Available online at www.IJournalSE.org

Emerging Science Journal

Vol. 3, No. 3, June, 2019

Investigation of Carmine Dye Removal by Green Chitin Nanowhiskers Adsorbent

Seyyed Salar Meshkat [a*], Mojtaba Nasiri Nezhad [a], Mohammad Reza Bazmi [b]

[a] *Faculty of Chemical Engineering, Urmia University of Technology, Urmia, Iran*

[b] *Department of Chemical engineering, Payame Noor University, Tehran, Iran*

Abstract

A green adsorbent was evaluated to remove the carmine dye. Chitin nanowhiskers were synthesized via acid hydrolyzed method. The diameter of the synthesized chitin whiskers was about 20 nm and had 200 to 400 nm length. The morphology and chemical structure of the synthesized adsorbent were investigated by Field Emission Scanning Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM), Fourier Transform Infrared (FT-IR), X- Ray Diffraction (XRD). The adsorption process parameters of the carmine dye removal were optimized as follow: adsorption time (3 h), initial carmine dye solution concentration (100 ppm), mass loaded of the chitin whiskers suspension 1% weight of chitin nanowhiskers, as an adsorbent (1.4 g). The removal efficiency of the carmine dye adsorption was about 85% which is modified 15% better than the previous researches. The results indicated that carmine dye molecules were absorbed by hydrogen bonding mechanism due to the N-H bond in the chitin nanowhiskers structure.

Keywords:

Adsorption;
Dye Removal;
Carmine;
Nanaochitin.

Article History:

Received:	13	March	2019
Accepted:	19	May	2019

1- Introduction

A very small amount of dye can affect as a toxic material in water and influence the human life. The removal of dye from waste water has an important role in environmental safety [1]. Adsorption is deliberated as well-known as an adsorbent for water and wastewater treatment. Researchers have used chitin as an adsorbent for the removal of dyes and heavy metal contaminants. The morphology and chemistry play an important role on the effectiveness of adsorbents used in adsorption processes [2].

The researchers have announced some chemical and physical methods to remove dye such as coagulation, flocculation, adsorption, photodecomposition and filtration [2-3]. Due to the low cost and high efficiency in removing the various dyes, the adsorption method is so appropriate [4]. Because of the low cost adsorbents such as chitosan, clay, zeolite and coal have introduced in order to remove the organic and inorganic pollution from water effluents [5].

Chitin is the second most abundant polysaccharides in the world that can be produced from waste marine residuals. Because of its low solubility, it prefers to convert to chitosan that is deacetylation product of chitin. Chitin can turn to nanowhiskers through acid hydrolyzed, TEMPO mediated oxidation, ultrasonication, mechanical treatment, persulfate oxidation, ionic liquids and methods. CNW is so similar to cellulose nanowhiskers except in the existence of acetamide group in chitin structure. It is more resistant towards chemical reagents. The CNW has a poor solubility in common solvent. In addition, after cel-9lulose, Chitin is the most mutual and common organic material in nature. Its polysaccharide structure increases the emphasis on environmental application of the chitin [6-9].

S. Kumari et al. designated the chitin extraction and chitosan from Fish Scales. The researchers synthesized the chitin via 1% of HCl solution for 36 h and 0.5 N of NaOH solutions for 18 h for demineralization and deproteinization sections.

* **CONTACT**: S.meshkat@che.uut.ac.ir

DOI: http://dx.doi.org/10.28991/esj-2019-01181

The chitin was rinsed with 50% of NaOH solution for 2 h at 80 °C with oil autoclave [10]. Application of chitin as an adsorbent for dye removal has been investigated in many researches. McKay et al removed acid blue 25 (0.45 mol/kg) and Smith et al. used chitin to remove Acid red 1(0/13 mol/kg) [11-12]. Akkaya et al, could reach 38 mg/g and 65 mg/g adsorbent for reactive yellow 2 and reactive black5, respectively. Dolphen et al, eliminated synthetic reactive dye wastewater 133-167 mg/g chitin. Modification of chitin using sodium hypochlorate let them reach 59-124 mg/g. Prado et al removed Indigo Carmine to 1.24 mol/g chitin. [13]. Some chitin composites also have been used to remove dyes from wastewater, Xu et al. used chitin-clay microsphere to remove 10ppm methylene blue by yield of 99.99% in 20 min [14]. Dassanayake et al. used chitin-MnO2 to remove 20ppm methylene blue with 99% efficiency by 8mg chitin composite [15]. Jesionowski used chitin-lignin composite for removal of direct blue71. They also found that composite adsorbent has better efficiency than alone chitin, so 91% removal was obtained in 1h [16].

With emergence of nanotechnology in many industries, application of chitin Nano whiskers in this region was done by some worthy works. Dhananasekaran et al. used chitin nano particles for removal of three types of dyes. They found that maximum capacity of this type of nanomaterials was 6.9 mg/g, 22.72 mg/g and 8.55 mg/g for methylene blue, bromophenol blue and coomassie brilliant blue respectively [17]. Gopi et al removed crystal violet by nano whiskers with adsorption capacity 39.56 mg/g and yield of 79.13%. Chitin nanocomposites were also used for this purpose. Gopi et al, used electro spun PVDF-CNW (1%-15%) to remove Indigo Carmine contamination. Based on their findings, adsorption capacity was 72.6 mg/g and 88.9% enhanced compared to neat PVDF [18].

In this work, we chose chitin nanowhiskers (CNW) as a green nano adsorbent to remove the carmine dye from waste water. Carmine dye is categorized in organic dyes. They are observed as common pollutants of water which can damage the health of human and ecosystems [2-3]. Due to the structure of the CNW, the high adsorption capacity of the CNW was evaluated by carmine dye removal experiments. The novelty of the synthesized green adsorbent is focused on the high removal efficiency of the carmine dye via low cost method. The effect of the adsorption parameters such as mass loaded of adsorbent; adsorption time and initial concentration of the carmine dye was considered on the removal efficiency.

2- Experimental

2-1- Materials

Chitin powder from shrimp shell was purchased from Sigma. Hydrochloric acid, HCl, potassium hydroxide, KOH acetone and ethanol were labratory grade and purchased from Merck Co. and were used without any purification. Carmine dye was purchased from Merck Co.

2-2- Synthesis of Chitin Nano Whiskers

Chitin Nano whiskers (CNW) from shrimp shells were synthesized with acid hydrolyze method that was reported by Morin and Dufresne [19]. Briefly, 5 g of air dried chitin was added to 100 ml KOH for more deproteinizing in room temperature for 24h. The deproteinized chitin was washed with deionized water until neutral pH achieved and was dried in oven in 60 ^{o}C overnight. Dye removal of chitin was done by adding derived chitin in 200 ml (50:50v/v) ethanol and acetone mixture. Resultant chitin was treated with boiling 3N hydrochloric Acid (30 ml acid/g chitin) for 90 min under reflux. The reaction was squeezed with dilution of mixture with cold deionized water. The slurry was centrifuged for 15 min in 4000 rpm and decanting residue was diluted with deionized water to remove soluble chitin and excess acid. This process was repeated two more times. After this stage the slurry was transferred to dialyze tube (12000 Dalton) and dialyzed against deionized water for 7 days until the pH 6 reached. For better dispersion, the final suspension was sonicated for 30 min in sonication bath and stored in refrigerator in 4 ^{o}C for further uses. The concentration of suspension was set in 1 %. The yield of chitin whisker synthesis was about 65%.

3. Results and Discussion

3-1- Characterization

In order to study the formation of the chitin nanowhiskers, the X-Ray Diffraction (XRD) patterns were taken utilization of Bruker with Cu Kα radiation (λ=1.540 Å) at room temperature. The morphology and particle size of CNW was determined by Field Emission Scanning Electron Microscopy (FESEM) with Mira 3-XMU model with accelerating potential 7.0 kV by Quanta FEG 250 Field Emission Scanning Electron Microscope (FESEM), FEI Company and Transmission Electron Microscopy (TEM) images. The surface bonding and surface chemicals was evaluated by Fourier Transform Infrared (FT-IR) spectra using a Bruker spectrometer in the wavenumber range from 400 to 4000 $cm^{-1}$by KBr pellets. The carmine dye concentration was measured by UV-Visible spectrophotometer. Carmine dye solution was analyzed at 415 nm.

3-2- Characterization of Synthesized Adsorbent

The XRD pattern of the synthesized CNW was presented in Figure 1. The intense peak of CNW was observed at 2θ= 19.6^0 and 9.7^0 [20]. In FTIR pattern (Figure 2) of derived CNW, the peaks at 1620 $cm^{-1}$and 1661 cm^{-1} correspond to amide I regions and peak at 1558 cm^{-1} corresponds to amide II regions of α-chitin [20]. The FESEM and TEM images were shown in Figure 3. It is evident from Figure 3 that the synthesized CNW was in whisker shape and their size was in 20 nm diameter and 300 nm in length.

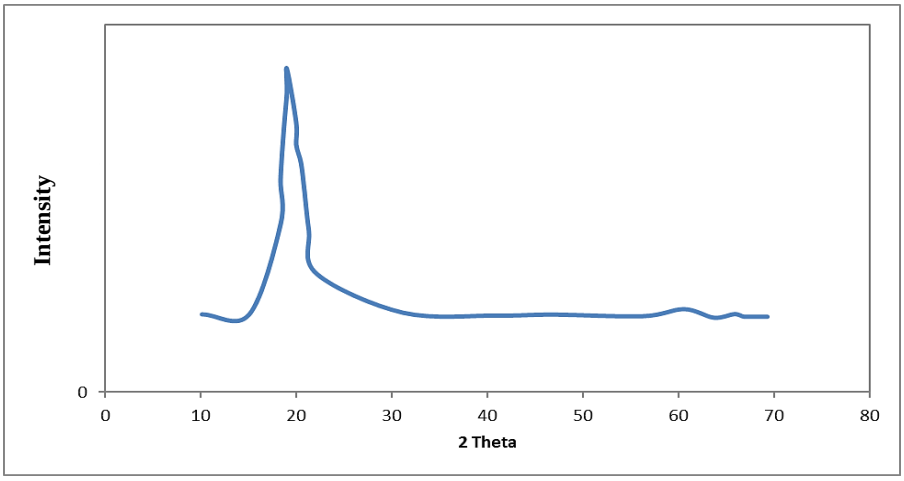

Figure 1. The XRD pattern of CNW.

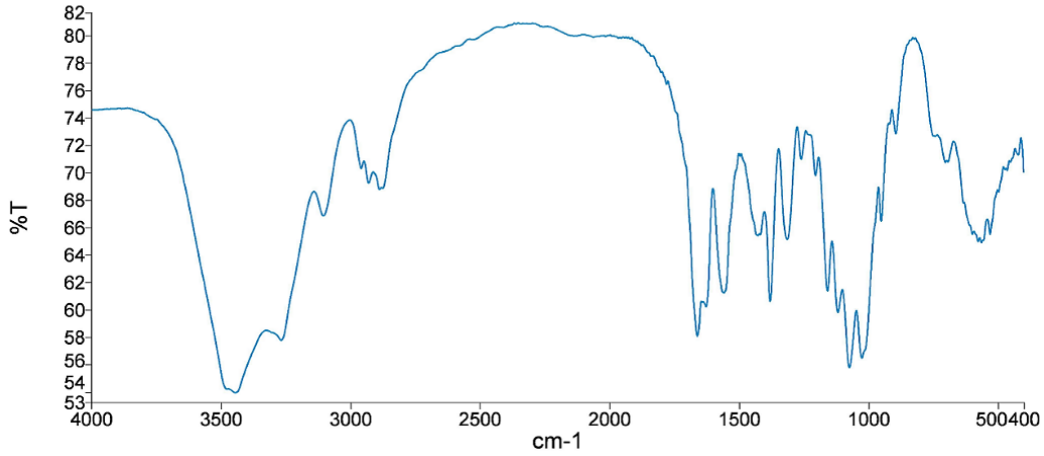

Figure 2. The FTIR pattern of synthesized CNW.

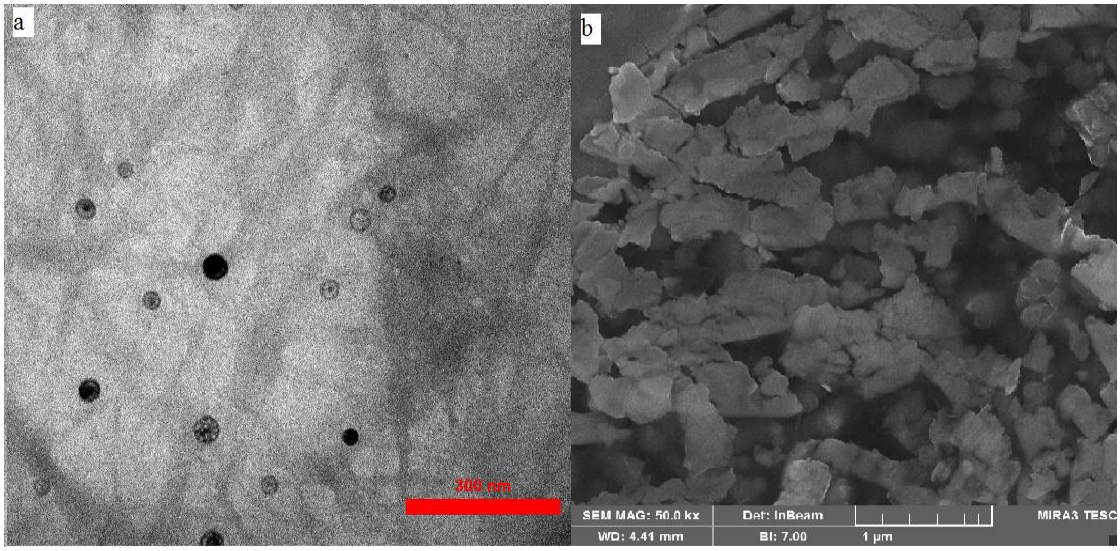

Figure 3. a) TEM image b) FESEM image of the synthesized nanochitin.

3-3- Effect of Mass Loaded

The effect of the adsorbent mass loaded on the dye removal efficiency was studied with various amount of mass adsorbent at 25 ^{0}C for 3 h with 100 ppm. The results were plotted in Figure 4a. The results indicated that by increasing the amount of the mass of the CNW, the removal efficiency increased. Due to the enhancement of the adsorption sites and the hydrogen bond effect the removal efficiency increased. Although the amount of the mass loaded become constant after increasing of the mass loaded to 2 g. The optimum value of the mass loaded to remove the carmine dye by CNW suspension was 1.4 g.

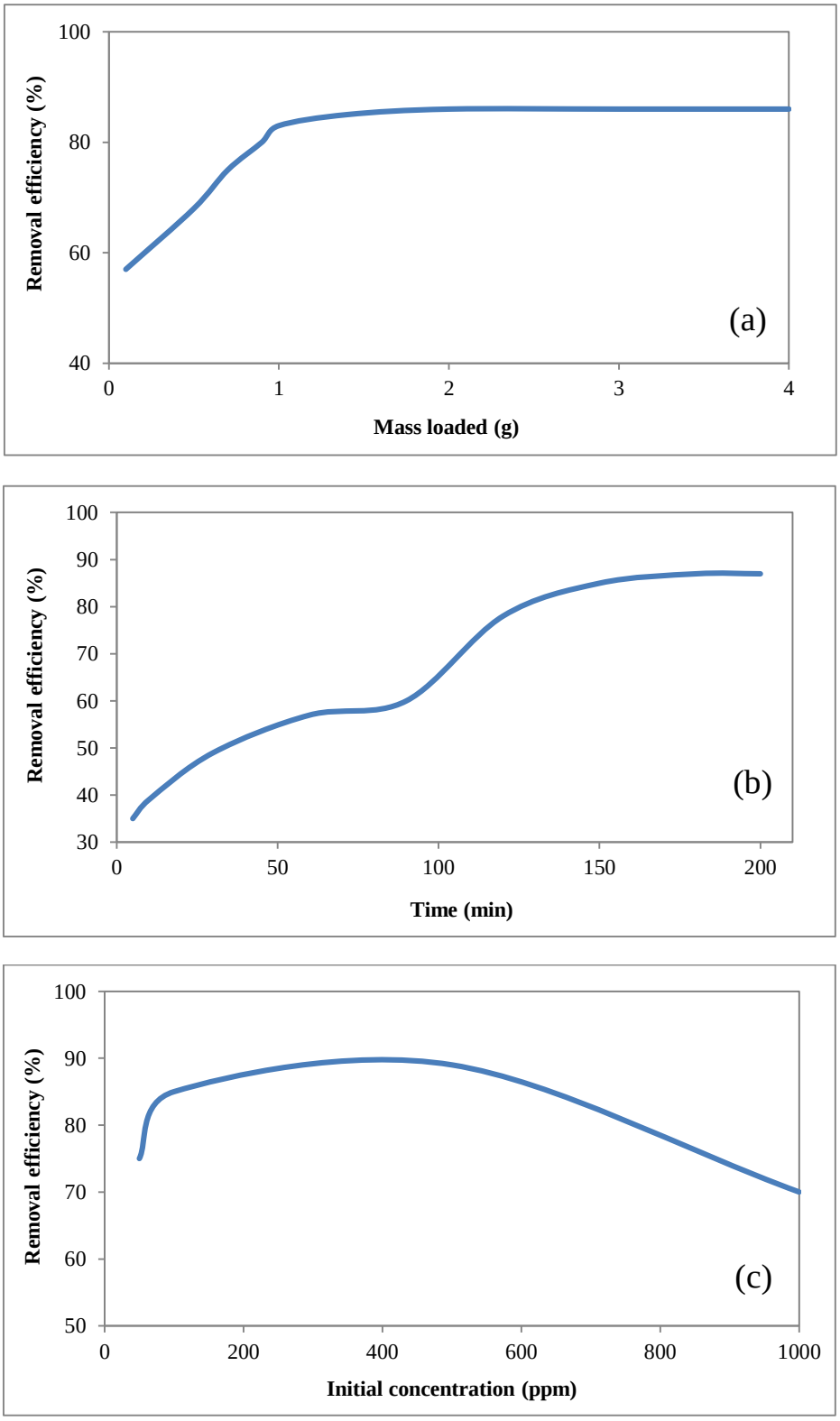

Figure 4. a) The effect of mass loaded; b) Time; c) initial concentration on removal efficiency.

3-4- Effect of Time and Kinetic Study

In order to study the time effect on removal efficiency of the carmine dye adsorption, some experiments were carried out at 25 ^{0}C, 100 ppm and 1.4 g of adsorbent. The results were shown in Figure 4b. The Figure 4b showed that after 180 min, the adsorption removal efficiency process became constant, which indicated the equilibrium time. The equilibrium time of carmine dye removal by CNW was about 180 min. Adsorption takes place rapidly for the adsorbent at the 180 min. This can be explained by hydrogen bonding in N-H bond.

For determination the adsorption process, rate and rate controlling step, and uptake rate of dye were evaluated using of different kinetics models. The results of the adsorption time experiment were used to obtain the adsorption kinetic models. Figure 5 depicts the application of pseudo first order and pseudo second order model to fit the experimental data. The linearized equation of the models is achieved in Equations 1 and 2. The kinetic data were summarized in Table 1. The pseudo second order model was fitted the experimental data [21].

$$Ln(q_e - q) = Ln(q_e) - k_1 t \quad (1)$$

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

Different mechanisms supply and determine adsorption kinetics in which diffusion mechanisms including external diffusion, boundary layer diffusion and intraparticle diffusion are the most effective parameters. The diffusion from bulk to the pores is the rate controlling step in the dye molecules adsorption process [21, 22].

Table 1. The kinetic data of the carmine dye adsorption.

	Pseudo first order			Pseudo second order		
q_e (Experimental) (mg/g)	q_e (mg/g)	K_1(mg/g.min)	R^2	q_e (mg/g)	K_2(mg/g.min)	R^2
78.6	42.5	$5.49*10^{-2}$	0.81	78.4	$3.45*10^{-3}$	1.0

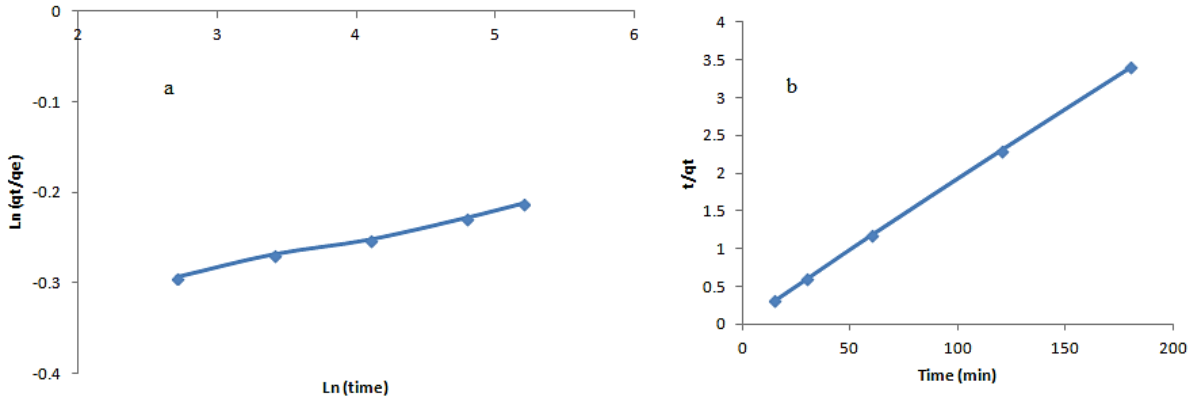

Figure 5. The kinetic data a) pseudo first order; b) pseudo second order.

3-5- Effect of Initial Concentration of Carmine Dye and Isotherm Study

The initial concentration of carmine dye solution affected the removal efficiency and adsorbent capacity. Due to the enhancement of the adsorption driving force in high concentration, the removal efficiency increased by enhancement of the carmine dye initial concentration. But after 500 ppm the removal efficiency declined to 70% in 1000 ppm. It is obvious that in high concentration amounts, the adsorption sites are covered by dye molecules and the sites are occupied [22].

An adsorption mechanism was described by isotherm models. In this study we used the Langmuir and Frendulich models to explain the isotherm investigation. In Table 2 the isotherm data was summarized. The comparison of R^2 (regression coefficient) indicates that the Langmuir model is suitable to illustrate the equilibrium data and is determined to explain the adsorption mechanism. In Figure 6 isotherm models are plotted. The linearized form of Langmuir and Frendulich are given in Equations 3 and 4 respectively [23].

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \quad (3)$$

$$Ln(q_e) = Ln(K_F) + \frac{1}{n} Ln(C_e) \quad (4)$$

In these models, adsorption capacity at equilibrium is corresponded by q_e in mg/g, C_e is the concentration of adsorbent, the solution at equilibrium in mg/l; in Langmuir isotherm, the maximum monolayer adsorption capacity in mg/g is depicted by Q_o, and b is Langmuir constant. In the Frendulich model, K_F and n replicate the Frendulich parameter in which n refers to the evaluation of the adsorbent surface heterogeneity.

The capacity of nanochitin as an adsorbent was considered by Equation 3 [21]:

$$q_e = \frac{C_0 - C_e}{m} * V \quad (3)$$

Table 2. The isotherm parameters of carmine dye adsorption.

	Langmuir				Frendulich		
Adsorbent	**b**	**Q_0**	**R^2**	**R_L**	**K_F**	**n**	**R^2**
CNW	$7.68*10^{-2}$	157.82	0.999	0.257	1.897	2.14	0.890

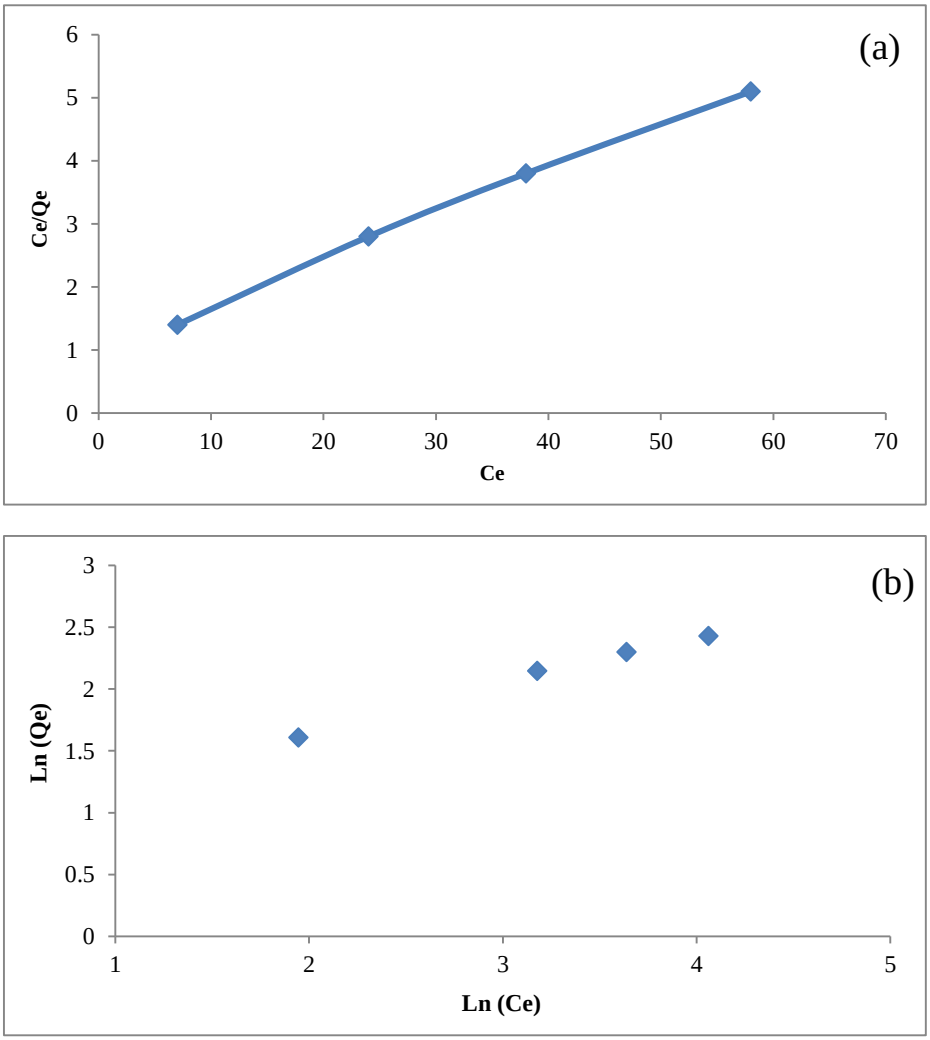

Figure 6. The isotherm data a) Langmuir; b) Frendulich.

4- Conclusion

In this work the functionalized nanochitin was synthesized. The size of the CNW was in 20 nm range. The carmine dye was removed by CNW. The parameters of the adsorption process were studied and the optimum value of the parameters was obtained. The time of the dye adsorption was about 3 h which introduces as an equilibrium time and the

optimum amount of the carmine dye concentration was 100 ppm. The mass of the synthesized nanochitin was obtained 1.4 g. In addition, the nanochitin adsorbed the carmine dye, by formation of the hydrogen band, which caused the fast adsorption process in spite of the previous literatures. The equilibrium adsorbent capacity was about 78.6 mg/g within the 180 min. The Langmuir model was fitted the isotherm data of the adsorption process. The evaluation of the kinetic data indicated that the pseudo second order model was so suitable for the study of kinetic study.

5- Conflict of Interest

The authors declare no conflict of interest.

6- References

[1] Mahdy Samar, M., M.H. El-Kalyoubi, M.M. Khalaf, and M.M. Abd El-Razik. "Physicochemical, Functional, Antioxidant and Antibacterial Properties of Chitosan Extracted from Shrimp Wastes by Microwave Technique." Annals of Agricultural Sciences 58, no. 1 (June 2013): 33–41. doi:10.1016/j.aoas.2013.01.006.

[2] Haldorai, Yuvaraj, and Jae-Jin Shim. "An Efficient Removal of Methyl Orange Dye from Aqueous Solution by Adsorption onto chitosan/MgO Composite: A Novel Reusable Adsorbent." Applied Surface Science 292 (February 2014): 447–453. doi:10.1016/j.apsusc.2013.11.158.

[3] Abd El-Magied, Mahmoud O., Ahmed A. Galhoum, Asem A. Atia, Ahmad A. Tolba, Mai S. Maize, Thierry Vincent, and Eric Guibal. "Cellulose and Chitosan Derivatives for Enhanced Sorption of erbium(III)." Colloids and Surfaces A: Physicochemical and Engineering Aspects 529 (September 2017): 580–593. doi:10.1016/j.colsurfa.2017.05.031.

[4] Shajahan, A., S. Shankar, A. Sathiyaseelan, Karthik S. Narayan, V. Narayanan, V. Kaviyarasan, and S. Ignacimuthu. "Comparative Studies of Chitosan and Its Nanoparticles for the Adsorption Efficiency of Various Dyes." International Journal of Biological Macromolecules 104 (November 2017): 1449–1458. doi:10.1016/j.ijbiomac.2017.05.128.

[5] Tran, Hai Nguyen, Sheng-Jie You, Ahmad Hosseini-Bandegharaei, and Huan-Ping Chao. "Mistakes and Inconsistencies Regarding Adsorption of Contaminants from Aqueous Solutions: A Critical Review." Water Research 120 (September 2017): 88–116. doi:10.1016/j.watres.2017.04.014.

[6] Zeng, Jian-Bing, Yi-Song He, Shao-Long Li, and Yu-Zhong Wang. "Chitin Whiskers: An Overview." Biomacromolecules 13, no. 1 (December 20, 2011): 1–11. doi:10.1021/bm201564a.

[7] Kadokawa, Jun-ichi, Akihiko Takegawa, Shozaburo Mine, and Kamalesh Prasad. "Preparation of Chitin Nanowhiskers Using an Ionic Liquid and Their Composite Materials with Poly(vinyl Alcohol)." Carbohydrate Polymers 84, no. 4 (April 2011): 1408–1412. doi:10.1016/j.carbpol.2011.01.049.

[8] M. Mincea, A. Negrulescu, V. Ostafe, Preparation, Modification, and Applications of Chitin Nanowhiskers: A Review, Rev. Adv. Mater. Sci. 30 (2012) 225-242. http://eproceedings.chemistry.utm.my.

[9] Oun, Ahmed A., and Jong-Whan Rhim. "Effect of Isolation Methods of Chitin Nanocrystals on the Properties of Chitin-Silver Hybrid Nanoparticles." Carbohydrate Polymers 197 (October 2018): 349–358. doi:10.1016/j.carbpol.2018.06.033.

[10] Kumari, Suneeta, and Pradip Kumar Rath. "Extraction and Characterization of Chitin and Chitosan from (Labeo Rohit) Fish Scales." Procedia Materials Science 6 (2014): 482–489. doi:10.1016/j.mspro.2014.07.062.

[11] McKay, G., H. S. Blair, and J. R. Gardner. "Adsorption of Dyes on Chitin. I. Equilibrium Studies." Journal of Applied Polymer Science 27, no. 8 (August 1982): 3043–3057. doi:10.1002/app.1982.070270827.

[12] Smith, Brent, T. Koonce, and S. Hudson. "Decolorizing dye wastewater using chitosan." American Dyestuff Reporter 82, no. 10 (1993): 18-36.

[13] Bhatnagar, Amit, and Mika Sillanpää. "Applications of Chitin- and Chitosan-Derivatives for the Detoxification of Water and Wastewater — A Short Review." Advances in Colloid and Interface Science 152, no. 1–2 (November 2009): 26–38. doi:10.1016/j.cis.2009.09.003.

[14] Xu, Rui, Jie Mao, Na Peng, Xiaogang Luo, and Chunyu Chang. "Chitin/clay Microspheres with Hierarchical Architecture for Highly Efficient Removal of Organic Dyes." Carbohydrate Polymers 188 (May 2018): 143–150. doi:10.1016/j.carbpol.2018.01.073.

[15] Dassanayake, Rohan S., Erandathi Rajakaruna, Hanna Moussa, and Noureddine Abidi. "One-Pot Synthesis of MnO 2 –chitin Hybrids for Effective Removal of Methylene Blue." International Journal of Biological Macromolecules 93 (December 2016): 350–358. doi:10.1016/j.ijbiomac.2016.08.081.

[16] Wawrzkiewicz, Monika, Przemysław Bartczak, and Teofil Jesionowski. "Enhanced Removal of Hazardous Dye Form Aqueous Solutions and Real Textile Wastewater Using Bifunctional Chitin/lignin Biosorbent." International Journal of Biological Macromolecules 99 (June 2017): 754–764. doi:10.1016/j.ijbiomac.2017.03.023.

[17] Dhananasekaran, Solairaj, Rameshthangam Palanivel, and Srinivasan Pappu. "Adsorption of Methylene Blue, Bromophenol Blue, and Coomassie Brilliant Blue by α-Chitin Nanoparticles." Journal of Advanced Research 7, no. 1 (January 2016): 113–124. doi:10.1016/j.jare.2015.03.003.

[18] Gopi, Sreerag, Preetha Balakrishnan, Anitha Pius, and Sabu Thomas. "Chitin Nanowhisker (ChNW)-Functionalized Electrospun PVDF Membrane for Enhanced Removal of Indigo Carmine." Carbohydrate Polymers 165 (June 2017): 115–122. doi:10.1016/j.carbpol.2017.02.046.

[19] Morin, Arnaud, and Alain Dufresne. "Nanocomposites of Chitin Whiskers fromRiftiaTubes and Poly(caprolactone)." Macromolecules 35, no. 6 (March 2002): 2190–2199. doi:10.1021/ma011493a.

[20] PM V, Thomas S. "Preparation and characterization of chitin nanowhiskers and their polymer nanocomposites." Int J Polym Technol 3, no. 1 (2011): 35-44.

[21] Pang, Jiabin, Fenglian Fu, Zecong Ding, Jianwei Lu, Na Li, and Bing Tang. "Adsorption Behaviors of Methylene Blue from Aqueous Solution on Mesoporous Birnessite." Journal of the Taiwan Institute of Chemical Engineers 77 (August 2017): 168–176. doi:10.1016/j.jtice.2017.04.041.

[22] Gupta, V. K., O. Moradi, I. Tyagi, S. Agarwal, H. Sadegh, R. Shahryari-Ghoshekandi, A. S. H. Makhlouf, M. Goodarzi, and A. Garshasbi. "Study on the Removal of Heavy Metal Ions from Industry Waste by Carbon Nanotubes: Effect of the Surface Modification: a Review." Critical Reviews in Environmental Science and Technology 46, no. 2 (June 18, 2015): 93–118. doi:10.1080/10643389.2015.1061874.

[23] Shankar, Shiv, and Jong-Whan Rhim. "Facile Approach for Large-Scale Production of Metal and Metal Oxide Nanoparticles and Preparation of Antibacterial Cotton Pads." Carbohydrate Polymers 163 (May 2017): 137–145. doi:10.1016/j.carbpol.2017.01.059.