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Adsorption of Cobalamin onto Synthesized Carbon Nanotubes (CNT)

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ABSTRACT

The adsorption efficiency of synthesized carbon nanotubes at different doses and contact time were investigated. The amount of adsorbed dye increased with the increasing of CNTs dosage and reached a plateau region when the CNTs dosage achieved 0.175g L⁻¹. Equilibrium adsorption data were analyzed by Langmuir and Freundlich isotherm of the results revealed that Langmuir isotherm fitted the experimental results well. Kinetic analyzes were tested using pseudo-first order, pseudo second order and the intraparticle diffusion model. Kinetic studies showed that the adsorption kinetics were more accurately represented by a pseudo second order model.

Keywords: Adsorption, carbon nanotubes, titanium dioxide, cobalamin, kinetics, isotherms.

INTRODUCTION

Dyes are extensively used in different types of industries. During dye production and textile manufacturing processes, a large quantity of wastewater containing high concentration of organic compounds. These dyes are difficult to remove due to high solubility in water [1-7]. Many researches have been devoted in recent years to remove dyes from wastewaters, using different techniques such as adsorption. The adsorption removal is an effective and simple technique for dye treatment but usually produces large amount of sludge, which may cause secondary pollution. The individual treatment technique is not perfectly enough to remove the dyes from wastewaters efficiently without producing secondary contaminants. The photo degradation technique is more effective to get high removal of dyes from wastewater [8-12]. One of the most important factor of adsorption is surface area and pore volume. The carbon nanotubes that were used in this studies consist of mixture of single wall carbon nanotubes SWCNT and multi wall carbon nanotubes MWCNT. The first have larger surface area and pore volume as compared with the second type, while the later have large diameter than SWCNTs [13]. Much effort was kept in the last few years to remove many components that cause pollution for the air and water. There were many methods used to reach this aim. The photo catalytic degradation which needs source of energy. Carbon nanotubes were occupying specific attention from the scientists in the entire World. It has unique chemical structure and excellent physical and chemical properties. The physical properties like the porosity and large surface area, tubular structure. The interaction between carbon nanotubes and organic pollutant is due to π bonding. The most important condition is to increase the efficiency and selectivity of adsorption by carbon nanotubes was represented by surface area [14-17]. Titanium dioxide widely used as adsorbent

for organic substances(including dyes), due to its high adsorption capacity, high specific surface area , small interfibrous porous size, nontoxic and relatively inexpensive [18,19]. Therefore it has high application in the field of environmental pollution control [20].

In this study, Carbon nanotubes and titanium dioxide were used for the adsorption of cobalamin. The objective of this study was to compare the adsorption capacity of TiO₂ and CNTs. The adsorption equilibrium was fitted by Langmuir and Freundlich models. The adsorption kinetic was tested by pseudo-first-order kinetic, pseudo second- order kinetic and intraparticle diffusion model.

MATERIALS AND METHODS

Materials: Crystalline carbon nanotubes (CNT) powder with diameter of 20-30nm and length of 10-30μm was purchased from NANOSHEL. Graphite (99.995%) was purchased from (NGS) German, NaNO₃ (99%) from Fluka, H₂SO₄ (98.%) from Himedia lab. Pvt. Lem, H₂O₂ (40%) from SIGMA, HNO₃ (69.5%), from Scharlau, KMnO₄ and KClO₃ from Aldrich.

Synthesis of carbon nanotubes: CNT was prepared according to chemical precipitation method. Graphite 5g suspended in cold (2-5 °C) concentrated sulfuric acid 115 mL in a 500 mL round-bottom flask equipped with a mechanical stirring rod. Potassium permanganate 15g was added gradually with stirring and cooling so that the temperature did not exceed 20°C. The stirring was then continued for 2 h at 35°C followed by addition of distilled water 230 mL and stirred for an additional 15 min. The mixture was poured into 700 mL distilled water. Hydrogen peroxide 30% was added to remove the excess of permanganate which is indicated by change the color of solution from dark to yellow. In these steps the product was graphite oxide which was isolated by filtration and washed with a 10% HCl solution. 1g from graphite oxide and 70% HNO₃ solution 100 mL were added to a 500 mL bottle. This was sealed and then sonicated in a bath sonicator at room temperature for 4 h at 60 Hz. The mixture was poured into 3L of water. To remove the acid from carbon nanotubes the solution was centrifuged at 15000 rpm.

Synthesis of nanoparticle TiO₂: The titania nanoparticles were synthesized by drop wise addition of titanium tetrachloride TiCl₄ in isopropanol. The reaction was performed at room temperature while stirring under a fume hood due to the large amount of Cl₂ and HCl gases evolved in this reaction. The resulting yellow solution was allowed to settle and cooled to room temperature till the gas evolution ceased. The suspensions obtained were dried in an oven for two hours at 80°C until amorphous and dried TiO₂ particles were obtained. The obtained powder samples were calcined for one hour in a furnace at temperature ranging from 450 to 650°C in an ambient atmosphere.

Adsorption experiments: The adsorption experiments in this work were done to study the effect of experimental conditions on cobalamin adsorption and determining the conditions that achieve the maximum amount of cobalamin removal. The adsorption tests were conducted in magnetic mixer. The concentration of cobalamin was 40ppm and the amount of adsorbent was included the ratio 0.05, 0.075, 0.1, 0.15, 0.175, and 0.2 g for carbon nanotubes and titanium dioxide. In all experiments, the required amount of the adsorbent was suspended in 100 cm³ of aqueous solution of cobalamin. 2mL was taken from the reaction suspension, centrifuged at 4,000 rpm for 15 minutes in an 800 B centrifuge and filtered to remove the particles. The second centrifuge was found necessary to remove fine particle of the CNT or titanium dioxide. After the second centrifuge, the absorbance of the cobalamin was measured at 550 nm, using Cary 100Bio UV - visible spectrophotometer Shimadzu. The efficiency of cobalamin, % removal was calculated as [21,22]

$$\% \text{ Removal} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

Where C_i is the initial concentration and C_f is the final concentration. q is the amount of metal adsorbed per specific amount of adsorbent (mg g^{-1}). The sorption capacity at time t , q_t (mg g^{-1}) was obtained as follows:

$$q_t = \frac{(C_i - C_t) \times v}{m} \quad (2)$$

Where C_i is the initial concentration of cobalamin, C_t represents cobalamin concentration at time t , V is the solution volume and m is the mass of CNT (g). The amount of adsorption at equilibrium, q_e was given by:

$$q_e = \frac{(C_i - C_e) \times v}{m} \quad (3)$$

Where C_e was the cobalamin concentration at equilibrium.

Photocatalytic reactions: Photocatalytic reactions were carried out in a batch photo reactor with the radiation source (mercury lamp, containing 6 lamps with 15W for each type) Philips (CLEO), Poland. Aqueous suspensions of CNT or TiO_2 containing cobalamin in beaker, under magnetic stirring, were irradiated in light of wavelength 365nm with an irradiation intensity of $2.1 \text{ mW}\cdot\text{cm}^{-2}$. In all experiments, the required amount of the catalyst was suspended in 100 cm^3 of aqueous solution of cobalamin. After illumination, 2mL was taken from the reaction suspension, centrifuged at 4,000 rpm for 15 minutes in an 800 B centrifuge, filtered to remove the particles. The second centrifugation was found necessary to remove fine particles of the CNT or TiO_2 . Then the absorbance of the cobalamin was measured at 550 nm.

RESULTS AND DISCUSSION

Effect of contact time: Fig. 1 shows the effect of contact time on cobalamin removal. Removal increased with an increase in contact time. Adsorption was very rapid in the first 10 min for the synthesized carbon nanotube and for the first 20 min for the commercial carbon nanotube, then increased slowly with time until reaching equilibrium. It was found that the equilibrium time for both carbon nanotubes was more than 20 min. To ensure full equilibration, a shaking time of 60 min was used for all concentrations of carbon nanotubes in this study [23-25].

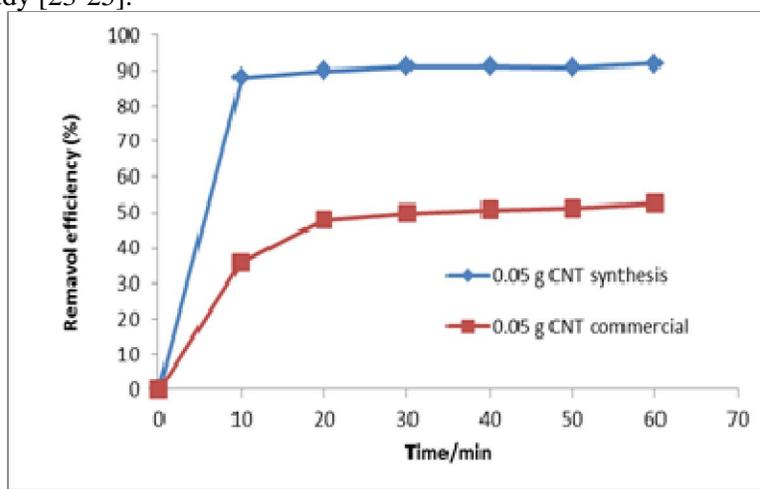


Fig. 1. Effect of contact time on cobalamin removal by carbon nanotube: Cobalamin concentration 40 ppm, adsorbent dosage 0.05 g, pH 7.8, and temperature 27°C.

Effect of CNT dosage on adsorption of cobalamin: The effect of CNT dose was studied for varying the dose between 0.05 g and 0.2g in 100 mL aqueous solution. These tests were conducted at a temperature of

27 °C, with pH 7.8 for cobalamin. The initial cobalamin concentration was 40 ppm. It was observed that the adsorption efficiency percentage of cobalamin onto the CNT increased rapidly with the increase of adsorbent concentration as shown in fig. 2. This result is expected because the increase of adsorbent dose leads to greater surface area. When the adsorbent concentration was increased from 0.05g to 0.2g, the percentage of cobalamin adsorption increased from 35.94 to 53.53. At higher concentrations, the equilibrium uptake of cobalamin did not increase significantly with increasing CNT. So, there was no any appreciable increase in the effective surface area resulting due to the conglomeration of exchanger particles. So, 0.15 g 100 mL⁻¹ was considered as optimum dose. The results shown in fig. 3 and fig. 4 as C_t/C_0 against time per min. where C_0 and C_t represent the concentration of cobalamin at time zero and different times of irradiation respectively [26].

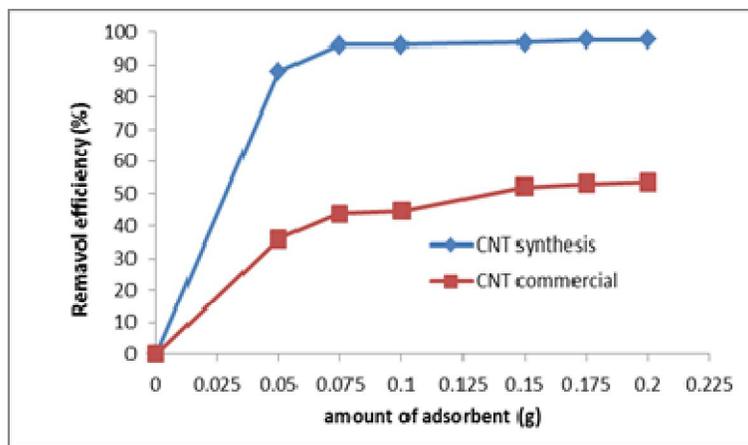


Fig. 2. The effect of dosage of adsorbent on the removal efficiency (the initial cobalamin concentration 40 ppm, pH 7.8, and temperature 27°C).

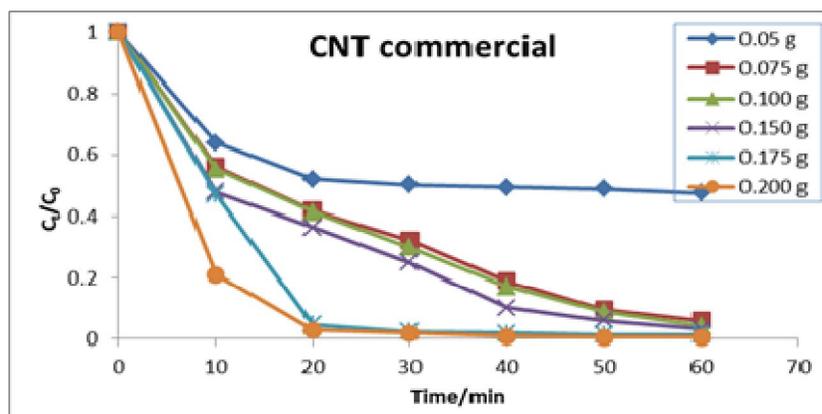


Fig. 3. Effect of CNT dose on cobalamin adsorption. [Conditions: 27°C, pH 7.8, initial cobalamin 40 ppm]

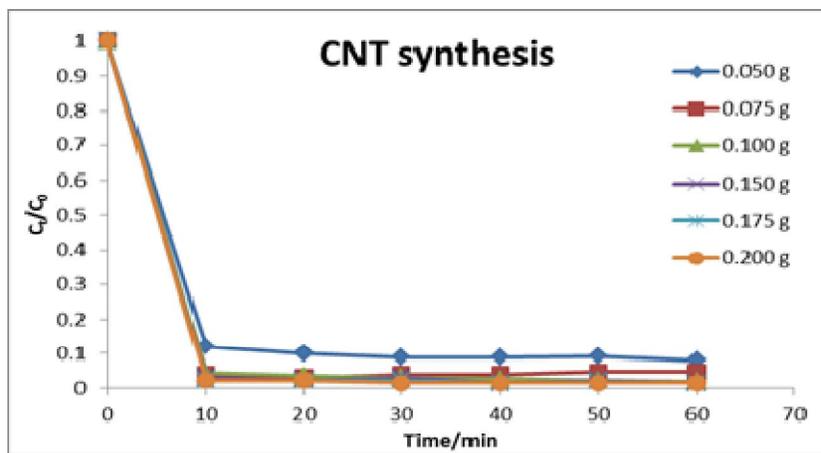


Fig. 4. Effect of CNT dose on cobalamin adsorption.
[Conditions: 27°C, pH 7.8, initial cobalamin 40 ppm]

Effect of TiO₂ dosage on adsorption of cobalamin: The effect of TiO₂ dose was studied for varying the dose between 0.05 g and 0.2g in 100 mL aqueous solution. These tests were conducted at a temperature of 27 °C, with pH 7.8 for cobalamin. The initial cobalamin concentration was 40 ppm. It was observed that the adsorption efficiency percentage of cobalamin onto the TiO₂ was increase slightly with the increase of adsorbent concentration as shown in Fig.5 and 6.

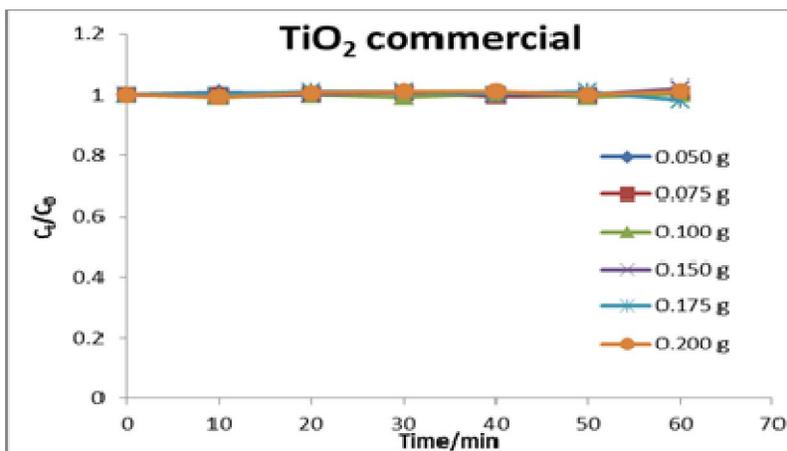


Fig. 5. Effect of TiO₂ dose on cobalamin adsorption.
[Conditions: 27°C, pH 7.8, initial cobalamin 40 ppm]

Photocatalytic Activity of the TiO₂: The photocatalytic efficiency percentage of cobalamin onto the TiO₂ increased rapidly with the increase of adsorbent concentration as shown in fig. 7. The effect of TiO₂ dose was studied for varying the dose between 0.05 g and 0.2g in 100 mL aqueous solution. This result is expected because the increase of TiO₂ dose leads to greater surface area. One possible explanation for such behavior is that it is believed that an increase in the number of catalyst will increase the number of photons absorbed and the number of cobalamin molecules adsorbed. Therefore, the photodegradation rate can be expected to be enhanced on increasing the amount of catalyst due to the increase in total surface area available for contaminant adsorption. However, a further increase of the catalyst concentration may cause light-screening effects [27]. These screening effects reduce the specific activity of the catalyst [28-30].

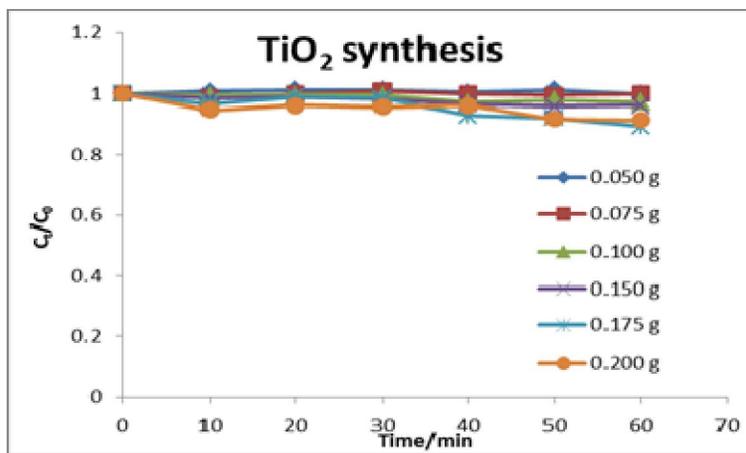


Fig. 6. Effect of TiO_2 dose on cobalamin adsorption
[Conditions: 27°C , pH 7.8, initial cobalamin 40 ppm]

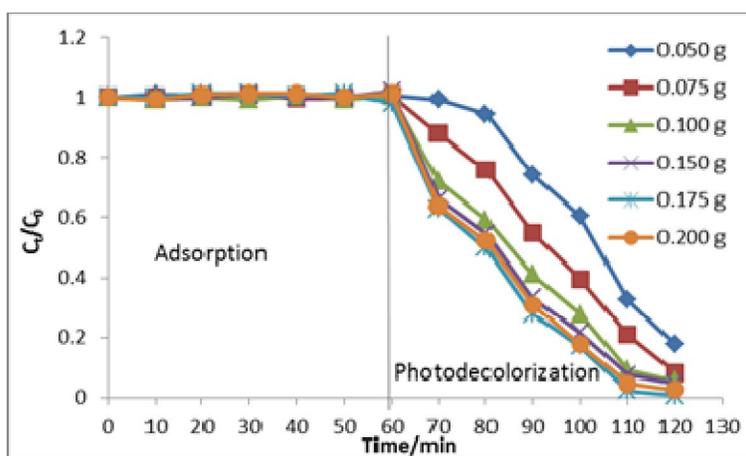


Fig. 7. Effect the masses of TiO_2 on photodecolorization of cobalamin.

Comparative study of adsorption activity of CNT and TiO_2 in degradation of cobalamin: The results in fig. 8 show the relationship between the adsorption efficiency of cobalamin with time by using two types of adsorbent CNT and TiO_2 , under the experimental conditions. CNT and TiO_2 concentrations 0.05 g. The results show that the activity of different types of adsorbent used in this study was of the sequence- CNT (synthesized) > CNT (commercial) > TiO_2

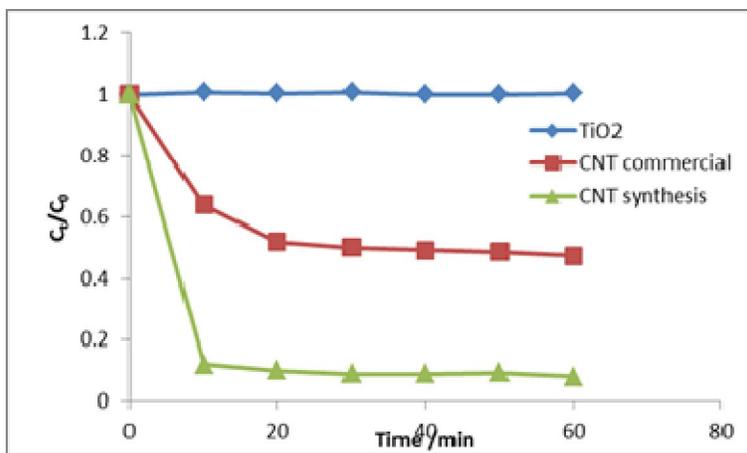


Fig. 8. Effect of adsorbent dose on cobalamin adsorption.

Kinetics of cobalamin adsorption on CNT: The kinetics of cobalamin adsorption on CNT were determined under the same conditions. It was found that the equilibrium time for both carbon nanotubes was more than 20 min. To ensure full equilibration, a shaking time of 60 min was used for all concentrations of carbon nanotubes in this study. The experimental data were processed with respect to three different kinetic models namely pseudo-first order [31], pseudo-second order [32], and intra-particle diffusion [33]. The equations (4) and (5) represent the linear forms of the pseudo-first order and pseudo-second order models respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

Where, q_e (mg g^{-1}) and q_t (mg g^{-1}) are amounts of cobalamin adsorbed at equilibrium and at time t respectively. k_1 (min^{-1}) and k_2 (g per min.mg) are the pseudo-first order and pseudo-second order adsorption rate constant respectively. Fig. 9 and 10 show pseudo-first order and pseudo-second order plots respectively for the experimental data. Various rate constants derived from the slopes and intercepts along with correlation coefficients are given in table 1 and table 2. The pseudo-second order plot in fig. 10 has better correlation coefficient, R^2 . The calculated value of adsorption capacity from the plot in fig. 10 is found to be closer to the experimentally determined value than that calculated from fig. 9. This suggests that the pseudo-second order model represents the kinetic data more accurately.

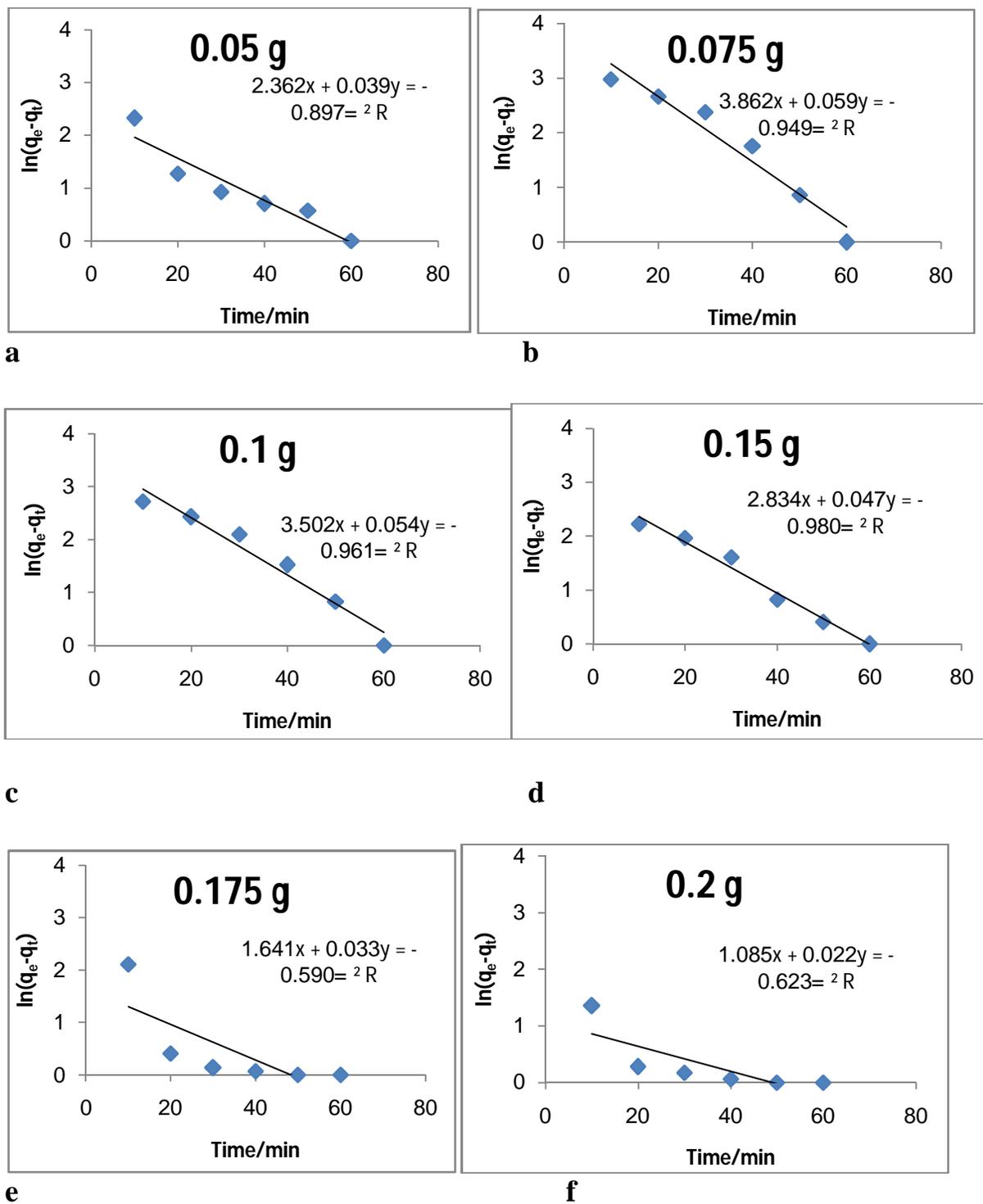
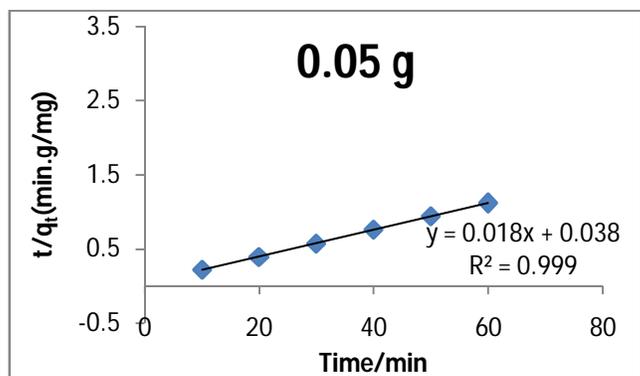
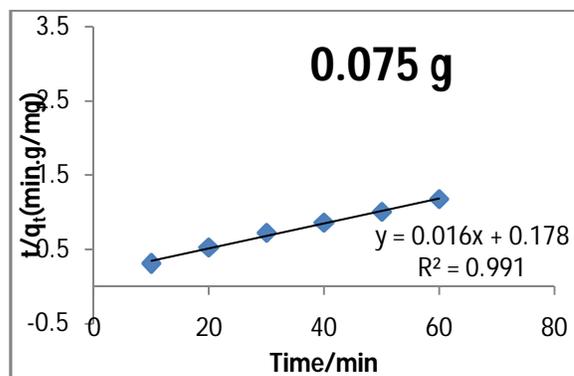


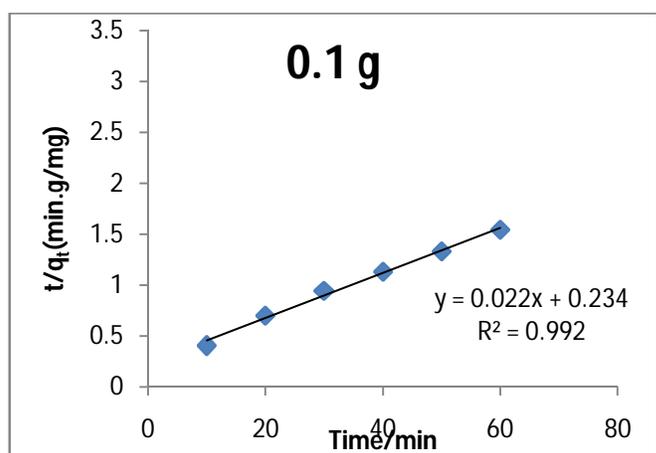
Fig. 9. Plot of (a,b,c,d,e and f) pseudo-first-order-kinetic model, for the adsorption of cobalamin onto CNTs. [Conditions: 27 °C, adsorbent dose (0.05-0.2 g/L), initial [cobalamin] 40 ppm, pH 7.8]



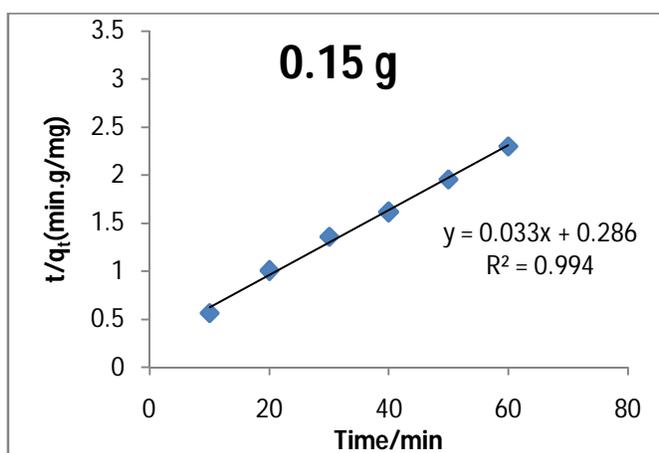
a



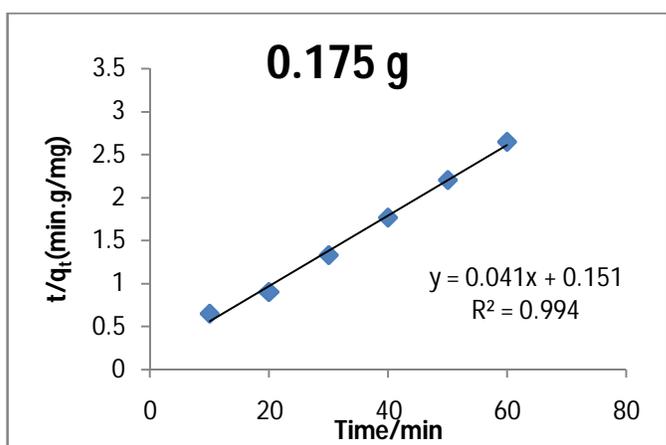
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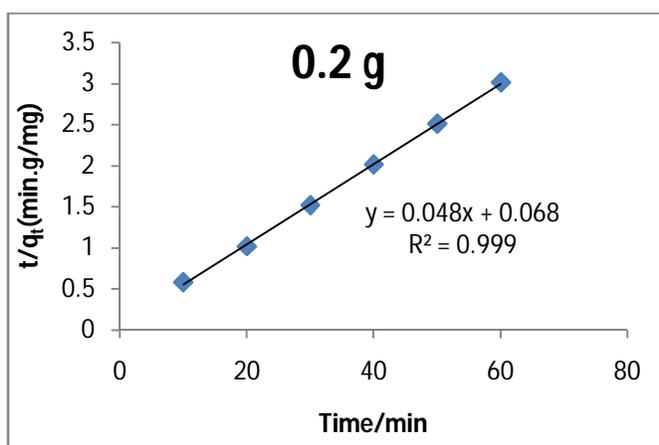
c



d



e



f

Fig. 10. Plot of (a,b,c,d,e and f) pseudo-second-order-kinetic model for the adsorption of cobalamin onto CNTs. [Conditions: 27 °C, adsorbent dose (0.05-0.2 g/L), initial [cobalamin] 40 ppm, pH 7.8]

Table 1. The pseudo-first-order-kinetic model, for the adsorption of cobalamin onto CNT at different adsorbent dose.

| Pseudo-first-order kinetic | | | | |
|-----------------------------|-----------------------|-------------------------|--------------------------------|--------|
| adsorbent dose (g/100ml) | $q_{e,exp}$ (mg/g) | $q_{e,calc.}$ (mg/g) | k_1 (min^{-1}) | R^2 |
| 0.050 | 53.589 | 10.610 | 0.0399 | 0.8974 |
| 0.075 | 51.111 | 47.580 | 0.0597 | 0.9494 |
| 0.100 | 38.846 | 33.200 | 0.0543 | 0.9615 |
| 0.150 | 26.068 | 17.015 | 0.0474 | 0.9802 |
| 0.175 | 22.637 | 28.940 | 0.0339 | 0.5902 |
| 0.200 | 19.935 | 2.960 | 0.0221 | 0.6237 |

Table 2. The pseudo-second-order-kinetic model, for the adsorption of cobalamin onto CNTs at different adsorbent dose.

| Pseudo-second-order kinetic | | | | |
|-----------------------------|-----------------------|-------------------------|---------------------|--------|
| adsorbent dose (g/100ml) | $q_{e,exp}$ (mg/g) | $q_{e,calc.}$ (mg/g) | K_2 (g/mg.min) | R^2 |
| 0.050 | 53.589 | | | |
| | | 55.24862 | 0.473822 | 0.9997 |
| 0.075 | 51.111 | | | |
| | | 59.52381 | 0.094382 | 0.9919 |
| 0.100 | 38.846 | | | |
| | | 45.04505 | 0.094589 | 0.9929 |
| 0.150 | 26.068 | | | |
| | | 29.67359 | 0.117832 | 0.9949 |
| 0.175 | 22.637 | | | |
| | | 24.39024 | 0.174691 | 0.9944 |
| 0.200 | 19.935 | | | |
| | | 20.49180 | 0.170629 | 0.9995 |

The intraparticle diffusion model [33], is expressed as

$$q_t = k_{id} t^{1/2} + C \quad (6)$$

Where, k_{id} is the intraparticle diffusion rate constant ($\text{mg per g} \cdot \text{min}^{1/2}$) and C is a constant related to boundary layer thickness (mg g^{-1}). If intraparticle diffusion is involved in the adsorption process, the q_t versus $t^{1/2}$ plot should be linear and should go through the origin if intraparticle diffusion is the sole rate-controlling step. Fig. 11 shows that the plot of q_t vs. $t^{1/2}$ is not linear over the entire time period. This

implies that more than one process is controlling the adsorption. The dotted line is indicative of the intraparticle diffusion on the CNT, for which the rate constant and intercept are given in Table 3.

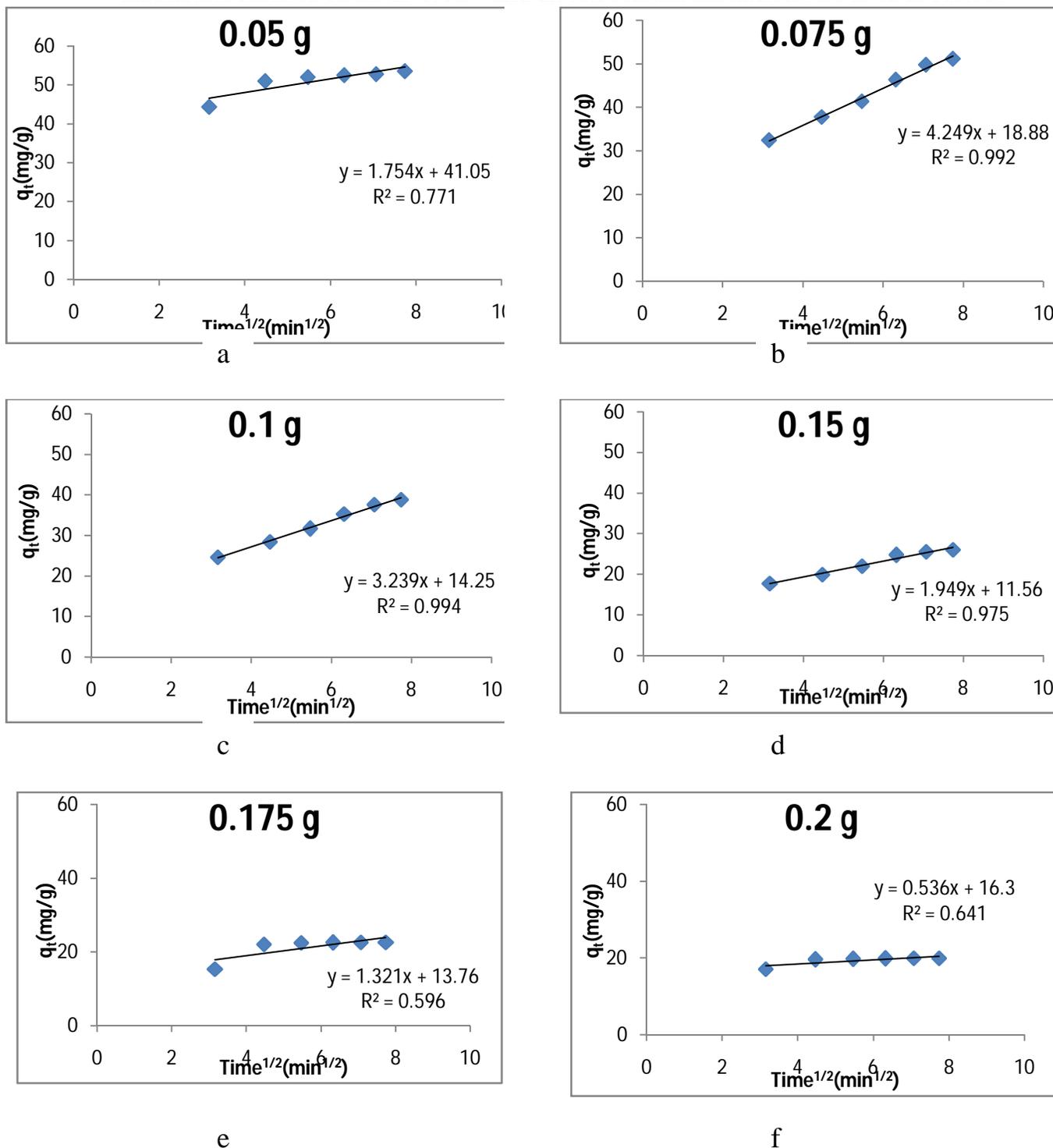


Fig. 11. Plot of (a,b,c,d,e and f) Intraparticle diffusion model, for the adsorption of cobalamin onto CNTs. [Conditions: 27°C, adsorbent dose (0.05-0.2 g/L), initial [cobalamin] 40 ppm, pH 7.8]

Table 3. The intraparticle diffusion model, for the adsorption of cobalamin onto CNTs at different adsorbent dose.

| adsorbent dose (g/100ml) | Intraparticle diffusion | | | |
|-----------------------------|-------------------------|-------------|--|----------------|
| | $q_{e,exp}$ (mg/g) | C (mg/g) | K_{id} (mg/g.min ^{1/2}) | R ² |
| 0.050 | 53.589 | 41.056 | 1.7549 | 0.7713 |
| 0.075 | 51.111 | 18.889 | 4.2497 | 0.9922 |
| 0.100 | 38.846 | 14.256 | 3.2391 | 0.9943 |
| 0.150 | 26.068 | 11.568 | 1.9498 | 0.9758 |
| 0.175 | 22.637 | 13.767 | 1.3215 | 0.5966 |
| 0.200 | 19.935 | 16.3 | 0.5361 | 0.6418 |

Adsorption isotherms: The adsorption isotherms are studied through various models such as the Langmuir and Freundlich isotherms. The Langmuir model is based on the assumption of homogeneous monolayer coverage with all sorption sites to be identical and energetically equivalent. The Freundlich model assumes physicochemical adsorption on heterogeneous surfaces. The linear forms of the two models are [34-40].

$$\text{Langmuir} \quad 1/q_e = 1/q_m + 1/K_L q_m C_e \quad (7)$$

$$\text{Freundlich} \quad \log q_e = \log K_F + 1/n \log C_e \quad (8)$$

Where, q_e (mg g⁻¹) is amounts of cobalamin adsorbed at equilibrium, q_m (mg/g) is the monolayer adsorption capacity, K_L (L mg⁻¹) is the Langmuir adsorption constant related to the free energy of adsorption and C_e (mg L⁻¹) is equilibrium cobalamin concentration in the solution. K_F and (1/n) are Freundlich adsorption isotherm constants being indicative of extent of adsorption and intensity of adsorption, respectively. The Langmuir isotherm equation was used to estimate the maximum adsorption capacity of the CNT under the same conditions by varying adsorbent dose from (0.05 to 0.2 g). The values of the isotherm constants and R² are given in table 4. The linear plot is shown in fig. 12, of 1/q_e versus 1/C_e along with high value correlation coefficient indicate that Langmuir isotherm provides a better fit with the equilibrium data. The adsorption data when fitted to the Freundlich isotherm the plot of log q_e versus log C_e in figure 1 shows that Freundlich isotherm gives a poor fit to the experimental data as compared to Langmuir isotherm. The isotherm parameters as derived from the slope and intercept of the plots are listed in table 4.

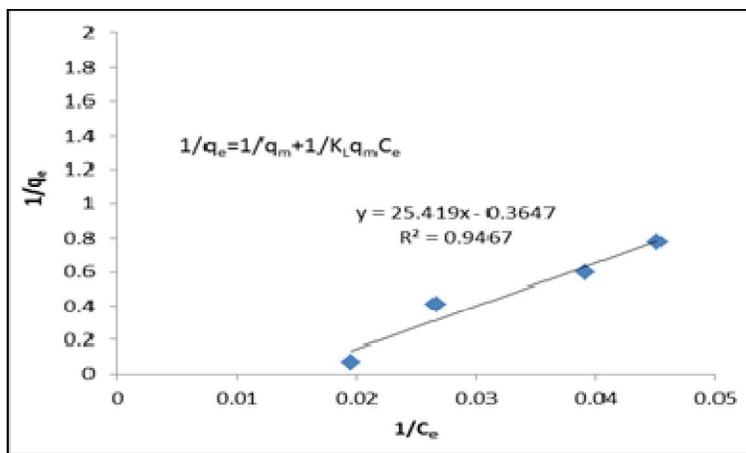


Fig. 12. The linear Langmuir adsorption isotherms for cobalamin adsorption by the CNT.

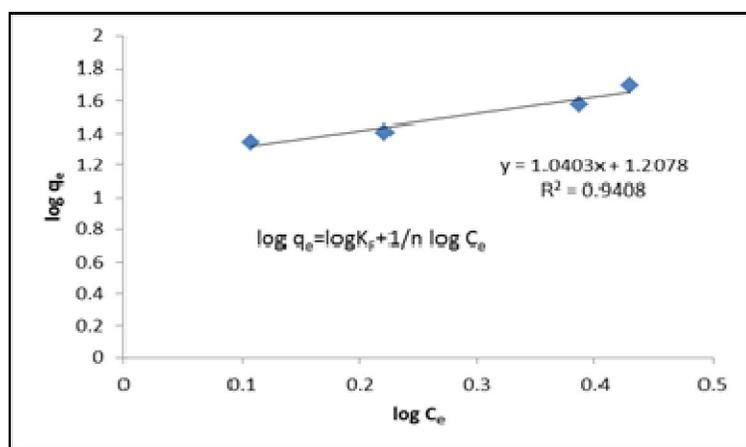


Fig. 13. The linear Freundlich adsorption isotherms for cobalamin adsorption by the CNT.

Table 4. Langmuir and Freundlich isotherm constants.

| Isotherms | Constants/Correlation coefficients | Values |
|------------|------------------------------------|--------|
| Langmuir | R^2 | 0.9467 |
| | q_m | 2.741 |
| | K_L | 0.018 |
| Freundlich | R^2 | 0.9408 |
| | K_F | 16.136 |
| | n | 0.961 |

AFM Measurements: AFM is a powerful method for investigation and examination of carbon nanotubes [41, 42]. This was used as an indirect method for morphological analysis of the sample [43]. AFM represents a powerful tool for studying the fibrillation pathway since the wide range and coexistence of relatively large

structural species is difficult to probe using diffraction methods [44]. The synthesis process of carbon nanotubes by chemical precipitation method was tested by using AFM techniques, which include forming CNTs Fig.14 from graphene oxide, Fig. 14 for two dimension and three dimensions. The diameter which obtained from these method for commercial CNTs was 81.59 nm, while for synthesis CNTs was 91.48 nm, O-CNTs was 64.09nm, for graphene oxide was 108. 51nm.

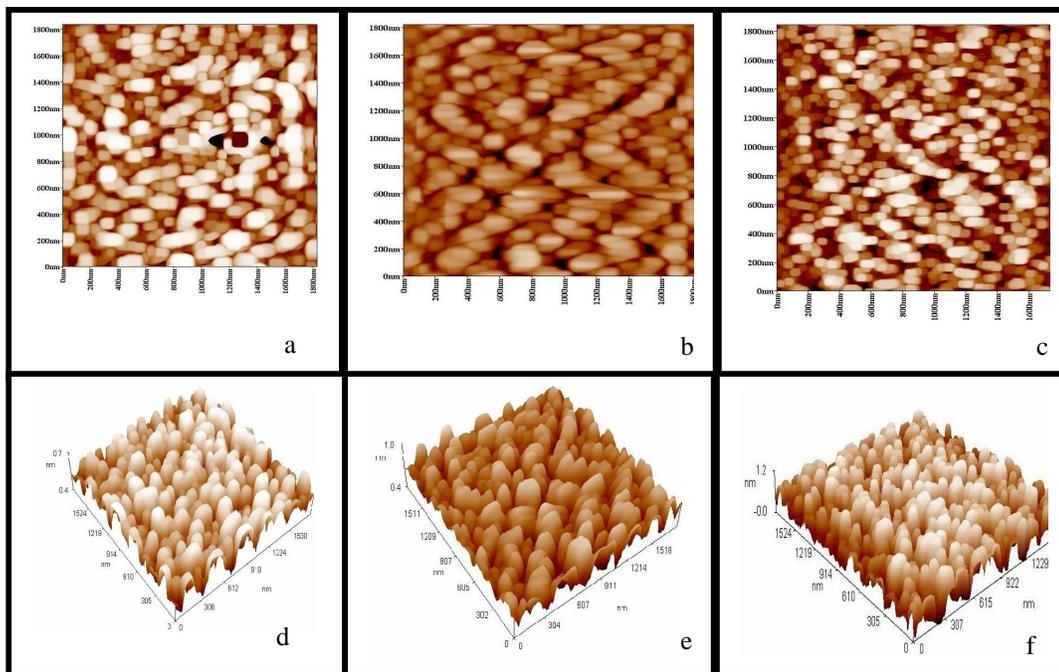


Fig.14 .(a, d) AFM image of graphene oxide, (b,e) AFM image of synthesis CNT, (c, f) AFM image of commercial CNT.

APPLICATIONS

The application of CNT shows high efficiency for the cobalamin removal in the wastewater.

CONCLUSIONS

Carbon nanotubes and titanium dioxide were used as adsorbents for the removal of cobalamin from aqueous solution in the present study. The optimum conditions of adsorption were found to be an adsorbent dose of 0.15 g in 100 mL of solution. The optimum contact time and pH were 20 min and 7.8 respectively. The pseudo-second-order-kinetic model equation is the best to describe adsorption of cobalamin on CNT. The results show that the best fit was achieved with the Langmuir isotherm equation. Also application of CNT shows high efficiency for the cobalamin removal in the wastewater. The efficiency of color removed increase with increasing adsorbent dosage, increase with increasing contact time. The removal efficiency of cobalamin was found equal to 92% for CNT (synthesis) and 52% for CNT (commercial). The results indicate that the adsorption efficiency percentage of cobalamin with carbon nanotubes was markedly higher than of titanium dioxide. The results show that the activity of different types of adsorbent used in this study was of the sequence- CNT (synthesis) > CNT (commercial) > TiO₂

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