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Application of Synthetic Layered Sodium Silicate Magadiite Nanosheets for Environmental Remediation of Methylene Blue Dye in Water

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Abstract: The removal of methylene blue (MB) dye from water was investigated using synthetic nano-clay magadiite (SNCM). SNCM was synthesized by hydrothermal treatment under autogenous pressure. A rosette-shaped single mesoporous magadiite phase with 16.63 nm average crystallite size and 33$m^2.g^{-1}$ BET-surface area was recorded. The adsorption results indicated the pronounced affinity of the SNCM to the MB dye molecules which reached adsorption uptake of 20.0 mg MB dye/g of SNCM. The elimination of MB dye by the SNCM was kinetically and thermodynamically considered; a pseudo second order kinetic model was attained, and a spontaneous, chemical, and exothermic in nature was verified.

Keywords: adsorption; magadiite; cationic clay; methylene blue; remediation

Introduction

Water pollution is one of the most serious problems that threaten the life of mankind and other living organisms on earth. This is mainly due to the extensive industrialization of all aspects of our lives, and the spreading of all classes of pollutants in the ecosystem. One of the most dangerous classes of pollutants is the organic ones, which greatly affects the human health and causes many diseases due to their persistence nature against biological systems. This class of pollutants is introduced to the aquatic environment from the discharge of many industries such as textiles, pharmaceuticals, packaging, tanning, etc. Currently, more and more severe limits on the extent of organic pollutants have been established. There are different methods used to treat industrial waste water containing organic dyes; photo-degradation [1], reverse osmosis [2], biological treatment [3], and oxidative degradation [4]. However, most of these methods generally suffer from disadvantages such as low efficiency, extraordinary cost, emerging of ancillary contaminants, revival problem, and long retention periods. One of the most promising and efficient method of treatment of wastewater is the adsorption, which characterized with the simplicity of utilization, little cost, facility to revive both adsorbent, and

pollutants [5-7]. Nowadays, research scientists world-wide are looking for innovative classes of adsorbents which characterized with high adsorption efficiency as well as the strong affinity towards certain environmental pollutants such as the organic dyes.

Synthetic clay minerals are a new class of nanomaterials characterized with the purity of their structure and the well-designed composition, which enable them to be used in different applications such as catalysis [8, 9], nanocomposites reinforcement [10-12], antibacterial agents [13]. Moreover, different clays were used for environmental remediation for the removal of heavy metals [14,15], the antimicrobial peptides nisin and pediocin [16], herbicides [17], vitamin B1 [18], and different organic dyes [19-23].

However, the application of synthetic nano-clay magadiite(SNCM) for the elimination and remediation of different contaminants from the water environment is rare in the literature [24-26]; extra effort is desired to discover the adsorption capabilities of synthetic nano-clay magadiite as an effective adsorbent for the elimination of organic dye, as an specimen of organic contaminants—a main class of ecological contaminants that are insistent in the environment and cause antagonistic possessions on both fauna and flora.

Na-magadiite ($Na_2Si_{14}O_{29}.nH_2O$) is one of the most significant aluminum-free layered silicates with unknown exact crystal structure. However, three probable structures have been anticipated [27]. Furthermore, the layered appeal and the swelling behavior of Na-magadiite are well designated in the literature [28-31]. It is well recognized that the layers of Na-magadiite can be prolonged by suitable treatment by intercalation of guest molecules among the sheets of Na-magadiite, which open the gate for possible adsorption affinity.

In the present work, synthetic nanoclay Na-magadiite (SNCM) was synthesized, characterized with dissimilar methods; scanning electron microscope (SEM), surface area analyzer (SAA), and x-ray diffraction (XRD), and then used for elimination of methylene blue dye (MB)—as an example or organic contaminants—from a model solution and a wastewater sample. The influence of the different operational parameters affecting the removal process was studied and optimized. The adsorption of the MB dye from the model solution by SNCM was revealed kinetically; using altered kinetic models, and thermodynamically, to gain a well sympathetic of the adsorption process.

2 Experimental

2.1. Materials

All chemicals were of analytical grade and obtained from Sigma-Aldrich. The experiments were performed by using de-ionized water with resistivity that did not exceed 18.2 MΩcm and that was obtained with a Millipore Milli-Q system (Billerica, USA). A stock solution; 100 mg

L^{-1}, was prepared by dissolving a known quantity of MB dye in de-ionized water. The stock solution was further diluted to the desired concentration for other experiments.

2.2. Synthesis of SNCM

SNCM was synthesized using hydrothermal treatment under autogenous pressure at 150ºC of viscous weak alkaline and SiO_2-rich area of the ternary system $Na_2O/SiO_2/H_2O$ [32]. The molar gel composition was 5 SiO_2: Na_2O: 75 H_2O. From the chemical and thermogravimetric analysis (TGA), it was found that the chemical composition of the Na-magadiite synthesized was 13.8 SiO_2: Na_2O: 9.8 H_2O.

2.3. Characterization

XRD diffraction pattern was obtained using X'pert Pro diffractometer from Phillips Analytical. CuK α radiation (λ=1.54056 Å) was used. The sample is measured in sample holder with a small exposure area. Diffraction pattern of the sample was measured by using the following program: 2 Theta angle from 2 to 50° with a step of 0.02° and duration of 3s per step. Morphology of the samples was determined by using Carl Zeiss Gemini ULTRA 55 SEM equipment at a 3-kV voltage and SE 2 detector. Nitrogen-sorption measurements were taken by first carrying out a pre-treatment of the samples. During pre-treatment, the samples were heated with a 1 °C per minute rate to 250 °C under high vacuum, and kept at these conditions for 12 hours. Analysis measurement was performed at a temperature of -176 °C in liquid nitrogen with Quadrasorb SI equipment.

2.4. Adsorption Studies

The adsorption experiments were carried out in batch mode by mixing a specific amount of SNCM and 10 mL of MB dye solution in the stoppered conical flask under constant shaking (120 rpm) in a thermostat shaker. The effects of contact time, SNCM dosage, pH, ionic strength, and temperature of the MB dye solutions were investigated. For determination of the equilibrium time of adsorption, the experiments were carried out specific time intervals using 0.25 mg of the SNCM and 5 mg/l MB dye solution. For the effect of SNCM dosage experiments, 1-70 mg of SNCM, 10 ml of 5 mg/l MB dye solution, 20ºC, and contact time of 60 min. was used. For the effect of solution pH, 10 mg of SNCM, 10 ml of 5 mg/l MB dye solution, 20ºC, and contact time of 60 min. was used. For the effect of ionic strength, 10 mg of SNCM, 10 ml of 5 mg/l MB dye solution, 20ºC, and contact time of 60 min. was used. The temperature effect was investigated kinetically at three different temperatures, 20ºC, 35ºC, and 50ºC. After the completion of the adsorption experiment, the solution was immediately filtered to collect the supernatant; and the residual MB dye concentration in the supernatant using UV-vis instrument at 370 nm was measured. The removal efficiency expressed as % MB dye

removed and the uptakes of SNCM (q_e, mg/g) were calculated by the equations (1), and (2); respectively.

$$\%\ \text{MB dye removed} = \frac{(C_0 - C_e)}{C_0} \cdot 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (2)$$

Where C_0 and C_e (mg/l) are initial concentration and equilibrium concentration of MB dye in solution; respectively, V (l) is the volume of the MB dye solution; m (g) is the SNCM dosage.

3. Results and Discussion

3.1 Characterization of the SNCM

X-ray diffraction pattern of as-synthesized dried sample showed the characteristic peaks of magadiite at 5.6°, 11.3°, and 17.11° 2Θ corresponding to (001), (002) and (003) diffraction planes, respectively [33]. A crystalline nature of magadiite phase layer was indicated by the found peaks between 23 and 30° 2Θ. In addition, a basal spacing of 1.54 nm corresponding to the d_{001} reflection was detected as shown in Fig. 1[34]. The average crystallite size was 16.63 nm and the lattice strain was 0.0416 as deduced from scherrer equation [35]. The small crystallite size of SNCM indicates the presence of the anionic sheets as nano-sheets.

Fig. 1

SEM image (Fig. 2) of SNCM showed a well crystallized rosette-shaped Na−magadiite particles (SEM), with a diameter for "flower" and "pedal" of about 5-7 µm. The single magadiite crystalline phase was obtained as a result of the controlled hydrothermal reaction temperature at 150°C. It was reported in literature that the effect of temperature is much important than the reaction time and concentration in order to synthesize single magadiite phase and the reaction temperature must be below 170°C [36].

Fig. 2

N_2 sorption isotherm and BJH pore size distribution shown in Fig.3 were obtained for SNCM sample. The preliminary monolayer-multilayer adsorption on the mesopores walls, which receipts the similar track as type II isotherm, is shadowed by pore condensation with H_3 hysteresis according to IUPAC classification in 1985[37]. This loop shape is due to the non-rigid aggregates of Na-magadiite plate-like particles and macropores which are not entirely

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occupied with pore condensate [38]. SNCM has BET-surface area of 39 m^2g^{-1}, total pore volume of 0.3 cm^3g^{-1}. The small surface area of Na-magadiite is identical to the alkaline magadiite reported elsewhere [39]. Surface areas of magadiite couldn't entirely attributed to the exterior surface since the layered structure, in which the nitrogen has contact. Hereafter the small surface area of SNCM is a significance of the adsorption nonporous exterior surfaces. Multi-modal pore size structure was shown inset Fig. 3. The average pore size of SNCM is ca. 28 Å.

Fig. 3

3.2. Effect of operational parameters

Environmental and operational parameters greatly affect the removal and adsorption of pollutants from water using any solid adsorbent. Therefore, the study of adsorption contact time, SNCM dosage, solution pH, and ionic strength are of great importance. The effect of time on the adsorption of MB dye from an aqueous solution by SNCM was studied to explore the time required to reach equilibrium and the results were presented in Fig. 4. As shown in the figure 4, the % MB dye removed from the solution reached 46.3% within 1 minute and significantly increased to 90.3% after 25 min. to 91.0% within 30.0 min.Further increase in the contact time did not alter significantly the % MB dye removed, which reached 94.0% after 60 min., and consequently, a contact time of 30 min. was selected for further studies. Figure 5 shows the effect of the SNCM dosage on the removal of MB dye from aqueous solution. It is clear that most of the % MB dye removed from the solution using 5 mg of the SNCM; 97.5% of the MB dye was removed, and this removal percentage did not change with further increase in the SNCM dosage. This means that 5 mg of the SNCM was adequate to remove the MB dye completely from the solution, and was selected for further studies.

Fig. 4

Fig. 5

The effect of solution pH on the removal of MB dye by SNCM was investigated due to its significant effect to the adsorption process and the results were presented in Fig. 6. The results show that increasing the solution pH accompanied by a slight enhancement in the % MB dye removal; 95.1%, 96.4%, and 98.6%, at pH values of 2, 4, and 6; respectively. This indicated the insignificant competition between the hydronium ions (H_3O^+) and the MB molecules for the adsorption on the SNCM surface at low pH values. Further increase in the solution pH to 8 was associated with a slight decrease in the % MB dye removed; where it decreased to 93.8%, which significantly decreased to 62.4% upon increasing the solution pH to 10. This decrease in the adsorption capacity upon elevating the pH values could be attributed to the competition between the MB dye molecules and the hydroxyl ions present at pH values, as the MB dye molecules are insensitive to the pH change [40]. The effect of ionic strength on the

removal of organic pollutants such as MB dye from water by solid adsorbent such as SNCM is significant. That is because it sheds light on the nature of the interactions between the MB dye molecule and the SNCM surface and explains if it is electrostatic; attractive, or repulsive [28].

Fig. 6

The effect of the ionic strength on the removal of MB dye from water using SNCM was studied using different concentration of KNO_3 and the results were presented in Fig. 7. It is clear that the % MB dye removed was insignificantly affected by an increase in KNO_3 from 0.005 M to 0.01 M; 95.0% and 94.2%; respectively. Further increase in KNO_3 concentration to 0.05 M and 0.1 M caused the decrease in the % MB dye removed to 88.6% and 73.2%; respectively. This is may be due to the hindering effect of high concentration of K^+ and NO_3^- ions, indicating the electrostatic nature of the MB dye adsorption by the SNCM surface.

Fig. 7

3.3.Kinetics and thermodynamics studies

The variation of the amount of MB dye adsorbed by SNCM as a function of the adsorption time was studied at three different temperatures; 293 K, 308 K, and 323 K, and the experimental results were shown in Fig. 8. It is clear from the figure that the amount of MB dye removed from solution by SNCM reached equilibrium within 30 minutes; 18.5, 19.6, and 19.9 mg MB/g SNCM; at 20°C, 35°C, and 50°C; respectively, and no significant improvement in the amount MB dye removed was observed with further increase in time. Also, it was clear that the adsorption was endothermic in nature as the amount MB dye removed enhanced with rising the solution temperature; 18.8, 19.8, and 20.0 mg MB/g SNCM; at 20°C, 35°C, and 50°C after 60 min.; respectively.

Fig. 8

The experimental results of the effect of contact time on the removal of MB dye by SNCM were used to study the adsorption kinetically using the most used kinetic models, namely; pseudo first order kinetic model, and pseudo second order kinetic model, as it is presented in Equation (3) and (4); respectively.

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where q_e and q_t are the values of the amount MB dye adsorbed per unit mass of SNCM at equilibrium and at any time t, respectively, k_1 (min^{-1}), k_2 (g/(mg·min)), are the pseudo first order adsorption rate coefficient, and pseudo second order rate coefficient; respectively. Applying the pseudo first order kinetic model; equation (3), to the experimental results; Fig.

9, the plot of $\ln(q_e - q_t)$ vs. t for MB dye at different temperatures did not converge well and did not give straight lines as it is clear from Fig. 9 with unacceptable regression coefficients as it is presented in Table 1. Also, the estimated values of the amount adsorbed at equilibrium ($q_{e,\,calc}$) were far from the experimental values ($q_{e,\,exp}$). This indicated that pseudo first order kinetic model is not appropriate for the description of MB dye removal by SNCM from water. Applying the pseudo second order kinetic model; equation (4), to the experimental data, the plot of t/q_t vs. t converged well, with straight lines and an excellent regression coefficient higher than 0.99, as presented in Fig. 10 and Table 1. In addition, there was an excellent correlation between the calculated amount of MB adsorbed by the SNCM($q_{e,calc}$)and the experimental values ($q_{e,exp}$) as it is shown in Table 1.These findings confirmed the suitability of the pseudo second order kinetic model for describing the removal of MB dye from the model solution by the SNCM.

Fig. 9

Fig. 10

There are many previous studies showed also the suitability of the pseudo second order kinetic model for the description of MB dye from water by the different solid adsorbents such as; Fe_3O_4-graphene@mesoporous SiO_2 nanocomposites [41], low cost agricultural by-product [40], porous soy protein isolate based composite beads [42], novel manganese oxide nanocorals [43],zeolite synthesized from electrolytic manganese residue [44], zinc oxide nanorods loaded on activated carbon [45], activated carbon [46], poly(sodium p-styrene sulfonate)/poly(methyl methacrylate) particles [47], and many other adsorbents. Also, since the removal of MB dye by the SNCM was fast and followed the pseudo second order kinetic model, the adsorption mechanism could be chemical in nature [48].

The thermodynamic parameters include enthalpy change (ΔH), free energy change (ΔG), and entropy change (ΔS), were calculated to evaluate the thermodynamic feasibility and the spontaneous nature of the MB dye removal by SNCM according to the following equations:

$$D = \frac{q_e}{C_e} \tag{5}$$

$$\ln D = \left(\frac{\Delta S}{R}\right) - \frac{\Delta H}{R} \cdot \frac{1}{T} \tag{6}$$

$$\Delta G = \Delta H - T\,\Delta S \tag{7}$$

D is the distribution coefficient, R is the gas constant (8.314 J mol^{-1} K^{-1}); T is the temperature (K). The values of ΔH and ΔS are determined from the slope and the intercept of the plots of ln D versus 1/T, which associated with a good correlation coefficient; r2 equal 0.956, as it is shown in Fig. 11. The removal of MB dye using SNCM from water associated with ΔH value of +139.5 kJ/mol, this indicated the adsorption process was endothermic and chemical in nature, as the enthalpy value is much more than 50 kJ $mole^{-1}$[49]. This finding confirmed the

above-mentioned result that the adsorption is fast and obey the pseudo second order kinetic model. The ΔS value of +507.7 J /mol.K indicating the increase in the degree of disorder upon the adsorption of the MB dye molecules by the SNCM. The ΔG value was calculated based on equation (7) at 20°C, and the value was found to be negative, -9.23 kJ/mol indicate the process was spontaneous, and this value became more negative by rising the solution temperature; -16.9 kJ/mol, and -24.6 kJ/mol, at 35 and 50°C; respectively. It could be concluded here that the more negative the ΔG value, the more spontaneous the removal, which accompanied by higher value of MB dye uptake by the SNCM. Also, the negative values of the ΔG, positive value of the ΔH, and positive value of the ΔS, indicated that the removal of MB dye by the SNCM is an entropy-driving process. According to the kinetics and thermodynamics study, the MB dye removal by the SNCM could be described by the pseudo second order kinetic model, and was spontaneously, endothermic, and chemical in nature.

Fig. 11

4. Conclusions

The removal of the organic dye methylene blue (MB) from water was studied using synthetic nano-clay magadiite (SNCM). Firstly, SNCM was synthesized by hydrothermal treatment under autogenous pressure and then characterized using different characterization technique in order to explore its physical and morphological structure. The XRD showed the characteristic peaks of magadiite with average crystallite size 16.63 nm, and the SEM image showed a well crystallized rosette-shaped Na–magadiite particles with a diameter for "flower" and "pedal" of about 5-7 µm, and BET-surface area $33 m^2 g^{-1}$. The effects of different operational and environmental parameters like removal time, SNCM dosage, contact time, pH, and ionic strength of the solution which affect the removal of MB dye were explored. The adsorption results showed the great affinity of the SNCM to the MB dye molecules which reached adsorption uptake of 20.0 mg MB dye/g of SNCM. The removal of MB dye by the SNCM was studied kinetically and thermodynamically, and found to follow the pseudo second order kinetic model, and was spontaneous, chemical, and exothermic in nature. Finally, SNCM showed that they can be considered as a promising adsorbent for the removal of MB dye, from an aqueous solution.

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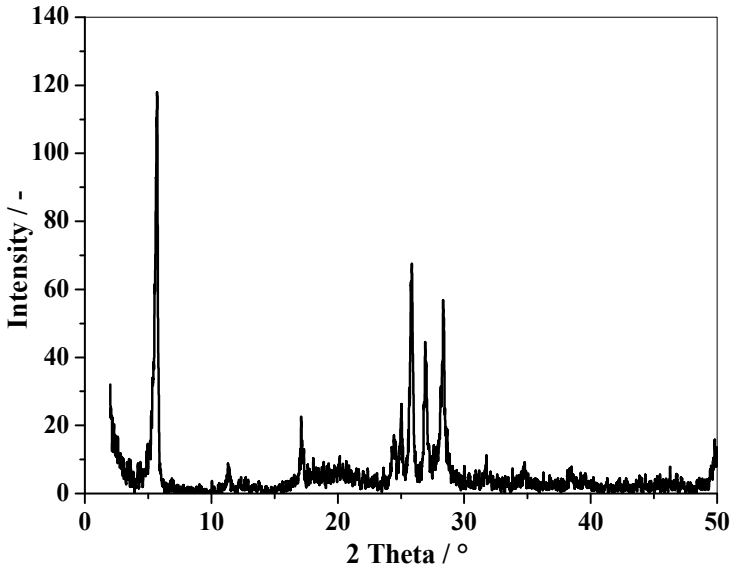

Fig. 1. X-ray diffraction pattern of as-synthesized layered sodium silicate magadiite

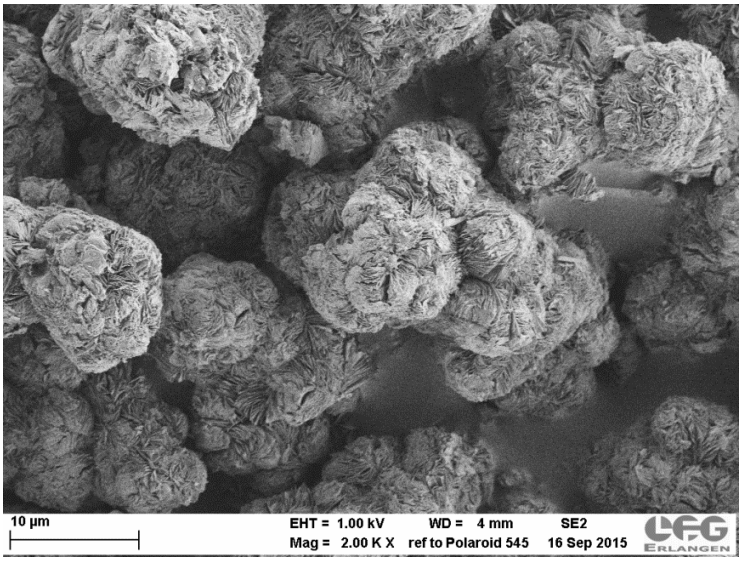

Fig. 2. SEM image ofas-synthesized layered sodium silicate magadiite

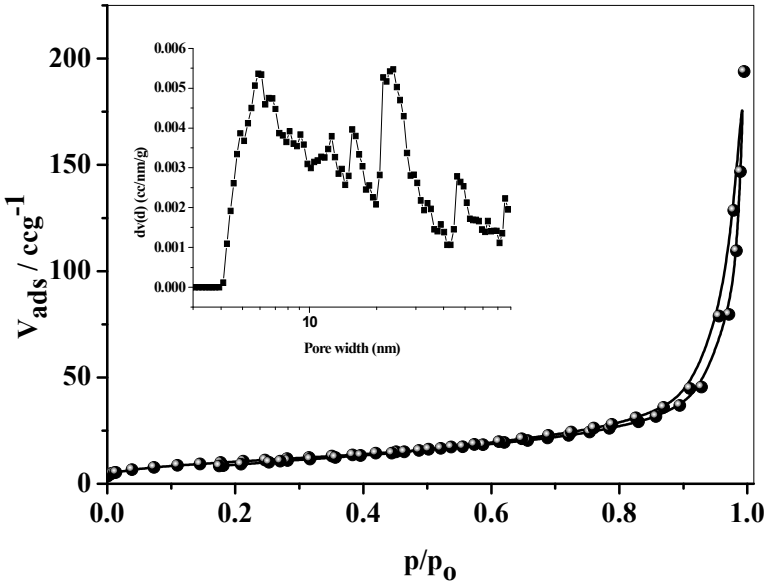

Fig. 3. N_2 sorption isotherm and pore size distribution curve for SNCM

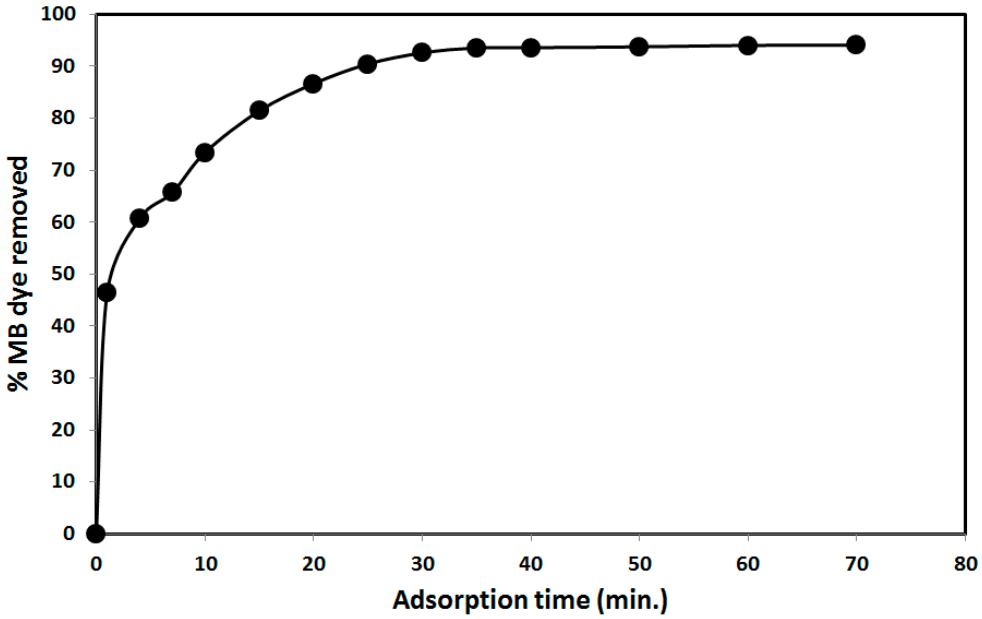

Fig. 4 Effect of adsorption time on the % methylene blue dye removed from an aqueous solution by SNCM.

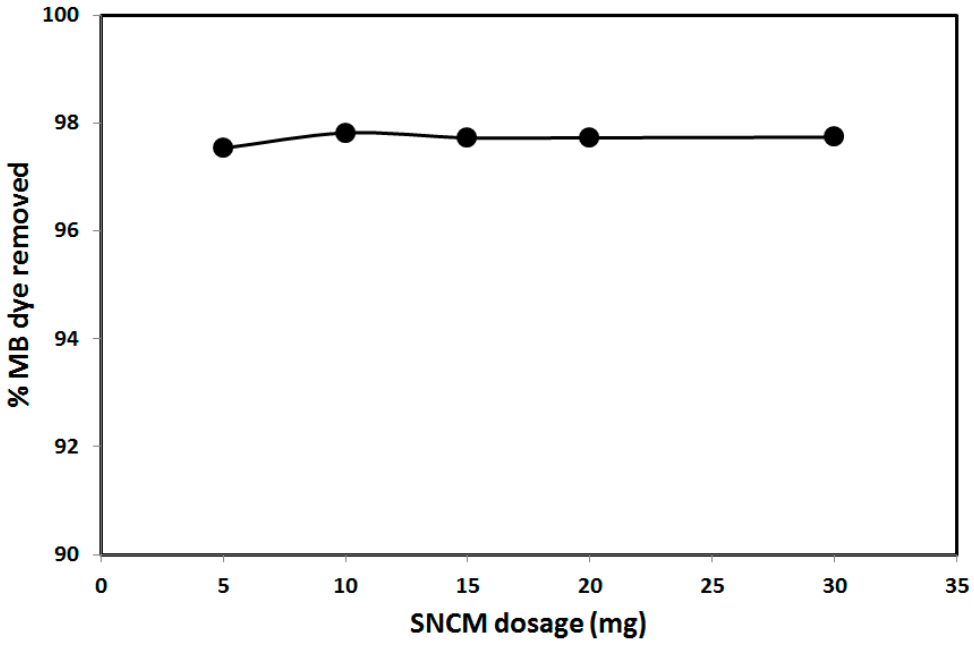

Fig. 5. Effect of SNCM dosage on the removal of methylene blue dye from an aqueous solution.

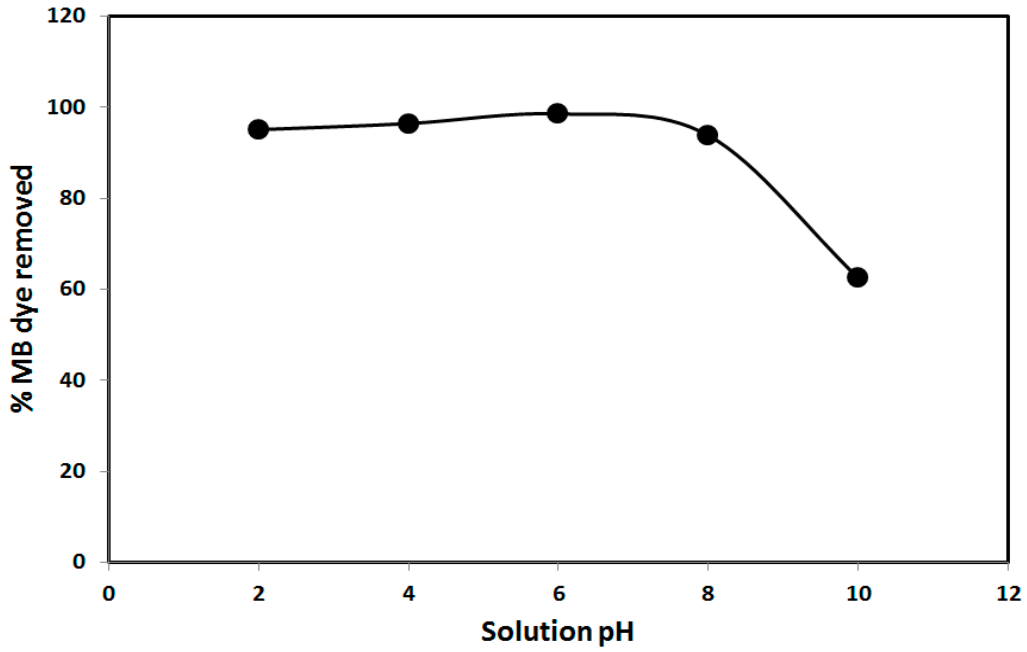

Fig. 6. Effect of solution pH on the % methylene blue dye removed from an aqueous solution by SNCM.

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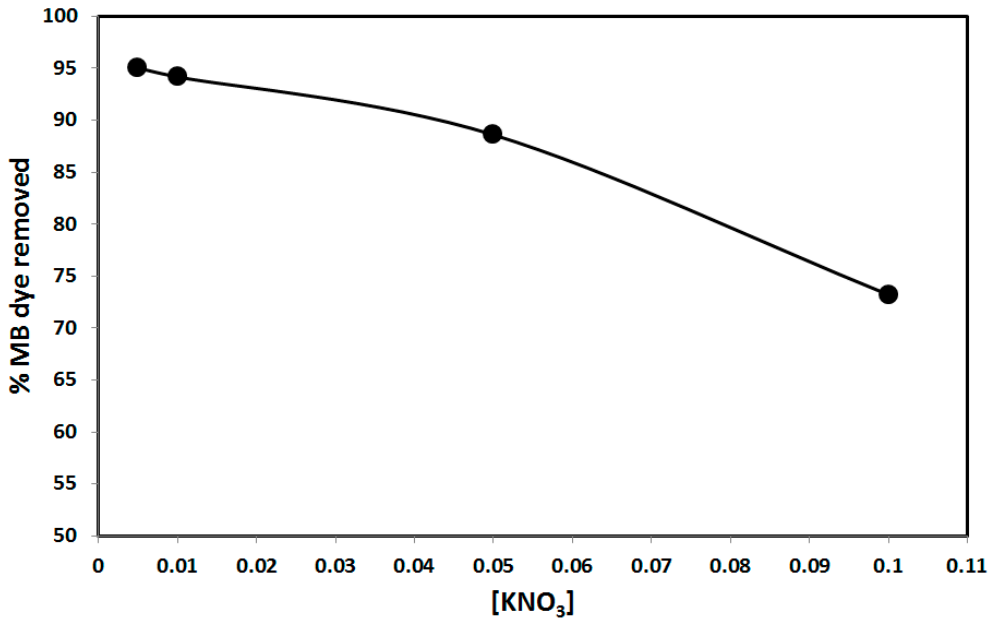

Fig. 7. Effect of solution ionic strength on the % methylene blue dye removed from an aqueous solution by SNCM.

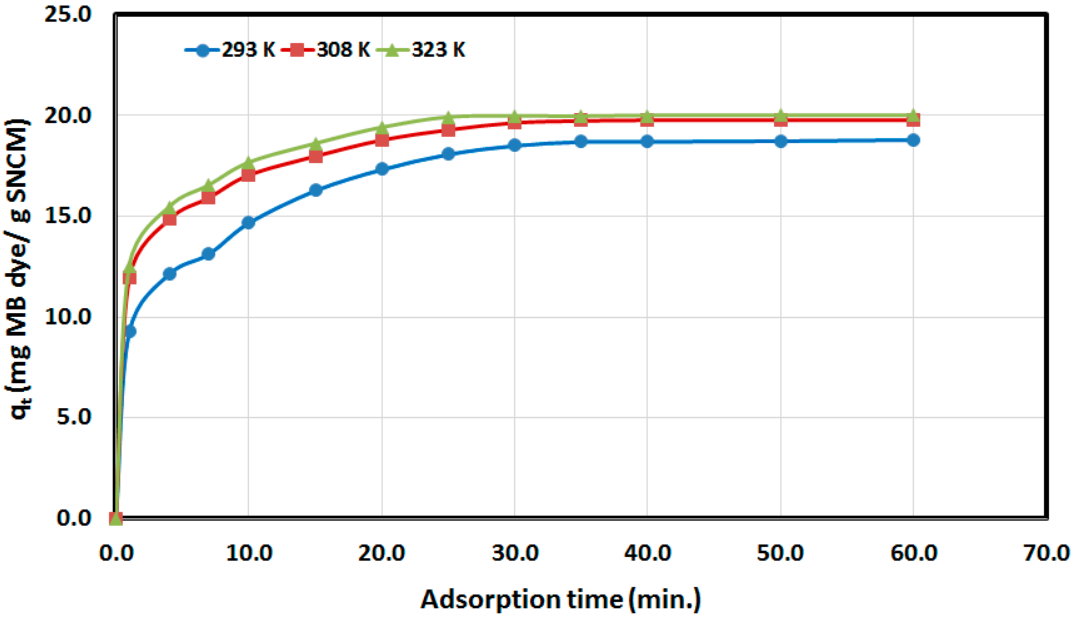

Fig. 8. Variation of the amount MB dye adsorbed per unit mass of SNCM (q_t) with time.

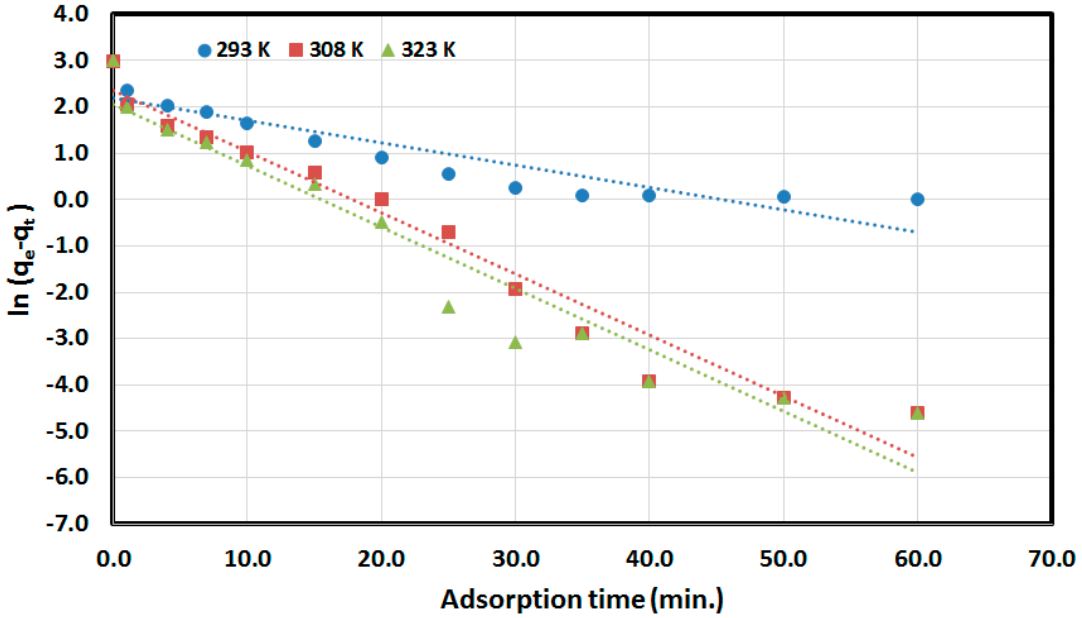

Fig. 9. The application of pseudo first order kinetic model for the MB dye removed from an aqueous solution by SNCM.

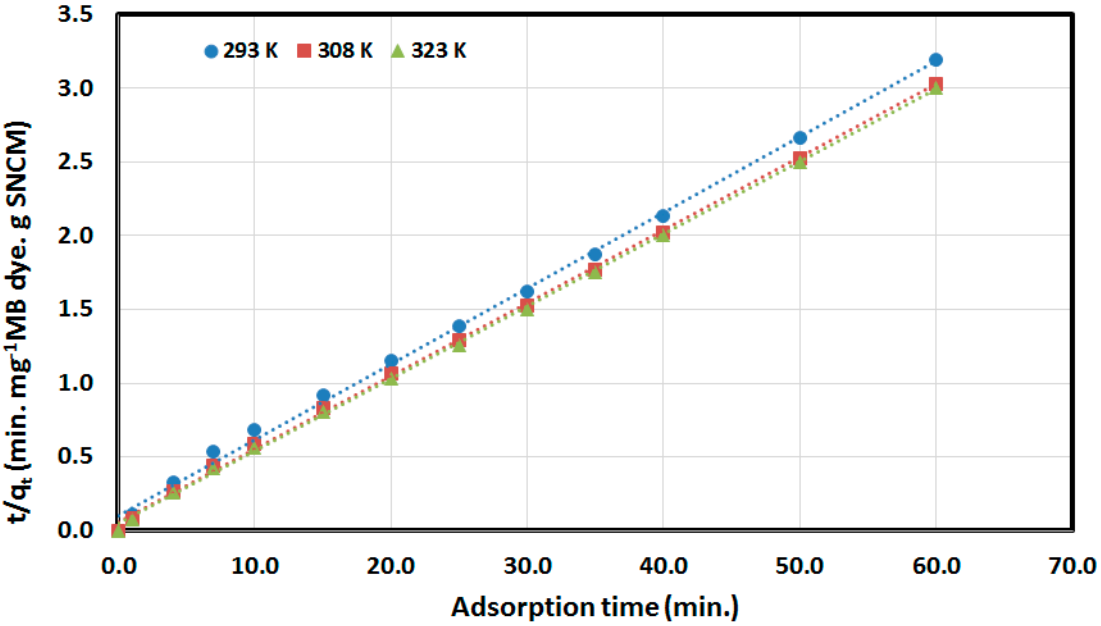

Fig. 10. The application of pseudo second order kinetic model for the MB dye removed from an aqueous solution by SNCM.

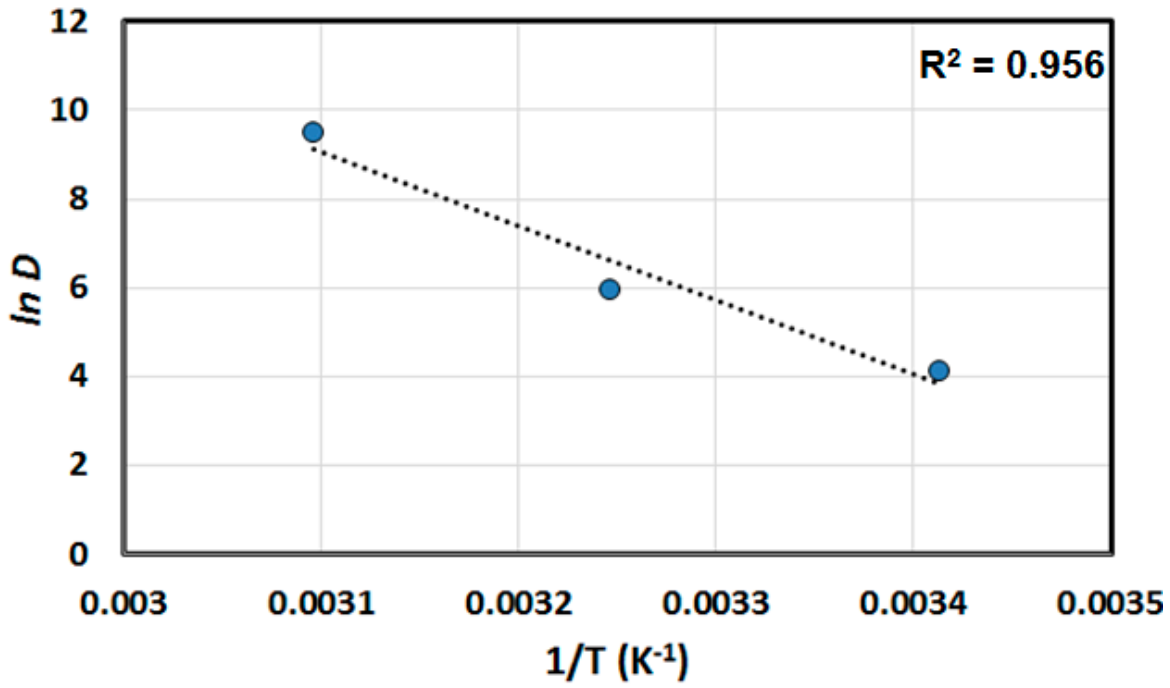

Fig. 11. Plot of ***ln D*** vs. $\mathbf{T^{-1}}$ for the MB dye removed from an aqueous solution by SNCM.