398, pp. 152–160, 2013

9 Deo N, Ali M. Adsorption by a new low cost material: congo red 1 and 2. Indian J Environ Protec 1997;17(5):328.

10 Santhi T and Manomani (2009) Removal of methylene blue from aqueous solution by bioadsorption onto riccinnus communis epicarp activated carbon. Chem Engg Res Bull 13: 1-11

11 Bazrafshan E, Mostafapour K F and Zazouli A M (2012) Methylene blue adsorption into salvadora persica stems ash. African J Biotech. 11: 16661-68.

12 Hameed B. H.,Ahmed A. L., Latiff, K. N. A., Dyes and pigments 75 (2007) 143.

13 Yang J, Qiu K. Preparation of activated carbons from walnut shells via vacuum chemical activation and their application for methylene blue removal. Chem Eng J. 2010; 165(1): 209-17

14 Kalyani G, Babu Rao G, Vijaya Saradhi B. Equilibrium and kinetic studies on biosorption of zinc onto gallus domesticus shell powder. ARPN J Eng Appl Sci. 2009;4(1): 39-49.

15 M. S. El-Geundi. 1991. Colour removal from textile effluents by adsorption techniques. Water Research. 25(3): 271-273.

16 T. M. Elmorsi. 2011. Equilibrium isotherms and kinetic studies of removal of methylene blue dye by adsorption onto miswak leaves as a natural adsorbent. Journal of Environmental Protection,2(6): 817-827.

17 Weber WJ, Morris JC. In: Eckenfelder WW, editor. Advances in water pollution research. Oxford: Pergamon Press, 1964.

18 N.Thinakaran, P.Panneerselvam, P.Baskaralingam, D.Elango, S.Sivanesan; ‘Equilibrium and kinetic studies on the removal of acid red 114 from aqueous solutions using activated carbons prepared from seed shells’, J.Hazard.Mater., 158, 142-150 (2008)

19 Y.S.Ho, G.Mckay; ‘Kinetic models for the sorption of dye from aqueous solution by wood’, Trans.Inst.Chem.Eng.B, 76, 183-191 (1998).