Research Article

Inexpensive and Environment Friendly Chitosan-Bentonite Composite as A Potential Adsorbent for Thiomethoxam Removal

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Abstract

Thiamethoxam is a systemic neonicotinoid pesticide which is highly toxic and its entry into water environment can greatly endanger the aquatic ecosystems and human health. Adsorption on natural materials have attracted a great attention as eco-friendly and low cost process. Present paper deals with the synthesis of environmentally acceptable composites using chitosan and bentonite via sonication assisted technique. The composite was characterized by FT-IR, XRD, BET and FE-SEM. XRD analysis indicated the shifted reflections of bentonite to lower angles revealing the intercalated structure. The broadening of FTIR spectral bands with decreased intensity also confirmed the integration between bentonite and chitosan. The synthesized composite was used as the adsorbent surface for removal of thiomethoxam pesticide from aqueous solution. The maximum removal efficiency of about 75 % was obtained at 7 *p*H having 30 mg of chitosan/bentonite composite as adsorbent at 30°C for 60 minutes. The findings indicate that the chitosan/bentonite composite would potentially be an inexpensive and environment friendly adsorbent for pesticide removal from water environment.

Keywords: Chitosan, Bentonite, Composite, Adsorption, Thiomethoxam

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Introduction

Increasing water pollution is one of the serious concerns leading to the potential research in the different ways and techniques which can help to improve the quality of water. Pesticides are generally used to increase the food production by decreasing the effect of pests on crop. The conventional formulations of pesticides are not only dangerous to the target pests but also for the whole ecosystem. The overuse of pesticides causes deterioration of aquatic as well as terrestrial life leading to the imbalance in ecosystem [1]. These pesticides are classified into extremely, highly, moderately and slightly dangerous pesticides [2]. Thiomethoxam is one of the moderately dangerous neonicotenoid pesticide. The toxic effects of pesticides attracted the attention of researchers towards the development of cost effective and economically compatible way to remove them. The development of composites has attracted great attention in development of material to remove the pesticide from water resources via adsorption.

In this study, chitosan polymer was chosen as the macromolecular intercalant for the bentonite clay particles. Chitosan is a natural polysaccharide obtained by the N-deacetylation of chitin [3]. It is easily available, biodegaradable, highly biocompatible, low-cost polymer, and can be chemically modified.

Bentonite is a clay mineral which is abundantly available in whole of the continent. Clays also show non toxicity, good biocompatibility, high mechanical strength etc. It was reported that clays can improve all the physical and chemical properties of the polymers [4].

The aim of this study was to synthesize chitosan bentonite composites, and evaluation of its adsorptive capacity towards thiomethoxam.

Experimental

Materials

Chitosan, Bentonite powder and Glacial Acetic Acid were procured from Central Drug House (P) Ltd. Sodium Hydroxide Pellets (extrapure AR) were supplied by Sisco research laboratories Pvt. Ltd. Thiomethoxam pesticide was provided by Residual Lab, Entomology Department, College of Agriculture, Chaudhary Charan Singh Haryana Agricultural University, Hisar. Thiomethoxam concentrations were determined using the maximum absorbance (at 245 nm) through UV-Vis spectrophotometer, Shimadzu 2600i.

Synthesis of Chitosan/Bentonite composite

The synthesis of chitosan/bentonite composite was carried out by sonication assisted technique. Firstly, 5 g of bentonite was dispersed within 50 mL of distilled water under continuous stirring for 2 h. Then 100 mL of 0.75% *(w/v)* chitosan solution prepared using 0.2% *v/v* acetic solution was added to bentonite solution and stirring was provided for further 2 h. After addition of 0.1 M NaOH, the obtained solution was sonicated for 4 h and the product was filtered.

Characterization of composite

FTIR was employed for the identification of inorganic and organic species. The Infrared induced vibrations were recorded on a Thermo Scientific spectrometer (Nicolet-is 50), in the range of 400-4000 cm^{-1} at a scan speed of 4 cm^{-1}. The XRD analysis was performed on Bruker AXS D8 diffractometer equipped with CuKα radiation (λ= 0.154 nm). The diffractogram was collected in the 2θ range of 20-80°, at a scanning rate of 2° min^{-1}. FE-SEM study was carried out using a Quanta 200F microscope with an accelerating voltage of 20 kV. N_2 sorption analysis was performed using Quantachrome IQ-XR-XR (2 Stat.) BET analyser for the estimation of surface area and the pore volume using Brunauer-Emmett-Teller (BET) and Barrett, Joyner and Halenda (BJH) method, respectively.

Adsorption experiments

Adsorptive removal of pesticide was studied through batch experiments by using chitosan- bentonite composite as the adsorbent at room temperature of about 30 °C.

Results and Discussion

X-ray diffraction

XRD patterns of bentonite **Figure 1**(a) possess different peaks corresponding to different constituents of clay i.e. montmorillonite (M), quartz (Q) and calcite (Ca) at 20.02º, 22.16º, 27.8º, 29.52º 36.08º, 50.09º and 61.96º while in the chitosan-bentonite composite Figure 1(b), some of the peaks are shifted to some lower angles at 18.06º, 28.22º and 35.38º, with decreased intensity [5]. The peak at 50.09º and 29.52º are not available in case of composite, indicating the formation of intercalated composite with chitosan.

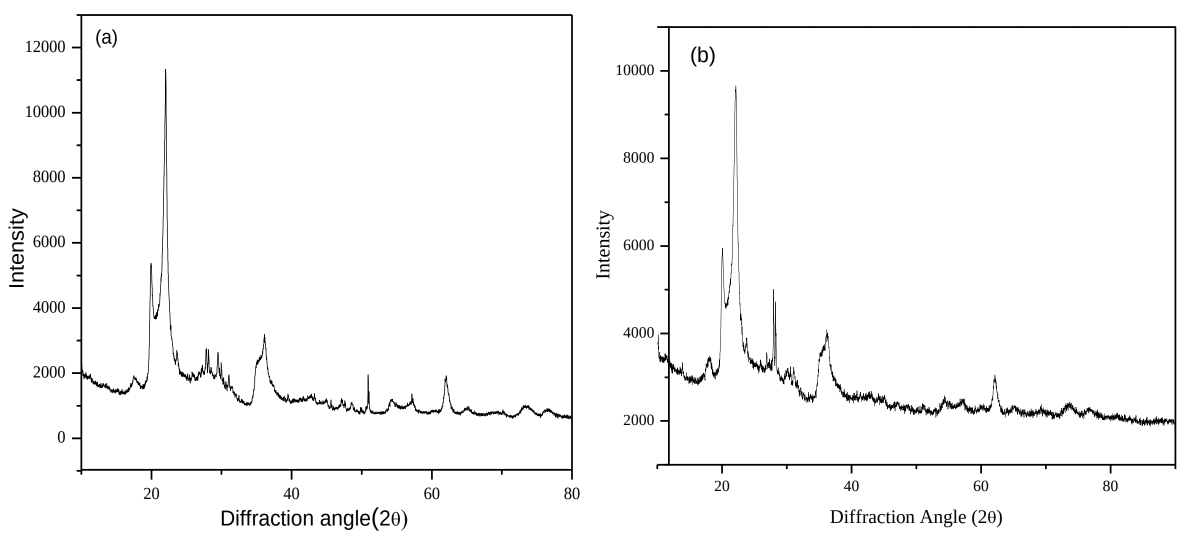

Figure 1 XRD of (a) Bentonite (b) Chitosan/Bentonite composite

FTIR Analysis

The FT-IR spectra of pristine chitosan, bentonite and chitosan/bentonite composite are shown in **Figure 2**. The spectrum of chitosan shows peaks at 3283 cm^{-1} due to overlapping of O-H and N-H stretching vibrations, at 2875 cm^{-1} due to aliphatic C-H stretching, at 1437 cm^{-1} due to N-H bending and at 1026 cm^{-1} due to C-O stretching [6]. The spectrum of bentonite shows peaks at 3630 and 3445 cm^{-1} due to inter-layer and intra-layer H-bonding, at 1638 cm^{-1} due to H-O-H bending, at 1040 cm^{-1} due to Si-O stretching, at 795 cm^{-1} due to (Al, Mg)-OH vibration modes, at 626 cm^{-1} for Al-OH and at 471 cm^{-1} due to Si-O bending [7, 8]. The spectrum of chitosan/bentonite composite revealed the creation of hybrid material having various functional groups related to both bentonite and chitosan. The broadening of band corresponding to the hydroxyl groups at 3420 cm^{-1} with decreased intensity confirmed the integration between bentonite and chitosan. The peak at 1660 cm^{-1} confirms the presence of water within the interlayers [9]. The characteristic peaks of bentonite are also present at 1043 cm^{-1} and 400-1000 cm^{-1} corresponding to Si-O, Mg-Fe-OH, Si-O-Al and Si-O-Mg groups.

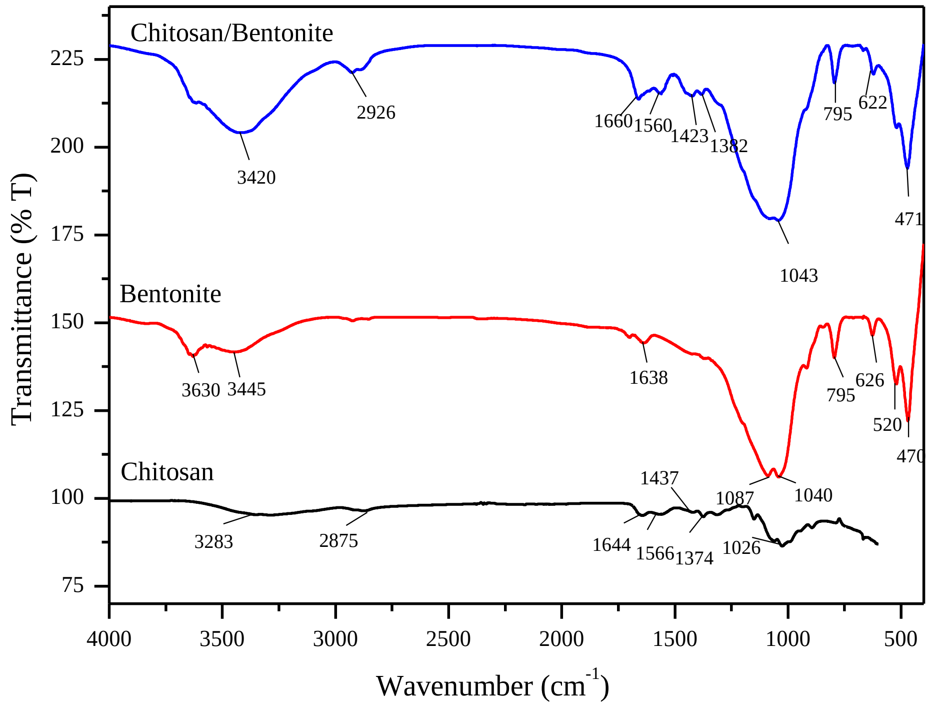

Figure 2 FTIR spectrum of chitosan, bentonite and chitosan bentonite composite

FE-SEM Analysis

The FE-SEM micrographs are present in **Figure 3**. The micrograph of bentonite shows that the surface possesses some layered structures which is probably due to the montmorillonite component of clay, while the image of bare chitosan indicates the presence sheet like morphology due to the polymeric nature of chitosan [10]. In the image of composite, it was found that the modification of bentonite with chitosan resulted into partially rounded particles of irregular topography over the sheet like structure [11].

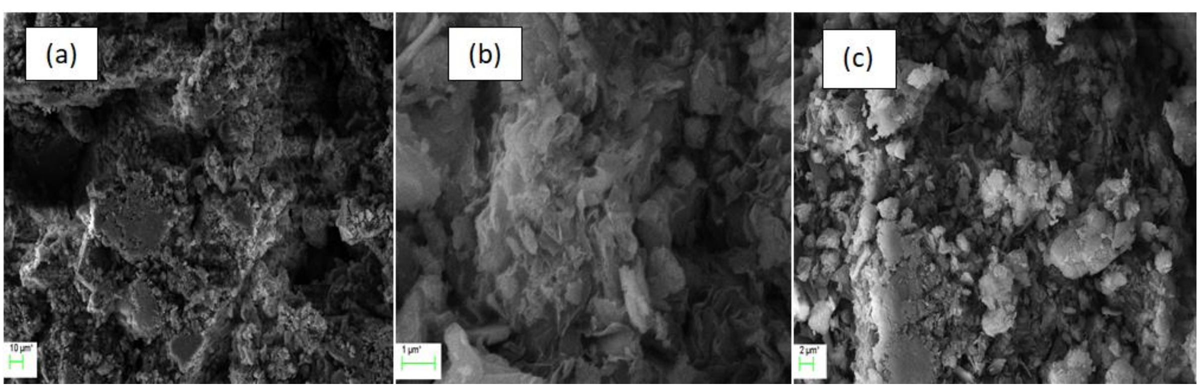

Figure 3 FESEM of (a) bentonite (b) chitosan (c) chitosan-bentonite composite

N_2 Sorption Analysis

The results indicate that the BET surface area of the chitosan/bentonite composite is 20.792 $m^2\ g^{-1}$ and the BJH pore volume is 0.115 cc g^{-1}. The curve obtained from the BET analysis is shown in **Figure 4** it follows the adsorption isotherm of type IV with H3 type hysteresis loop [12-13]. This type of isotherm indicates finite monolayer to multilayer adsorption on mesoporous materials with increase in the gas pressure while the type of hysteresis loop is associated with the capillary condensation in the mesopores [14].

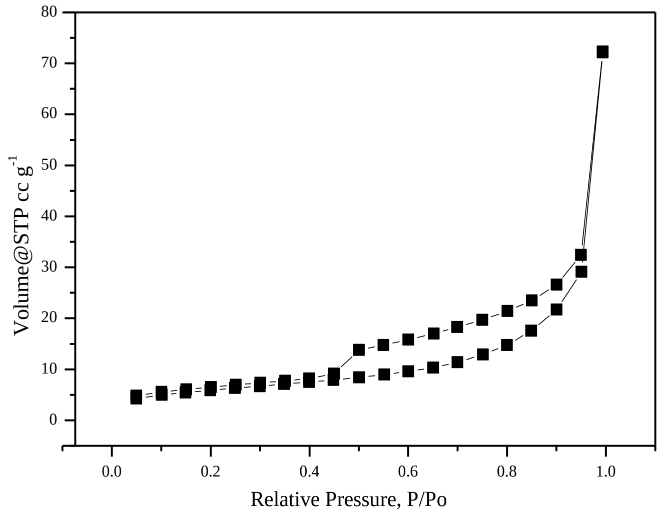

Figure 4 N_2 Sorption Analysis curve

Adsorption studies

Effect of pH

In order to get the most favourable *p*H for the removal of pesticide from water, the *p*H of thiomethoxam solution was optimized in the range of 3 to 9 by taking 10 mL solution of pesticide having concentration of 25 ppm added with 20 mg of the adsorbent. The results indicated that maximum percent removal of about 47.5% is at *p*H 7. This percent removal first increase with the *p*H and then starts to decrease again after *p*H 7, shown in **Figure 5**(a). As the change in *p*H can affect the speciations of the dissolved pesticide particles and also the surface properties of the adsorbent surface [15].

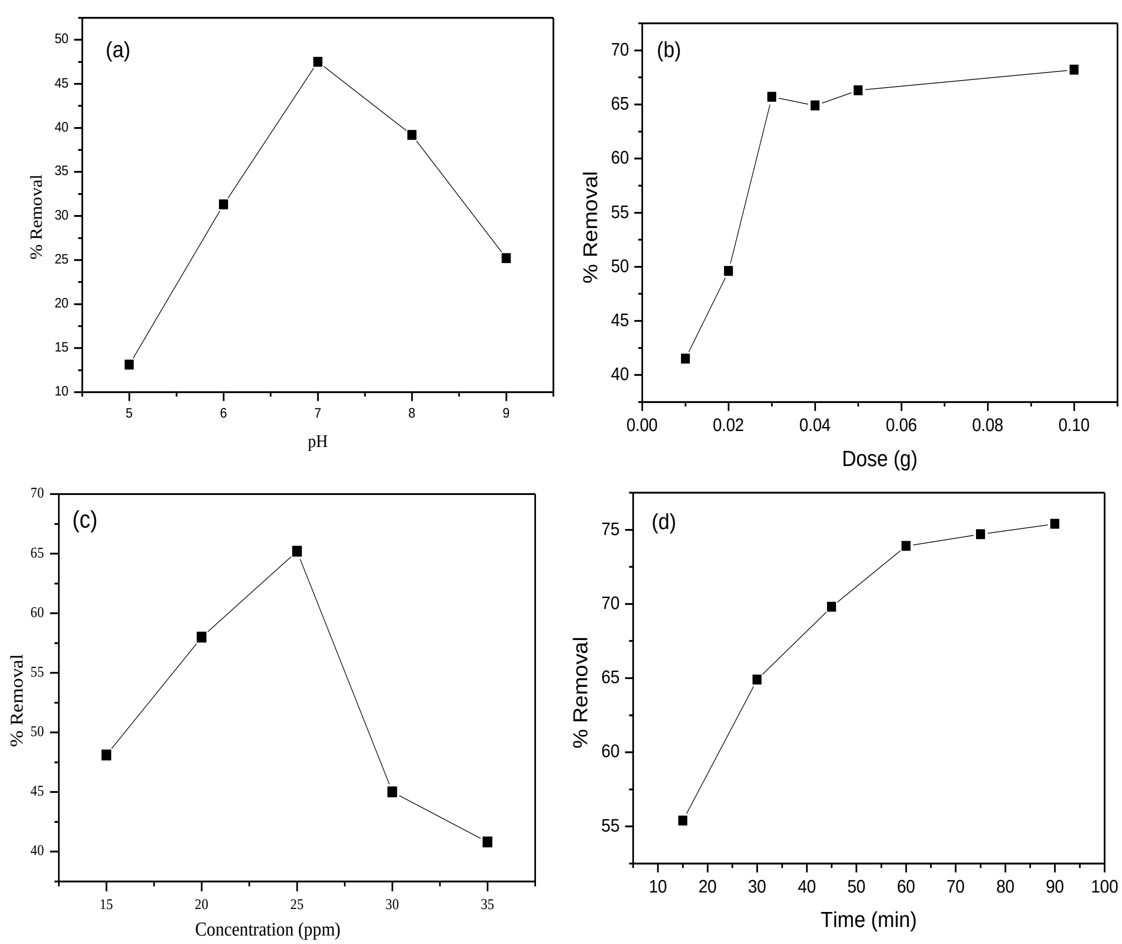

Figure 5 Effect of (a) *p*H of pesticide solution (b) dose of adsorbent (c) initial concentration pesticide and (d) contact time

Effect of amount of adsorbent

For this 10 mL solution of 25 ppm concentration at *p*H 7 was taken and stirred for 30 minutes having different doses as 0.01, 0.02, 0.03, 0.04, 0.05 and 0.1 g of the composite. Here, it can be seen in Figure 5(b) that removal percentage increases with the increase in adsorbent dose and after a particular point it becomes almost constant. The maximum removal efficiency was found almost equal to 65 %. This may be due to the increase in effective surface area and adsorption sites with increase in dose of the adsorbent and after that the concentration of pesticide being the limiting factor showing almost constant removal efficiency [16].

Effect of initial concentration of pesticide

The initial concentration of pesticide used was optimized at optimized pH, contact time and dose. For this, pesticide solutions having different concentrations in the range of 15 to 35 ppm were used and stirred for 30 minutes at other optimized conditions. The maximum percent removal of about 65 % is found at 25 ppm concentration and decreases with increase in concentration (Figure 5(c)). This is probably due to the reason of fully covered adsorption sites at 25 ppm concentration, making the adsorbent dose as the limiting factor [17, 18].

Effect of temperature and contact time

Finally, the percent removal of pesticide was calculated for different time intervals of 15, 30, 45, 60, 75 and 90 minutes. For this 10 mL solution of 25 ppm concentration at *p*H 7 having 30 mg of the composite were stirred for different time intervals and their absorbance was checked to calculate removal efficiency. The percentage of removal of the pesticide is found increasing upto approximately 75 % with the increase in contact time for the removal (Figure 5(d)). This is due to the increase in exposure time which further leads to increased interactions between the adsorbate and adsorbent. There is little increase in the percent removal after 60 minutes leading towards the slight equilibrium condition [19, 20].

Adsorption isotherm

The adsorption isotherms explain the type of interaction between adsorbate and adsorbent.

Langmuir Adsorption Isotherm

Data was fitted to Linear and Non-linear Langmuir Adsorption Isotherm equations and the obtained graphs are shown in **Figure 6**. The calculated values of Q_{max} (mg/g), Langmuir constant and R^2 in the linear curve fitting are 5.6705, 0.2538 and 0.9980, respectively while in non-linear curve fitting the values are 5.6975, 0.2507 and 0.9973, respectively.

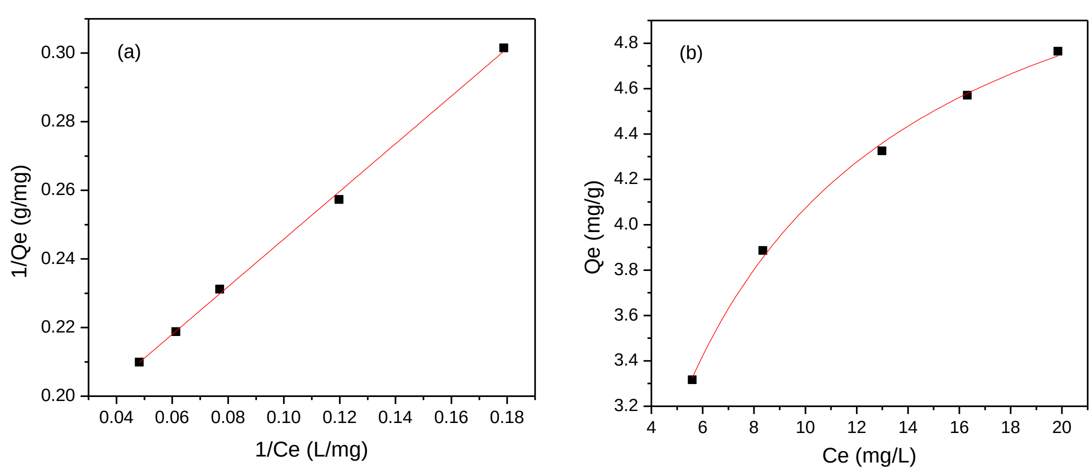

Figure 6 Fitting of data into (a) linear and (b) non-linear Langmuir adsorption isotherm

Freundlich Adsorption Isotherm

Data was fitted to Linear and Non-linear Freundlich Adsorption Isotherm equations and the graphs obtained are shown in **Figure 7**. The calculated values of Freundlich constant, 1/n and R^2 in the linear curve fitting are 14.791083, 3.5641 and 0.9788, respectively while in non-linear curve fitting the values are 20.58818, 3.6471 and 0.9807, respectively.

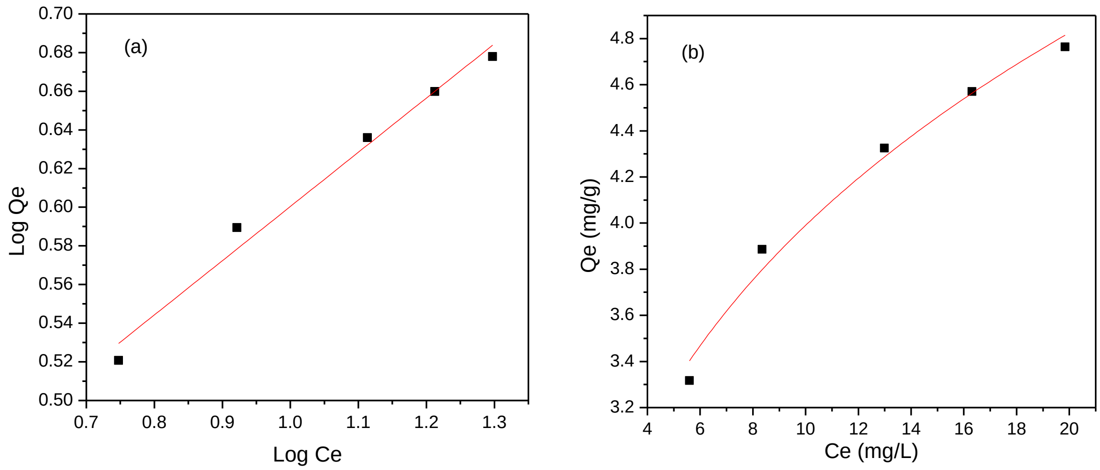

Figure 7 Fitting of data into (a) linear and (b) non-linear Freundlich adsorption isotherm

From above observations, it was revealed that the adsorption of thiomethoxam over chitosan/bentonite composite follows linear Langmuir plots. As value of R^2 (0.998) for Langmuir linear isotherm revealed the Langmuir behaviour for adsorption i.e. monolayer adsorption of thiomethoxam over chitosan/bentonite composite sites [21].

Kinetics Study

The data obtained from experiments was fitted into Pseudo Second Order (PSO) kinetic equations and the curves obtained are shown in the **Figure 8**. The kinetic parameters were calculated by using Pseudo second order models. It was found that the experimental data was fitted best to linear pseudo second order model with R^2 equal to 0.99953 and the closest approaching value of experimental and calculated adsorptive capacity (q_e) which is approximately equal to 4.0 mg/g. This data for adsorption indicates that there is chemical interaction between the pesticide and the composite surface [22].

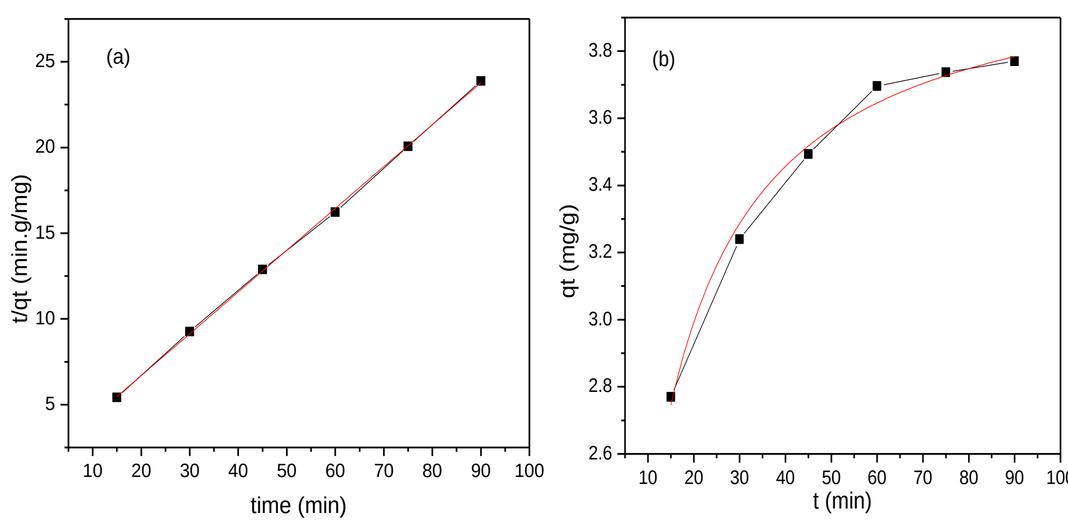

Figure 8 Pseudo second order (a) Linear and (b)Non-linear graph

Earlier, Ramos et al. [23] studied the adsorptive removal of Thiomethoxam from water matrix by utilizing the activated carbon magnetic nanocomposite. They reported 42 and 52% sorption of Thiomethoxam by nanocomposite under different operating conditions. Gámiz et al. [24] prepared a novel functional material by the modification of montmorillonite clay (SAz-1) with a cationic polymer hexadimethrine (SA-HEXAD). The prepared SA-HEXAD displayed a high affinity towards anionic pesticides where adsorption percentages were found to be 54 to 75%. In present study, around 75% removal of thiomethoxam was observed by utilizing the inexpensive and environment friendly material.

Conclusion

In this study, we have synthesized chitosan/bentonite composite by sonication assisted technique and its pysico-chemical properties were analyzed using FTIR, XRD, FE-SEM and N_2-sorption techniques. The results indicated the successful synthesis of chitosan/bentonite composite with good adsorption properties. The synthesized composite was used as an adsorbent for the removal of thiomethoxam pesticide from water. The optimization of various reaction parameters affecting adsorption process was done in order to establish its efficiency. The obtained data was found best fitted for the Langmuir (linear) adsorption isotherm and pseudo second order (linear) kinetic model, showing the monolayered chemisorption of the pesticide over the surface of chitosan/bentonite composite. Thus the use of chitosan/bentonite composite was found as an efficient way for the removal of thiomethoxam pesticide from water.

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Reference

[1] H. Chhipa. Nanofertilizers and nanopesticides for agriculture. Environmental Chemistry Letters, 2017, 15:15-22.
[2] R. Kaur, G. K. Mavi, S. Raghav, I. Khan. Pesticides classification and its impact on environment. International Journal of Current Microbiology and Applied Sciences, 2019, 8:1889-97.
[3] J. Cai, J. Yang, Y. Du, L. Fan, Y. Qiu, J. Li, J. F. Kennedy. Enzymatic preparation of chitosan from the waste Aspergillus niger mycelium of citric acid production plant. Carbohydrate Polymers, 2006, 64:151-157.
[4] E. Günister, D. Pestreli, C. H. Ünlü, O. Atıcı, N. Güngör. Synthesis and characterization of chitosan-MMT biocomposite systems. Carbohydrate Polymers, 2007, 67:358-365.
[5] M. R. Abukhadra, A. Adlii, B. M. Bakry. Green fabrication of bentonite/chitosan@ cobalt oxide composite (BE/CH@ Co) of enhanced adsorption and advanced oxidation removal of Congo red dye and Cr (VI) from water. International Journal of Biological Macromolecules, 2019, 126:402-413.
[6] P. Monvisade, P. Siriphannon. Chitosan intercalated montmorillonite: Preparation, characterization and cationic dye adsorption. Applied Clay Science, 2009, 42:427-431.
[7] B. A. Mansor, S. Kamyar, D. Majid, W.M. Z. W. Yunus, A. I. Nor. Synthesis and characterization of Silver/Clay/Chitosan bionanocomposites by UV irradiation method. American Journal of Applied Science, 2009, 6:2030-2035.
[8] X. Jin, M. Jiang, J. Du, Z. Chen. Removal of Cr (VI) from aqueous solution by surfactant-modified kaolinite. Journal of Industrial and Engineering Chemistry, 2014, 20:3025-3032.
[9] Y. Ma, C. Yan, A. Alshameri, X. Qiu, C. Zhou. Synthesis and characterization of 13X zeolite from low-grade natural kaolin. Advanced Powder Technology, 2014, 25:495-499.
[10] V. C. Kelessidis. Yield stress of bentonite dispersions. Rheol Open Access, 2017, 1:1-12.
[11] C. M. Hristodor, N. Vrinceanu, A. Pui, O. Novac, V. E. Copcia, E. Popovici. Textural and morphological characterization of chitosan/bentonite nanocomposite. Environmental Engineering and Management Journal, 2012, 11:573:578.
[12] H. Moussout, H. Ahlafi, M. Aazza, A. Amechrouq. Bentonite/chitosan nanocomposite: Preparation, characterization and kinetic study of its thermal degradation. Thermochimica Acta, 2018, 659:191-202.
[13] K. S. W. Sing. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Provisional). Pure and Applied Chemistry, 1982, 54:2201-2218.
[14] M. Kruk, M. Jaroniec. Gas adsorption characterization of ordered organic−inorganic nanocomposite materials. Chemistry of Materials, 2001, 13:3169-3183.
[15] H. Fu, Y. Yang, R. Zhu, J. Liu, M. Usman, Q. Chen, H. He. Superior adsorption of phosphate by ferrihydrite-coated and lanthanum-decorated magnetite. Journal of Colloid and Interface Science, 2018, 530:704-713.
[16] A. Alshameri, H. He, J. Zhu, Y. Xi, R. Zhu, L. Ma, Q. Tao. Adsorption of ammonium by different natural clay minerals: characterization, kinetics and adsorption isotherms. Applied Clay Science, 2018, 159:83-93.
[17] Z. Amghouz, C. Ancín-Azpilicueta, K. K. Burusco, J. R. García, S. A. Khainakov, A. Luquin, R. Nieto, J. J. Garrido. Biogenic amines in wine: individual and competitive adsorption on a modified zirconium phosphate. Microporous and mesoporous materials, 2014, 197:130-139.
[18] C. H. Giles, T. H. MacEwan, S. N. Nakhwa, D. Smith. 786. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in

measurement of specific surface areas of solids. Journal of the Chemical Society (Resumed), 1960, 3973-3993.
[19] R. A. Pepper, S. J. Couperthwaite, G. J. Millar. Re-use of waste red mud: Production of a functional iron oxide adsorbent for removal of phosphorous. Journal of Water Process Engineering, 2018, 25:138-148.
[20] M. Shaban, M. R. Abukhadra, A. A. P. Khan, B. M. Jibali. Removal of Congo red, methylene blue and Cr (VI) ions from water using natural serpentine. Journal of the Taiwan Institute of Chemical Engineers, 2018, 82:102-116.
[21] A. S. Yusuff, L. T. Popoola, E. O. Babatunde. Adsorption of cadmium ion from aqueous solutions by copper-based metal organic framework: equilibrium modeling and kinetic studies. Applied Water Science, 2019, 9:1-11.
[22] P. S. Abhari, F. Manteghi, Z. Tehrani. Adsorption of lead ions by a green AC/HKUST-1 nanocomposite. Nanomaterials, 2020, 10:1647.
[23] J.L. Ramos, J.O. Monteiro, G. Labuto, N.V.M.E. Carrilho. Removal of the pesticide thiamethoxam by activated carbon magnetic nanocomposite in water matrix. I Environment and Energy Symposium (SiMAE) November 26 to 28, 2020.
[24] B. Gámiz, M.C. Hermosín, J. Cornejo, R. Celis. Hexadimethrine-montmorillonite nanocomposite: Characterization and application as a pesticide adsorbent. Applied Surface Science, 2015, 332:606-613.

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