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Optimization of adsorption conditions for removal of total organic carbon from drinking water using polypropylene and titanium dioxide nano-composite by response surface methodology

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ABSTRACT

Identification of organic carbon in drinking water can indicate the presence of hazardous pollutants that are capable of threatening human health and aquatics. This study was conducted to optimize adsorption of total organic carbon (TOC) using polypropylene/titanium dioxide nano-composite from drinking water by response surface methodology (RSM). Activation of polypropylene (PP) fibers was achieved via wet heating. To synthesize the nano-composite, activated PP fibers were coated with nano-TiO_2 in sonication chamber. The morphology of the fractured surfaces of impact specimens was examined by field-emission scanning electron microscopy (FE-SEM). After FTIR spectroscopy and EDS test, the adsorption of TOC was evaluated in different spiked drinking water. The adsorption data were simulated using isotherm models. The pore size distributions and pore volume of synthesized nano-composite were measured using multiple point nitrogen gas adsorption/desorption analysis. In addition, central composite design (CCD) was applied to optimize the effects of the operating parameters, including contact time (5–60 min), adsorbent dose (0.5–4 g/l), and initial concentration of TOC (2–20 ppm), on responses which were adsorption rates (mg/kg). The FE-SEM micrographs showed that the dispersion of the nano-Tio_2 particles was relatively good and only few aggregations exist. The total pore volume of synthesized nano-composite was 2.06 cm^3/g (p/p_0 = 0.98) with an average pore diameter of 2.48 nm and a surface area of 51.52 m^2/g. Optimized conditions of initial TOC concentration, adsorbent dose, and contact time were found as 11.00 mg/L, 2.25 g/L, and 32.50 min, respectively. The isotherm evaluations revealed that the equilibrium data for TOC removal using PP/TiO_2 nano-composite could be fitted with the Langmuir model. The obtained results showed that the PP/TiO_2 nano-composite can be effectively used to remove TOC from relatively polluted water.

Keywords: TOC; Drinking water; PP/TiO_2 nano-composite; Response surface methodology

1. Introduction

"Access to safe drinking water is fundamental to human development and a basic human right. A lack of access to safe drinking-water sources, coupled with inadequate sanitation and hygiene, remains one of the most critical public health challenges globally" [1]. Today, water pollution caused by chemicals has been widely reported [2,3]. There are numerous organic compounds known in the environment which threaten human health [4]. Determination of these compounds in water bodies cannot be defined individually with considerable analytical effort in short time. Therefore, use is made of grass analysis, including biochemical oxygen demand (BOD), chemical oxygen demand

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(COD), and total organic carbon (TOC). TOC is a measure of the total amount of organic matter that reflects organic pollution on the basis of a direct carbon determination [5]. It has a direct effect on the production of disinfection by-products (DBPs) such as trihalomethanes (THMs) that are formed during the disinfection process [6]. Moreover, it can indicate the presence of many pollutants in water resources such as phenolic compounds, polycyclic aromatic hydrocarbons, and chlorinated hydrocarbons. The carcinogenicity of these compounds is proven by international agency for research on cancer (IARC) [7].

Some studies have attempted to determine TOC concentration in bodies of water [8]. He and Xu [9] investigated long-term variability of TOC from four major coastal rivers in Louisiana entering the Northern Gulf of Mexico. They found out that these rivers annually discharged a total of 13.0–104.0 tons TOC. Unfortunately, there is no plan for monitoring and removing TOC from potable water in many countries. Furthermore, international organizations such as WHO have not provided guidance on TOC concentration in drinking water [10,11].

Although removal of total organic matter from water resources has been reported in some studies, there is, to the best of our knowledge, no evidence of the use of PP/TiO_2 nano-composite to remove TOC from drinking water. It is proven that at extremely high loads of TOC, municipal chemical treatment by coagulation and sedimentation effectively reduces TOC to a manageable level for the public health [12,13]. What is more, it has been reported that some water utilities draw upon a conventional or direct filtration process to remove TOC from water resources [14]. Hakizimana et al. [15] assessed removal of organic matter from seawater by electrocoagulation (EC) and showed that the EC method can remove 70.8% dissolved organic carbon. In another study, TOC in coking wastewater was reduced by 33% using free graphitic carbon nitride/Sio_2 hybrid hydro-gel [16].

Owing to its good processability and mechanical properties, PP is used as one of the most important polymers in technical applications. Also, titanium dioxide is an inexpensive photo catalyst with high reactivity which improves the performance properties of PP. It depends on mixing patterns, particle size, and carbon contents of TiO_2 nano-powders [17–19]. Altan et al. [20] demonstrated that TiO_2 gave higher tensile strength to PP due to its stiff structure. After the synthesis of nano-composite, field-emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray-spectroscopy (EDS), Fourier-transform infrared (FTIR) spectroscopy, and BET analysis were employed to study the morphology and characteristics of the PP/TiO_2 nano-composite. Finally, the current study set out to model and optimizes the removal of TOC using PP/TiO_2 nano-composite from potable water by Response Surface Methodology (RSM) using Design-Expert 7.0 software.

2. Materials and methods

2.1. Drinking water origin

Qazvin (Iran) tap water was used as drinking water. To obtain TOC concentration levels in drinking water (2–20 mg/l), the potassium hydrogen phthalate (KHP, which was procured from Merck, Germany) were spiked from stock solutions (200 mg/L) in ultra-pure water. KHP is solid, air-stable, and easy to weigh accurately. For these reasons, KHP is used as an organic substance of synthetic wastewater and as a model compound in environmental studies [21]. Prior to the test, the TOC concentration of drinking water was determined. Further, domains of experiments were determined by implementing preliminary tests. Removal of TOC from spiked drinking water samples was evaluated in 5–60 min at 20°C with synthesized PP/TiO_2. At each stage, TOC concentration was measured in triplicate using a TOC analyzer (TOC ANATOC SeriesII, SGE International, PTY Ltd, Australia). TOC analysis was carried out at room temperature, injection volume of 1 ml, UV radiation at 300–400 nm, and presence of a dilute suspension of TiO_2 in solution (2%) as a catalyst.

2.2. Nano-composite synthesis

The PP fibers with a density of 0.91 g/cm^3, a length of 0.01 m, and a diameter of 330 micrometers (Razi Corporation, Iran) and nano-TiO_2 with a diameter of 20 nm and made up of 80% Anatase and 20% Rutile (NANOSANY, Iran) were used for nano-composite synthesis. PP/TiO_2 nano-composite was synthesized in three stages, including activation of PP fibers, coating of PP fiber with nano-TiO_2, and drying. The PP fibers were activated through wet heating for 90 min at 65°C in a stainless steel chamber. Increasing contact time and temperature in PP activation was limited to fiber deformation. In various studies, activation of PP has been reported with different methods such as dry heat and plasma [22, 23]. Then, activated fibers were coated with nano-TiO_2 with a diameter of 20 nm. This was performed at 26 kHz and 100 W at 40°C in a sonication chamber with nano-TiO_2 solution with 0.5, 1, and 2 mg/l concentrations. The feasibility of this method has already been proven by Szabova et al. [23]. Lastly, fibers were washed with distilled water and were dried using hot air. The morphology of the fractured surfaces was examined via FE-SEM. The pore size distributions and pore volume of PP/TiO_2 nano-composite were assessed using a multiple point nitrogen gas adsorption Brunauer-Emmett-Teller (BET) surface area analyzer (Belsorp Mini II, Japan). BET analysis was applied using the amount of N_2 gas adsorbed at different partial pressures (p/p_0) and a single condensation point ($p/p_0 = 0.98$). Additionally, particle distribution and titanium particle weight content in the PP/TiO_2 nano-composite were analyzed with image analysis and EDS, using a Mira 3-XMU device equipped with an EDS micro-analyzer (TESCAN-Corporation). FTIR spectroscopy was employed to identify fiber-forming substances, using an EQUINOX55 FT-IR (Bruker Optics, Ettlingen, Germany).

2.3. Study design and statistical analysis

Optimum conditions for the adsorption of TOC by synthesized PP/TiO_2 were determined by means of central composite design (CCD) under response surface methodology (RSM) with Design-Expert 7.0. RSM is a mathematical and statistical approach to analyze and evaluate the effects of variables and to obtain optimum conditions of variables to predict responses [24, 25].

In the present study, CCD was used as the most famous design method based on multivariate nonlinear analysis to optimize the effects of operating parameters, including contact time (5–60 min), adsorbent dose (0.5–4 g/l), and initial TOC concentration (2–20 ppm), on responses which were the adsorption rates of TOC on PP/TiO_2 nano-composite (mg/kg). Experiments were performed in 15 runs. The analysis of variable (ANOVA) was used to evaluate the predicted coefficient values of the model. The significance level was set at $p < 0.05$.

2.4. Isotherm studies and validity assessment

Langmuir, Freundlich, and Temkin isotherms were used to understand the mechanism of adsorption and to assess the transmission of TOC from the solution phase to the PP/TiO_2 nano-composite in equilibrium. The linear form of isotherm equations and employed plots are presented in Table 1, where C_e denotes equilibrium concentration (mg/L), q_e is amount of TOC adsorbed in equilibrium (mg/g), q_m indicates the maximum amount of adsorption (mg/g), b is the adsorption equilibrium constant (L/mg), K_f denotes adsorption capacity (Freundlich constant (mg/g) $(L/g)^{1/n}$), n is adsorption intensity, and K_T is the binding constant representing the maximum binding energy (Temkin isotherm constant as L/mg) [26].

The validity of isotherm equations was assessed by the correlation coefficient (R^2), average relative error (ARE), Marquardt's percent standard deviation (MPSD), and hybrid fractional error function (HYBRID) values, as presented in Eqs. (1)–(3), where $q_i^{\exp}$ and q_i^{cal} are experimental and calculated mass of TOC adsorbed by PP/TiO_2 nano-composite, N is the number of observations in the experimental isotherm, and P is the number of parameters in the regression model [26,27].

$$ARE = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{q_i^{\exp} - q_i^{cal}}{q_i^{\exp}}\right| \quad (1)$$

$$MPSD = 100\sqrt{\frac{1}{N-P}\sum_{i=1}^{N}\left(\frac{q_i^{\exp} - q_i^{cal}}{q_i^{\exp}}\right)^2} \quad (2)$$

$$HYBRID = \frac{100}{N-P}\sum_{i=1}^{N}\left[\frac{\left(q_i^{\exp} - q_i^{cal}\right)^2}{q_i^{\exp}}\right] \quad (3)$$

3. Results and discussion

3.1. Synthesized nano-composite

The surface structure of PP fibers before and after treatment with nano-TiO_2 was analyzed using FE-SEM. FE-SEM micrographs provide useful resolution and permit repeated multi-site imaging of surfaces [28]. As shown in Fig. 1a, the surface of crude PP fiber was smooth and without bumps; however, the surface of nano-composite was moldy and appeared to bulge after synthesis (Fig. 1b). The FE-SEM micrographs showed that the dispersion of the nano-TiO_2 particles was relatively good and only few aggregations exist. Fig. 2 shows the FTIR spectra of the synthesized PP/TiO_2 nano-composite. The presence of grafted regions on the composite surface can be confirmed by the vibration peak at 1570–700 cm^{-1} regions. According to the results obtained by Gao et al. (2004) and Randorn et al. (2004), these peaks are thought to be formed by adsorption of TiO_2on the PP fibers [19,29,30]. The nitrogen adsorption–desorption isotherms PP/TiO_2 nano-composite is displayed in Fig. 3, which presents the amount of gas adsorbed in equilibrium as a function of partial pressure (p/p_0). The maximum amount of adsorbed nitrogen increased with partial pressure. BET analysis showed that the total pore volume of synthesized PP/TiO_2 nano-composite was 2.06 cm^3/g ($p/p_0 = 0.98$), with an average pore diameter of 2.48 nm. The results demonstrated that the prepared PP/TiO_2 nano-composites have a high surface area (51.52 m^2/g). To validate the presence of Titanium on the PP surface, EDS was performed. Fig. 4 shows the EDS spectrum for the PP/TiO_2 nano-composite. The peaks corresponding to nitrogen, carbon, oxygen, and titanium can be observed in spectrum. Similar results were reported by Wei et al. [31]. Quantitative analysis of EDS spectrum revealed that the titanium weight content in the composite can be promoted from 3.4 to 3.71%. The sharp carbon and nitrogen peaks are ascribable to the dentin substrate [32].

Table 1
Isotherms and their expressions as applied for the adsorption of TOC by PP/TiO_2 nano-composite

Isotherm	Equations	Plot
Freundlich	$\log(q_e) = \log(K_f) + 1/n \log\log(C_e)$	q_e vs. log C_e
Langmuir	$C_e / q_e = 1/bq_m + C_e / q_m$	C_e/q_e vs. C_e
Temkin	$q_e = q_m \ln K_T + q_m \ln C_e$	q_e vs. ln C_e

3.2. Optimum conditions and statistical analysis

Performance of PP/TiO_2 nano-composite in the adsorption of TOC from drinking water was evaluated to be up to 3.6 mg/g of the adsorbent. As shown in Table 2, the observed and predicted values of responses are highly interrelated ($R^2 = 0.86$). In other words, the regression model provides a good explanation of the relationship between the independent variables (i.e., adsorbent dosage, contact time, and initial TOC concentration) and the response (i.e., TOC adsorption).The second order response surface model was obtained for optimum values from the results of multiple linear regressions. The summary output of ANOVA of TOC removal using PP/TiO_2 nano-composite showed that the model was significant ($p < 0.05$). Three factors of contact time (A), interaction between contact time and adsorbent dose (B), and interaction between adsorbent dose and initial TOC concentration (C) significantly influenced the response (Figs. 5a, b, and c). Of these variables, interaction between B and C had the strongest effect on TOC adsorption (F = 13.56).

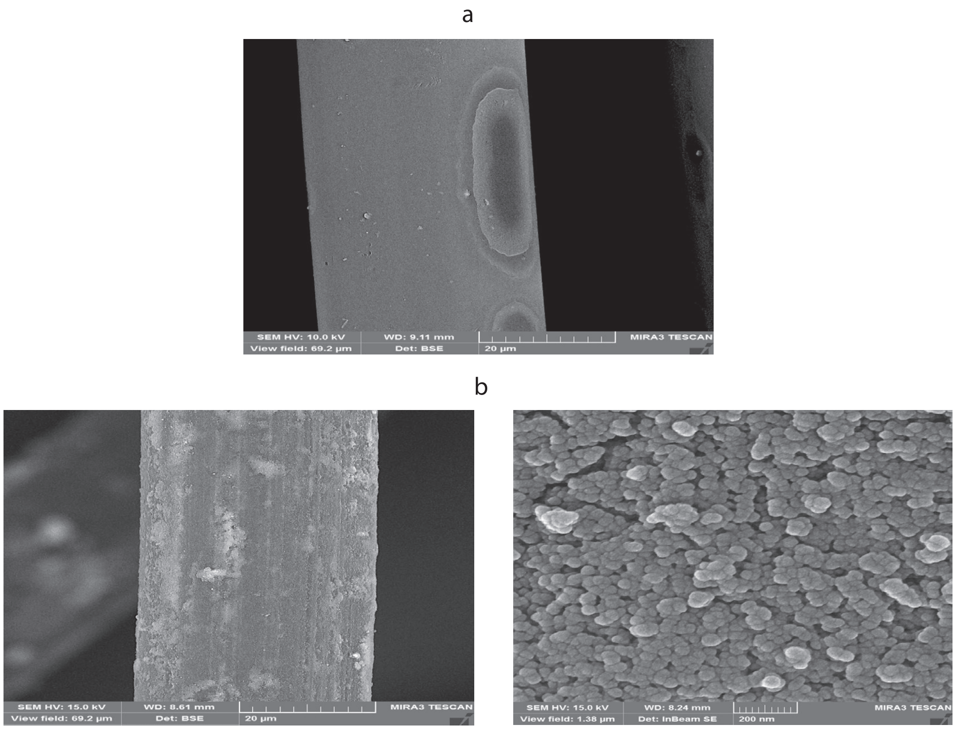

Fig. 1. SEM micrographs, surface of PP fiber before treatment (a) and surface of nano-composite after treatment (b).

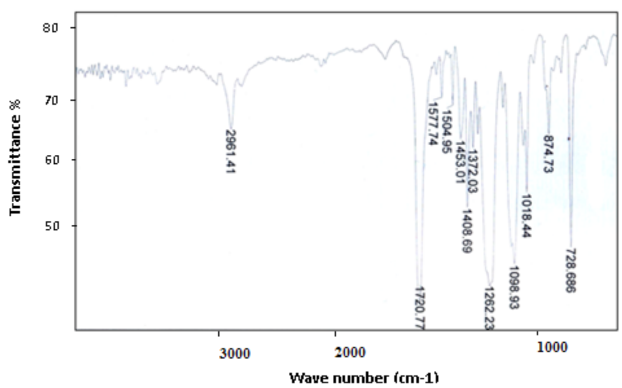

Fig. 2. FTIR spectra of the synthesized PP/TiO_2 nano-composite.

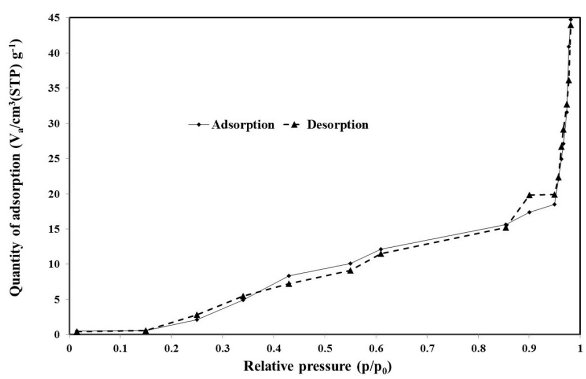

Fig. 3. Nitrogen adsorption/desorption isotherms of PP/TiO_2 nano-composite.

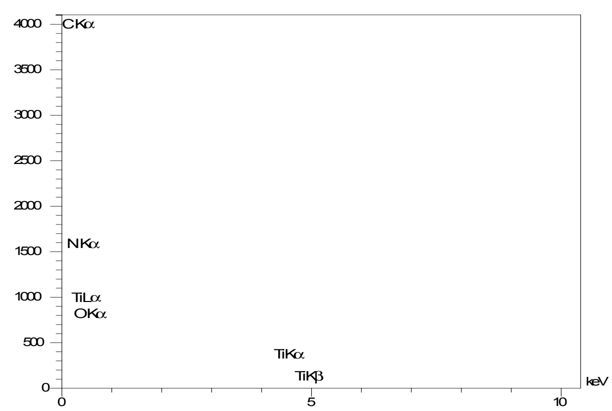

Fig. 4. EDS spectrum of synthesized PP/TiO_2 nano-composite.

The optimum conditions for TOC removal using PP/TiO_2 nano-composite were achieved using 2.25 g/l of the adsorbent, 11 mg/L of initial TOC concentration, and 32.50 min of contact time (Fig. 5d). The TOC removal efficiency was 73.6% under the optimum conditions at a prediction interval of between 68.5 and 78.9%. TOC adsorption using free graphitic carbon nitride/SiO_2 hybrid hydro-gel has been reported in the literature to be up to 33%, which was lower than the PP/TiO_2 nano-composite in the present study [16]. Polypropylene has been previously reported to remove organic matter from polluted water. In addition, the unique properties of the PP/TiO_2 has already been proven [19,20]. Muhandiki et al. [33] emphasized the ability of PP coated n-hexane to remove hydrophobic organic com-

Table 2
Analysis of variance and statistical analysis for response surface model

Source	Sum of squares	Mean squares	F value	p-value Prob > F
Model	15.78	2.63	0.93	0.004
A - Contact time	1.12	1.12	3.52	0.097
B - Adsorbent dose	0.038	0.038	0.12	0.738
C - Initial TOC	0.29	0.29	0.93	0.364
AB	3.04	9.58	9.58	0.015
AC	0.12	0.39	0.39	0.548
BC	4.31	13.56	13.56	0.006
Result, mean ± SD	0.96±0.56			
C.V., %	58.68			
Press	33.34			
R-squared	0.86			
Adjusted R-squared	0.76			
Predicted R-squared	0.82			
Pure error	6.85	2.28		

pounds from the effluent of municipal wastewater treatment plants.

The obtained results showed that a higher TOC removal efficiency occurred at higher values of initial TOC concentration. The higher initial concentration of organic matter leads to an increase in the mass transfer driving force. Consequently, the organic matter passes from the solution to PP/TiO_2 nano-composite surfaces. These results are consistent with the findings of the studies into the removal of phenol from aqueous solutions by adsorption onto organo-modified tirebolu bentonite [34].

The optimum conditions for the removal of TOC by PP/TiO_2 nano-composite is stated in Eq. (4). The validity of this equation was sustained by the residual point (Fig. 6, which statistically illustrates that residual point follow normal distribution). The obtained model can be developed due to the p-value of the lack of fit ($p > 0.05$).

$$\text{Adsorption dose (mg/g)} = 0.32 - 0.042\,(A) + 0.15\,(B) + 0.19\,(C) + 0.016\,(A{*}B) - 7.5\,E - 004\,(A{*}C) - 0.065\,(B{*}C) \quad (4)$$

Furthermore, the validity of the above model was assessed via the diagnostic analysis of outliers (Fig. 7).

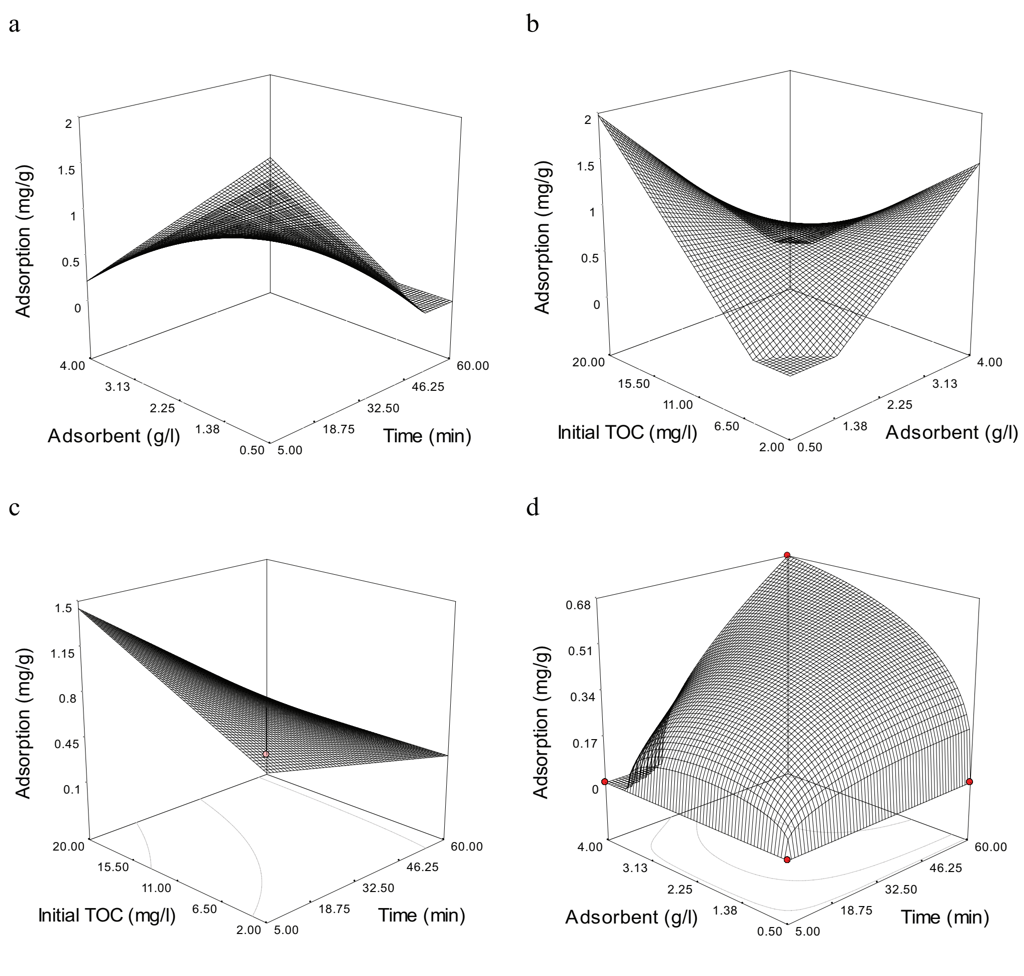

Fig. 5. Effect of the interaction between independent variables on TOC removal efficiency (a, b, and c) and the optimum condition graph (d).

Assessing the leverage versus run number (a) and Cook's distance versus run number (b) plots revealed some outlier (run order 1 and 5). The leverage versus run plot gives a perspective into whether a run is an influential data point. In addition, Cook's distance plot can be used to notice whether a run is significantly different from the other cases. The run values are relative. High values may indicate an outlier [35].

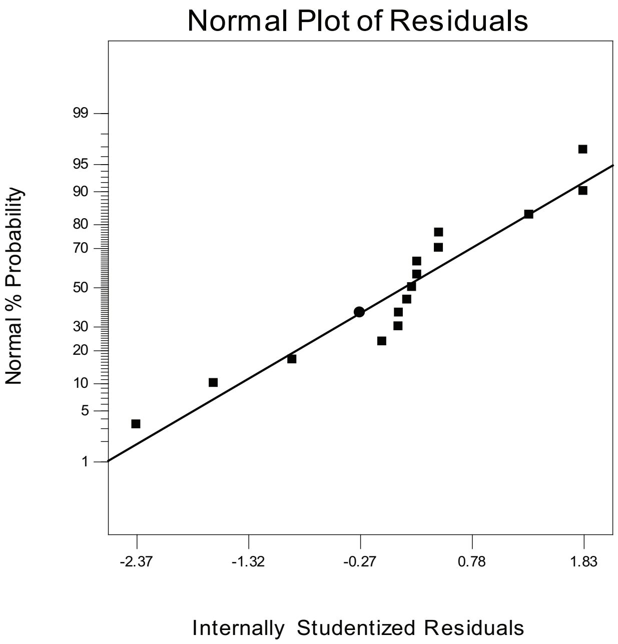

Fig. 6. Diagnostic plot-normal probability of the chosen model.

3.3. Effect of factors on TOC removal

The combined effects of contact time, adsorbent dose, and initial concentration of TOC on TOC removal by PP/TiO_2 nano-composite are illustrated in Fig. 5. The effects of adsorbent dose and contact time (Fig. 5a) and interaction between adsorbent dose and initial concentration of TOC (Fig. 5b) were significant (p < 0.05). However, the interaction between initial TOC concentration and contact time did not reach significance (p = 0.548, F = 0.39). Adsorbent dosage is a key parameter in batch studies. The obtained results showed that TOC adsorption increases with an increase in the mass of adsorbent from 0.5 to 4g/l. This can be attributed to an increase in the adsorption surfaces area. Although Abu Hasan et al. (2011) assessed RSM for optimization of COD removal from potable water using a biological reactor [36], the effect of the PP/TiO_2 nano-composite on the efficiency removal of TOC from drinking water has not been studied in the existing literature.

3.4. Equilibrium isotherms

The values of correlation coefficients are listed in Table 3. Linear regression analyses of three Langmuir (type 1), Freundlich, and Temkin models and a comparison of their correlation coefficients (R^2) formed the basis of judgment about the applicability of isotherm equations in describing the adsorption process. These models have been applied to many adsorption processes [26,27,37]. As shown in Table 3, Langmuir was better fitted than the Freundlich and Temkin models, suggesting that adsorption occur as the monolayer onto the homogenous adsorbent surface with a uniform distribution of energy level. Similar results was obtained from the removal of phenolic compounds from olive mill wastewater [37]. The essential features of the Langmuir isotherm were assessed by the equilibrium

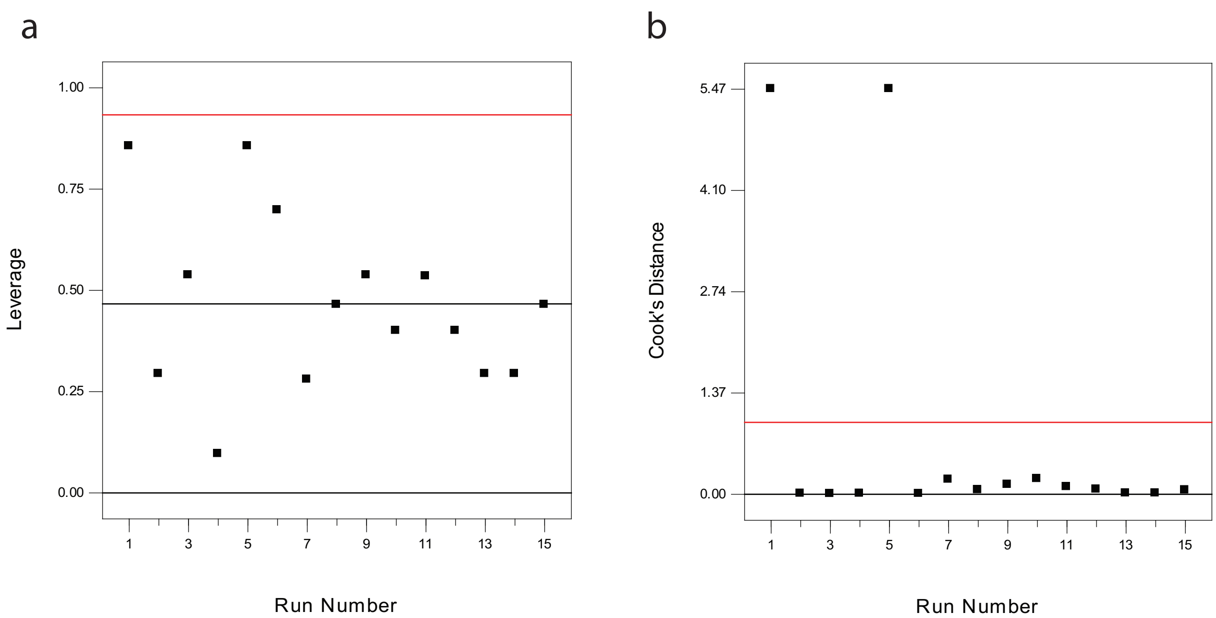

Fig. 7. Diagnostic plot-outlier T of the chosen model.

Table 3
Isotherm parameters as obtained using the linear regression method for the adsorption of TOC by PP/TiO_2 nano-composite

Isotherm	Parameters	R^2	MPSD	HYBRID	ARE
Freundlich	$n = 0.91$	0.992	1.46	38.77	4.39
	$K_f = 29.78$ (mg/g) (L mg^{-1})$^{1/n}$				
Langmuir	$b = 0.51$ L/mg	0.994	0.88	10.79	3.18
	$q_m = 0.1$ mg/g				
Temkin	$K_T = 0.26$ L/mg	0.812	1.88	46.07	3.54
	$q_m = 2.54$ mg/g				

parameter, R_L [Eq. (5)], where b is the Langmuir constant, C_0 denotes the initial TOC concentration (g/L), and R_L values indicate the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$) [37]. The result obtained here showed R_L to be 0.15, indicating that the adsorption of TOC on the PP/TiO_2 nano-composite was favorable.

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

The obtained values of MPSD, ARE, and HYBRID are given in Table 3. Lower values imply more accurate estimations [26]. The correlation coefficient of the Langmuir (type 1) model was higher than in the Freundlich and Temkin models, but the MPSD, ARE, and HYBRID values of the Langmuir model were lower than in the Freundlich and Remkin isotherms. This suggests that Langmuir model can more accurately predict the adsorption than do Temkin and Freundlich isotherms.

4. Conclusions

After PP/TiO_2 nano-composite was characterized via FTIR spectroscopy, EDS, SEM, and BET analysis, the conditions of TOC removal from potable water were optimized using RSM under the CCD method. In addition, to explain the relationship between initial adsorbent and adsorption, Langmuir, Freundlich, and Temkin models were used. According to AVOVA analysis, TOC removal is highly affected by contact time, interactions between contact time and adsorbate dose, and interactions between adsorbent dose and adsorbate dose. Optimized conditions of initial TOC concentration, adsorbent dose, and contact time were found as 11.00 mg/L, 2.25 g/L, and 32.50 min, respectively. Linear regression analyses revealed that Langmuir model provides the best fit in the explanation of TOC removal using the PP/TiO_2 nano-composite, implying that the surface of the PP/TiO_2 nano-composite for the adsorption of organic matter may be heterogeneous with a different energy distribution. Finally, the reported results indicate that the PP/TiO_2 nano-composite can be successfully used in the removal of TOC from drinking water and that it can be considered an effective adsorbents for organic pollutants.

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