American Journal of Polymer Science and Technology
2021; 7(4): 57-63
http://www.sciencepublishinggroup.com/j/ajpst
doi: 10.11648/j.ajpst.20210704.12
ISSN: 2575-5978 (Print); ISSN: 2575-5986 (Online)

Use of Novel and Environmental Friendly Natural Polymer and Its Alumina Nano-composite Synthesized from *Rhynchophorus phoenicis* in Waste Water Treatment

Osu Charles Ikenna, Ugwu Henry Chimezie, Iwuoha Godson Ndubuisi

Department of Pure and Industrial Chemistry, Faculty of Science, University of Port Harcourt, Port Harcourt, Nigeria

Email address:
Charles.osu@uniport.edu.ng (O. C. Ikenna), charsike@yahoo.com (O. C. Ikenna)

To cite this article:
Osu Charles Ikenna, Ugwu Henry Chimezie, Iwuoha Godson Ndubuisi. Use of Novel and Environmental Friendly Natural Polymer and Its Alumina Nano-composite Synthesized from *Rhynchophorus phoenicis* in Waste Water Treatment. *American Journal of Polymer Science and Technology*. Vol. 7, No. 4, 2021, pp. 57-63. doi: 10.11648/j.ajpst.20210704.12

Received: October 8, 2021; **Accepted**: October 29, 2021; **Published**: November 23, 2021

Abstract: Novel and environmental friendly natural polymer and its Alumina nano-composite were synthesized from hard tissue of *Rhynchophorus phoenicis* gathered from palm trees at Omuoko community in Aluu, Ikwerre Local Government Area, Rivers state, Nigeria using standard methods. Dyes which are coloured organic compounds employed to put in colour onto cloth contaminate most of the water used. The natural polymer and its nano composite were used in Removal of dye from waste water. The investigation showed that chitosan (44.05 mg/g) has a lower adsorption capacity compared to alumina-chitosan composite (56.18 mg/g). This signifies that alumina-chitosan nano composite is a better adsorbent than chitosan. Batch adsorption tests of crystal violet dye confirmed that the adsorption process followed the pseudo-second-order kinetic model. The q_e value ascertained for alumina-chitosan nanocomposite and chitosan for pseudo-second-order kinetic model, were 23.98 mg/g and 22.37 mg/g respectively. The optimum contact time for adsorption of crystal violet dye onto chitosan was attained at 40 minutes. Adsorption isotherms which are a very key tool for comprehending the circulation of the adsorbate on the adsorbent surface at equilibrium were used. Alumina-chitosan composite is better for the adsorption of crystal violet dye from wastewater than the chitosan. Going by the correlation coefficient, R^2 values, the adsorption isotherm studies of crystal violet dye onto the chitosan and alumina-chitosan composite abided by the Langmuir isotherm model.

Keywords: Waste Water, Dye, Chitosan, *Rhynchophorus phoenicis*

1. Introduction

Chitosan, chitin and other by-products have more than 200 applications at present and they are still growing [2]. The functionability of chitosan hinges highly on it molecular weight which consecutively affect its viscosity [22]. Its polycationic behaviour lets chitosan to be employed as heavy metal trapper and flocculating agent in wastewater treatment industry [23]. Chitosan with amine group in C-2 spot gives some exceptional attributes which have been affirmed in the application of dietary supplements, agriculture, food preservation, pulp and paper, wastewater treatment, medical applications and cosmetics [23]. With its antibacterial activity, chitosan is applied in medical application such as wound dressing and suturing thread [24]. In some studies, chitosan has been involved in the treatment of surface for non-woven fabric and polypropylene film to improve antibacterial properties [1]. It has as well been applied. In the treatment/removal of dyes/colours from wastewater.

Colour is a crucial feature of the human world. People love to put on attires of all types of hues, consume foods embellished with colours and medicines are multihued. Little wonder that numerous investigations have discussed the manufacturing of dye and colour. Presently, there exist over thousands of dyes obtainable commercially and quite a few loads of dyes are made yearly. Dyes are coloured organic compounds employed to put in colour onto cloth. The existing procedure for dyeing fabrics is effective, but uneconomical and detrimental. The main purpose of water in the dyeing course is to wash surplus dye off from the clothes that have been decorated. All of the recent viable dyeing procedures involve considerable volume of water, and contaminate most of that water in the course. Dyeing is the method of attaching colour to a fabric that usually entails big amount of water not just in the dye-bath, but likewise in the washing stage. Several chemicals like salts, metals, organic processing aids, surfactants, formaldehyde and sulphide, may be included to enhance dye uptake onto the fabrics based on the procedure [14]. The colour of fabric wastewater is largely caused by the existence of fabric pigments, dyes and other painted materials. A particular dyeing action can employ numerous dyes from diverse chemical classes bringing about a multifaceted wastewater.

Gentian violet or methyl violet 10B or crystal violet or hexamethyl pararosaniline chloride has a molar mass of 407.979 g/mol, a melting point of 205°C (478 K, 401°F) and the molecular formula $C_{25}N_3H_{30}Cl$ (Tris (4-(dimethylamino) phenyl) methylium chloride). Crystal violet is unsolvable in diethyl ether but dissolvable in hot & cold. Crystal violet is applied to dye paper and as a constituent of black and navy blue inks for ball-point pens, ink-jet printers and printing. It is as well applied to colour assorted products for instance anti-freezes, fertilizers, leather jackets and detergents. In addition, triarymethane dye is employed in Gram's technique of categorizing bacteria and as a histological stain [11].

Crystal violet dye with an absorption maximum at 420 nm is yellow in a strongly acidic solution while it is green with absorption maxima at 420 nm and 620 nm at a pH of 1.0. The dissimilar colours are because of the dissimilar charged states of the dye molecule. When the dye with two of the nitrogen atoms positively charged this form corresponds to the green colour while the yellow form have all the three nitrogen atoms charged positively with two, protonated. The two extra protons are lost to the mixture remaining just one of the nitrogen atoms positively charged, at neutral pH. The pKa's for the shortfall of the two protons are roughly 1.8 and 1.15. The colourless carbinol or triphenylmethanol type of the dye is formed when nucleophilic hydroxyl ions hit the electrophilic central carbon, in alkaline mixtures. Some triphenylmethanol is as well produced in extremely acidic situation when the positive charges on the nitrogen atoms brings about an enrichment of the electrophilic character of the central carbon which lets the nucleophilic attack by water molecules. This upshot causes a trivial declining of the colour yellow.

Methyl violet 10B has been employed as an antiparasitic and antifungal agent for healing of fish, and in addition as a relevant antibacterial, antifungal and antiseptic compound for cure of eye and skin illness in domestic animals. It could also be employed for cure of Ichthyophthirius multifiliis, which brings about "white spot disease" in freshwater fish can be cure by gential violet. It is not presently permitted for usage in aquaculture in most advanced nations. Nonetheless, owing to its antifungal and antibacterial behaviour, and its connections with malachite green, there is a likelihood for it to be applied in aquaculture to lessen fungal or bacterial viruses in some nations [15]. Fish produce brought into several nations, including EU member states, the United States of America and Canada, have irregularly confirmed positive for leucogentian violet, its metabolite, or crystal violet. Methyl violet 10B was earlier applied in poultry feedstuff to stall the development of fungus and mould; though, some nations have retracted endorsement or listing of this usage [8, 3]. It is at present forbidden for use in food making animals in the USA [8, 5]. Water pollution has grown to be a grave dilemma as numerous types of contaminants are present in water environment, including metal ions, dyes and microorganism amongst others. There are quite a lot of firms such as clothing, textile, leather, dyestuff, paper, plastic, cosmetic and food processing industries releasing organic dyes into the surroundings [21]. The occurrence of dyes in aqueous environments is one of the serious environmental issues as a result of the deadliness of dyes to aquatic life and low biodegradability in such environments [21]. A minute volume of dye in water is vastly observable and can be lethal to living things in water. Some dyes bring about harm of DNA that can bring about the start of nasty tumours. Besides being poisonous, dye wastes as well comprise substances that are mutagenic and cancer-causing to humans and different organisms.

Nitro and azo substances have been noted to be lessened in deposits of aquatic bodies because they increase to likely cancer-causing amines. Scores of dyes are created from recognized cancer-causing agents like benzidine and are as well acknowledged to accrue, hence, causing a severe risk. Dyes in general have a man-made source and an intricate structure which makes sure thermal, optical and physico-chemical stability because of the existence of aromatic groups [18]. Various dyes are also acknowledged to get lessened to lethal materials in living organisms [26]. Consequently, the need for the elimination of dye/colour from wastewater becomes environmentally important.

The relatedness of chitosan and its nanocomposites for getting rid of dyes have as well been looked into, as they are an efficient biosorbents owing to their basic attributes of –OH and $–NH_2$ groups [6, 20, 28, 31, 4, 16, 29, 10, 12].

The aim of this study is to compare the absorption capacity of chitosan and the alumina-chitosan nano-composite synthesised from *Rhynchophorus phoenicis* (palm weevil) for the elimination of dye from wastewater.

2. Materials and Methods

2.1. Collection and Preparation of Samples

Rhynchophorus phoenicis were gathered from palm trees at Omuoko community in Aluu, Ikwerre Local Government Area, Rivers state, Nigeria, and recognized at the Department of Animal and Environmental Biology, University of Port Harcourt, Rivers State, Nigeria. The samples were cleaned of adhering dirt and soft tissues, washed well with distilled water and kept in the oven at 50°C for two days. After drying, the dried samples were ground and sieved.

2.2. Demineralization

A 1000 mL beaker glass containing 650 mL of 1 M HCl solution was added 65g hard tissues of *Rhynchophorus phoenicis*. With a magnetic stirrer at room temperature for 3 hours, the mixture was stirred and then filtered with Whatman filter paper while constantly rinsed with distilled water until neutrality was gotten. The remains was kept in an oven at 65°C until dry to steady weight [19].

2.3. Deproteinisation

After the demineralisation step, the samples continued to the deproteinisation process. The residue was put into a 1000 mL beaker glass and added 650 mL of 1 M NaOH solution. The mixture was stirred and heated for 1 hour on a hotplate at 60°C and then sieved with filter paper. The remains were washed with distilled water until the pH was neutral, and then put in an oven at 65°C until dry to stable weight. After this step, the produce gotten is the chitin [19].

2.4. Deacetylation

Deacetylation of chitin gives chitosan. The sample from deproteinasi step was put into the glass beaker containing 50% NaOH solution at a ratio of 10:1 (w/v) between NaOH solution and the isolated chitin. The mixture was stirred and heated for 2 hours on hotplate at 110°C. The mixture was filtered and the remains were washed with de-ionized water until the chitosan was neutral. Chitosan was put in an oven at 65°C until it was dry to steady weight [19].

2.5. Synthesis of Alumina-chitosan Nanocomposite

120 mL of 10% oxalic acid was added 6 g of chitosan and then heated until it formed a gel using a hot plate at 55°C. Then, 120 mL distilled water was added to the gel solution, and heated for 20 minutes at 45°C. Next, 12g of Al_2O_3 was added to the solution and stirred for 240 minutes at 250 rpm and left for 2 hours. The precipitate was poured out, sieved, cleaned and dried in an oven for 5 hours at 55°C [7].

2.6. Effect of Contact Time

Crystal violet dye solution (30 mL) with concentration of 200 mg/L added 0.2 g of chitosan alumina nanocomposite and chitosan. The mixture was swirled at 150 rpm for 5, 10, 20, 30, 40 and 50 minutes. The solution was sieved and then the filtrate was evaluated by UV-Vis spectrophotometer at the maximum wavelength obtained was 670 nm.

2.7. Effect of Initial Concentration

A total of 30 mL crystal violet dye with variations in concentrations of 50, 100, 150 and 180 mg/L were added 0.2 g chitosan alumina nanocomposite and chitosan. The mixture was then stirred at 150 rpm at 25°C for 30 minutes. The solution was filtered and then the filtrate was computed by using a UV-Vis spectrophotometer. The following equation can be used to ascertain the removal percentage and adsorption capacities (mg/g) (1 and 2.):

$$\mathrm{qe} = (\mathrm{Co} - \mathrm{Ce})\ X\ \frac{\mathrm{V}}{\mathrm{M}} \quad (1)$$

$$\text{Removal } \% = \frac{\mathrm{Co} - \mathrm{Ce}}{\mathrm{Co}} \times 100 \quad (2)$$

Where:

C_e and C_t=Cconcentration of the dye (mg/L) at initial time and at any time t, respectively

q_e (mg/g)=Adsorption capacities is the amount of the dye adsorbed on the adsorbent

C_e=Equilibrium concentrations of dyes (mg/L)

V (mL)=Volume of dyes solution and M (g) is the weight of the chitosan and chitosan alumina nanocomposite.

2.8. Effect of Initial Concentration of Dye in the Wastewater

Figure 1 shows the effect of concentration on the adsorption of crystal violet by alumina-chitosan nanocomposite and chitosan. The adsorption procedure for alumina-chitosan nanocomposite and chitosan was done at a half an hour with the mass of each adsorbent as 0.2g. From the figure below, It is clear that the bigger the concentration of the dye, the lesser dyes removed. In addition, it is noted that the volume of crystal violet removed by the chitosan is lesser compared to alumina-chitosan nanocomposite. Addition of alumina brings about the accumulation of active groups which can react with the dye. This outcome is at odds with the research of [27] who affirmed that augmenting the concentration of dye (congo red) increases adsorption capacity by using bentonite inserted organometallic and bentonite. 44.05 mg/g and 56.18 mg/g were recorded as the adsorption capacity of chitosan and alumina-chitosan nanocomposite, correspondingly.

3. Results and Discussion

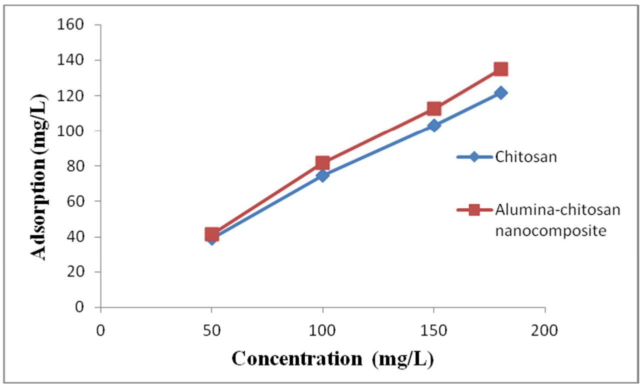

Figure 1. *Effect of Concentration of Dye in the Wastewater on Adsorption of Crystal Violet by Chitosan and Alumina-chitosan Nanocomposite.*

3.1. Adsorption Isotherm

The adsorption isotherm is a very key tool for comprehending the circulation of the adsorbate on the adsorbent surface at equilibrium [25]. Freundlich isotherm is a semi empirical equation based on the adsorption procedure that happens on heterogeneous surfaces whereas Langmuir isotherm connects with the monolayer adsorption course [13]. Freundlich and Langmuir isotherm was employed to ascertain the isotherm model that was apt for adsorption of crystal violet dye onto chitosan and alumina-chitosan nanocomposite. The linearized equation of Langmuir isotherm model is:

$$1/qe = (1/(qmax\ KL))\ 1/Cc + 1/qmax \qquad (3)$$

Where:

q_{max}=adsorption capacity (mg/g);

K_L=Langmuir constants related to adsorption energy (L/g)

If the plot between 1/qe and $1/C_e$ is linear, it proves aptness with Langmuir.

The Freundlich isotherm calculation is:

$$\text{Log } q_e = 1/n \text{Log } C_e + \text{Log } K_f \qquad (4)$$

Where:

qe=volume of dye absorbed per unit mass of adsorbent (mg/g)

K_f=Freundlich constants

1/n=adsorption intensity

The adsorption isotherm corresponds to freundlich if it is linearly plotted between log q_e and log C_e

Table 1. displays the isotherm values of adsorption of crystal violet on alumina-chitosan nanocomposite and chitosan.

Table 1. *The Parameters of Freundlich and Langmuir Isotherms.*

Samples	Isotherm					
	Langmuir			Freundlich		
	q_{max} (mg/g)	K_L (L/g)	R^2	$\frac{1}{n}$	K_f (mg/g)	R^2
Chitosan	44.05	0.0138	0.9940	0.661	1.2468	0.992
alumina-chitosan nanocomposite	56.18	0.0128	0.9889	0.6979	1.4431	0.9752

Based on the value of R^2 which confirms the link of linearity, the Langmuir isotherm is more appropriate to explain the crystal violet adsorption model on alumina-chitosan nanocomposite and chitosan. This is as the R^2 value of the Freundlich isotherm is lesser than that of Langmuir isotherm. The value of 1/n < 1 displays the adsorption procedure is encouraging. The table also gives 44.05 mg/g and 56.18 mg/g as the adsorption capacity of chitosan and alumina-chitosan nanocomposite, correspondingly. This signifies that alumina-chitosan nanocomposite is a better adsorbent than chitosan.

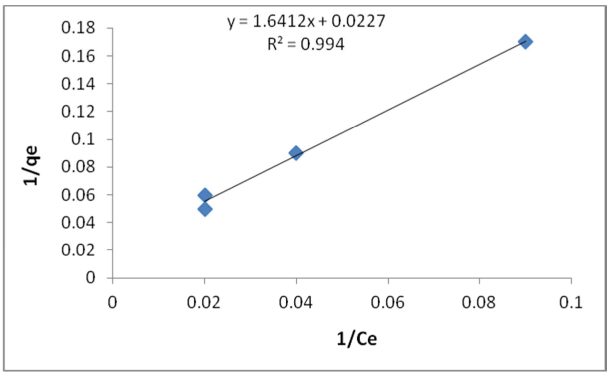

Figure 2. *Langmuir Plot for the Adsorption of Crystal Violet by Chitosan.*

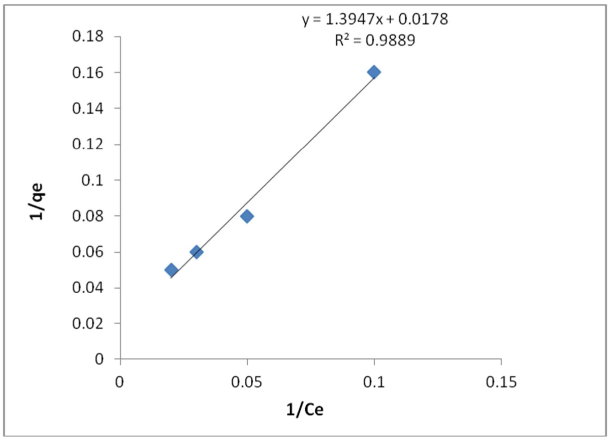

Figure 3. *Langmuir Plot for the Adsorption of Crystal Violet by Alumina-chitosan Nanocomposite.*

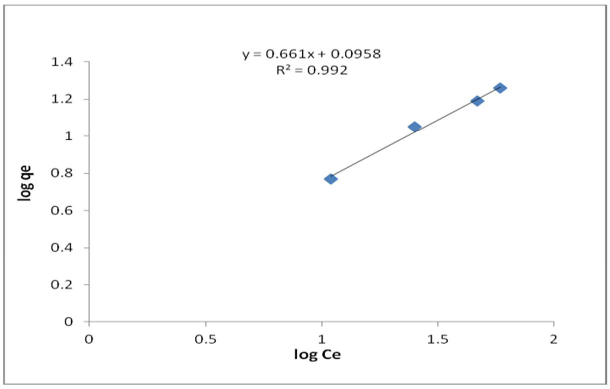

Figure 4. *Freundlich Plot for the Adsorption of Crystal Violet by Chitosan.*

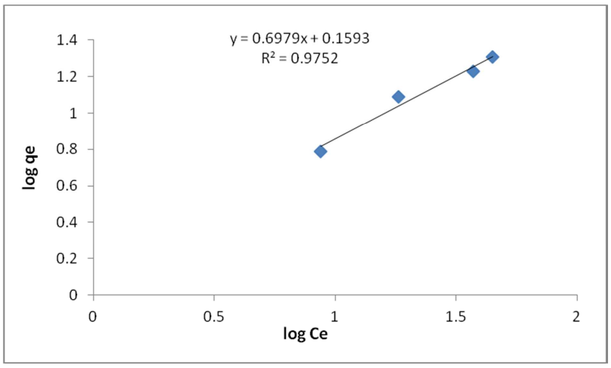

Figure 5. *Freundlich Plot for the Adsorption of Crystal Violet by Alumina-Chitosan Nanocomposite.*

3.2. Effect of Contact Time

At a concentration of 200 mg/L weight of adsorbent as 0.2 g, with volume of 30 mL, contact time variation of 5, 10, 20, 30, 40 and 50 minutes, and stirring speed of 150 rpm, the determination of the contact time was done. Figure 6 presents the important of contact time on the amount of dye removed by alumina-chitosan nanocomposite and chitosan. At the contact time of 30 minutes, the adsorption balance between the alumina-chitosan nanocomposite and the dye was reached so that the increase of contact time did not influence the adsorption. The optimum contact time for adsorption of crystal violet dye onto chitosan was attained at 40 minutes.

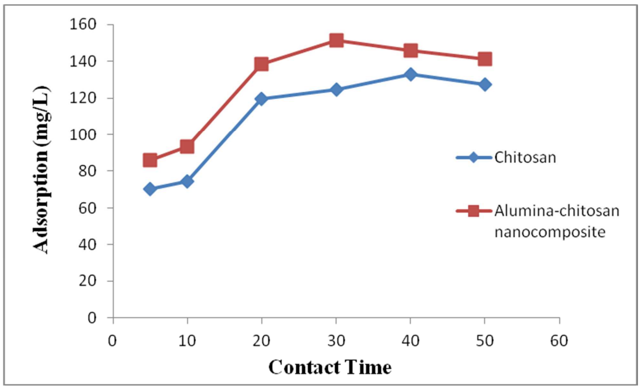

Figure 6. *Effect of Contact Time on the Amount of Dye Adsorbed by Chitosan and Alumina-Chitosan Nanocomposite.*

3.3. Adsorption Kinetics

Kinetic of adsorption is a noteworthy characteristic in describing the effectiveness of adsorption. Two kinetic models, pseudo-second-order kinetic model and pseudo-first-order kinetic model, were employed to examine the alumina-chitosan nanocomposite and chitosan adsorption kinetic behaviour on crystal violet dye.

Pseudo-first-order kinetic model is signified by following equation.

$$\text{Log}\,(q_e - q_t) = -\frac{K}{2.303}t + \text{Log}\,q_e \qquad (5)$$

Where;

q_e=amounts of dyes adsorbed (mg/g) at equilibrium

q_t=amounts of dyes adsorbed (mg/g) at time t (min)

K_L=rate constant (1/min).

Pseudo-second-order kinetic model is expressed, thus:

$$\frac{t}{qe} = \left(\frac{1}{qe}\right)t + 1/\,K_2qe^2 \qquad (6)$$

Where:

K_2=rate constant (g/mg.min)

The intercept and slope of the linear plots of t/q_e against t yield the values of $1/C_e$ and $1/K_2qe^2$.

The kinetic parameters are shown in table 2 and the plots of the pseudo orders are presented in Figures 7 and 8. Experimental data indicates that pseudo-second-order kinetic model has higher correlation coefficient values and is more valid to describe the removal of chitosan and alumina-chitosan nanocomposite. The values of q_e calculated from the pseudo-second order kinetic models were in good settlement with those resulted from experiment. For pseudo-second-order kinetic model, 23.98 mg/g and 22.37 mg/g were the q_e value ascertained for alumina-chitosan nanocomposite and chitosan.

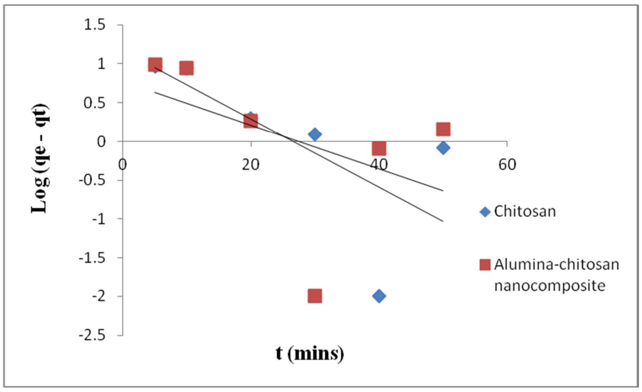

Figure 7. *Pseudo-first-order Kinetic Model Plots for the Adsorption of Crystal Violet Dye by Chitosan and Alumina-chitosan Nanocomposite.*

Table 2. *Kinetic Parameters of Chitosan and Alumina-chitosan Nanocomposite.*

Samples	**Adsorption Kinetics**					
	Pseudo-first-order-model			**Pseudo-second-order-model**		
	q_e (mg/g)	**K_1 (min^{-1})**	**R^2**	**q_e (mg/g)**	**K_2 (g/mg.min)**	**R^2**
Chitosan	14.80	0.1011	0.4946	22.37	0.0068	0.985
alumina-chitosan nanocomposite	5.92	0.0649	0.2024	23.98	0.0095	0.9861

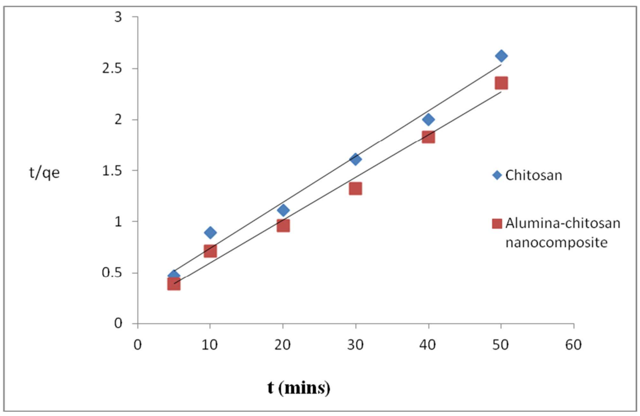

Figure 8. *Pseudo-second-order Kinetic Model Plots for the Adsorption of Crystal Violet Dye by Chitosan and Alumina-chitosan Nanocomposite.*

4. Conclusion

Alumina chitosan composite and chitosan have been fruitfully produced and employed for the elimination of crystal violet dye from wastewater. Going by the correlation coefficient, R^2 values, the adsorption isotherm studies of crystal violet dye onto the chitosan and alumina-chitosan composite abided by the Langmuir isotherm model. The investigation noted that chitosan (44.05 mg/g) has a lower adsorption capacity compared to alumina-chitosan composite (56.18 mg/g). Batch adsorption tests of crystal violet dye confirmed that the adsorption process followed the pseudo-second-order kinetic model. Finally, the study notes that alumina-chitosan composite is better for the adsorption of crystal violet dye from wastewater than the chitosan.

References

[1] Abdou, E. S., Elkholy, S. S., Elsabee, M. Z. and Mohamed, E. (2008). Improved antimicrobial activity of polypropylene and cotton nonwoven fabrics by surface treatment and modification with chitosan. *Journal of Applied Polymer Science, 108* (1), pp. 2290-2296.

[2] Al Sagheer, F. A., Al-Sughayer, M. A., Muslim, S. and Elsabee, M. Z. (2009). Extraction and characterization of chitin and chitosan from marine sources in Arabian Gulf. *Carbohydrate Polymers 77* (1), pp. 410-419.

[3] CFIA (Canadian Food Inspection Agency) (1992). Regulatory guidance RG-8: Contaminants in Feed. *Section 3: Gentian violet for use in livestock feeds*. Date modified: 2012-10-01. Available at: http://www.inspection.gc.ca/animals/feeds/regulatory-guidance/rg-8/eng/1347383943203/1347384015909?chap=3 Accessed 04-12-2019.

[4] Crini G. (2006). Non-conventional low-cost adsorbents for dye removal: a review. *Bioresour Technol*; 60: 67–75.

[5] Davis, J. L., Smith, G. W., Baynes, R. E., Tell, L. A., Webb, A. I. and Riviere, J. E. (2009). Update on drugs prohibited from extralabel use in food Animals. *Journal of the American Veterinary Medical Association*, 235: 528–534.

[6] Fan, L., Luo C., Sun M., Qiu H. and Li X. (2013). Synthesis of magnetic beta-cyclodextrin _ chitosan / graphene oxide as nanoadsorbent and its application in dye adsorption and removal. *Colloids Surf. B* 103, 601_607. Available at: https://doi.org/10.1016/j.colsurfb.2012.11.023.

[7] Fatma, Yuliasari N., Riyanti F., Hariani P. L., and Nurbaiti B. (2019). Synthesis of chitosan/alumina composite by sol gel method for adsorption of procion blue MX-R dye from wastewater songket industry. *Journal of Physics*: Conf. Series 1282 (2019) 012080.

[8] FDA (United States Food and Drugs Administration) (1991a). *Code of Federal Regulations*, Title 21, part 500.29–Gentian violet for animal drug use.

[9] FDA (1991b). *Code of Federal Regulations*. Title 21, part 500.30–Gentian violet for use in animal feed.

[10] Gao, Q., Zhu, H., Luo, W. J., Wang, S. and Zhou, C. G. (2014). Preparation, characterization, and adsorption evaluation of chitosan-functionalized mesoporous composites. *Microporous Mesoporous Mater. 193*, 15–26.

[11] Gessner, T. and Mayer, U. (2002), Triarylmethane and Diarylmethane Dyes. *Ullmann's Encyclopedia of Industrial Chemistry 6th Edition*, Weinheim: Wiley-VCH, doi: 10.1002/14356007.a27_179.

[12] Guibal E, Touraud E, Roussy J. (2005). Chitosan interactions with metal ions and dyes: dissolved-state vs. solid-state application. *World J Microbiol Biotechnol*; 21: 913–20.

[13] Gupta, V. K. and Ali, I. (2008). Removal of endosulfan and methoxychlor from water on carbon slurry. *Environ. Sci. Technol*. 42, 766–770.

[14] Henneman, S. A. and Kohn, F. S. (1975). Methylene blue staining of tissue culture monolayers. *Methods in Cell Science*1, doi: 10.1007/BF01352624, (2), 103.

[15] Khoshkho, Z. H. and Matin, R. H. (2013). Efficacy of medication therapy to control of Saprolegniasis on rainbow trout (*Oncorhynchus mykiss*) eggs. *Global Veterinaria*, 10 (1): 80–83.

[16] Kim T. Y. and Cho S. Y. (2005). Adsorption equilibria of reactive dye onto highly polyaminated porous chitosan beads. *Korean J Chem Eng*; 22: 691–6.

[17] Kumar, M. N. V. R. (2000). A review of chitin and chitosan applications. *Reactive and Functional Polymer,* 46 (1), pp. 1-27.

[18] Langhals, H. (2004). Color Chemistry. Synthesis, Properties and Applications of Organic Dyes and Pigments. 3rd revised edition. By Heinrich Zollinger, Angewandte Chemie International Edition, 43 (2004) 5291-5292.

[19] Mohadi R., Kurniawan C., Yuliasari N., Hidayati N. and Aldes Lesbani (2015). Synthesis of Nanocomposite Chitosan-Tio2 and its Application as Photodegradation Agent of Methilen Blue in Aqueous Medium. *Progress on Chemistry and Application of Chitin and its Derivatives*, Volume xx, doi: 10.15259/PCACD.20.21.

[20] Nagarpita, M. V., Roy, P., Shruthi, S. B., Sailaja, R. R. N. (2017). Synthesis and swelling characteristics of chitosan and CMC grafted sodium acrylate-co-acrylamide using modified nanoclay and examining its efficacy for removal of dyes. *Int. J. Biol. Macromol*. 102, 1226-1240.

[21] Nesic A. R., Velickovic S. J. and Antonovic D. G. (2012). Characterization of chitosan/montmorillonite membranes as adsorbents for Bezactiv Orange V-3R dye. *J Hazard Mater.* 2012; 209–210: 256–263.

[22] No, H. K. & Lee, M. Y. (1995). Isolation of chitin from crab shell waste. *Journal of the Korean Society of Food Science and Nutrition,* 24 (1), pp. 105-113.

[23] Pradip, K. D., Joydeep, D. and Tripathi, V. S. (2004). Chitin and chitosan: Chemistry, properties and applications. *Journal of Science and Industrial Research,* 63, pp. 20-31.

[24] Prashanth H., K. V. & Thanathan, R. N. (2007). Chitin/chitosan: modifications and their unlimited application potential - an overview. *Trends Food Science Technology,* 18, 117-131.

[25] Rabelo, R. B., Vieira, R. S., Luna, F. M. T., Guibal, E., and Beppu, M. M. (2012). Adsorption of copper(II) and mercury(II) ions onto chemically-modified chitosan membranes: Equilibrium and kinetic properties. *Adsorpt. Sci. Technol.*, 30, 1–12.

[26] Ratna and Padhi B. S. (2012). Pollution due to synthetic dyes toxicity & carcinogenicity studies and remediation. *International Journal of Environmental Sciences.* ISSN 0976-4402, doi: 10.6088/ijes.2012030133002, 3 (3), 940.

[27] Said M., Utami H. P. and Hayati F. (2017). Insertion of bentonite with Organometallic $[Fe_3O(OOC_6H_5)_6(H_2O)_3(NO_3).nH_2O]$ as Adsorbent of Congo Red. *IOP Conference Series: Materials Science and Engineering*, Volume 299, conference 1.

[28] Soltani, R. D. C., Khataee, A. R., Safari, M. and Joo, S. W. (2013). Preparation of bio-silica/chitosan nanocomposite for adsorption of a textile dye in aqueous solutions. *Int. Biodeterior. Biodegrad*. 85, 383_391. Available at: https://doi.org/10.1016/j.ibiod.2013.09.004.

[29] Wong Y. C., Szeto Y. S., Cheung W. H. and McKay G. (2004). Adsorption of acid dye on chitosan-equilibrium isotherm analyses. *Proc Biochem*; 39: 693–702.

[30] Wong Y. C., Szeto Y. S., Cheung W. H. and McKay G. (2004). Pseudo-firstorder kinetic studies of the adsorption of acid dyes onto chitosan. *J Appl Polym Sci*; 92: 1633–45.

[31] Wu F. C., Tseng R. L. and Juang R. S. (2000). Comparative adsorption of metal and dye on flake- and bead-types of chitosans prepared from fishery wastes. *J Hazard Mater*; B73: 63–75.