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A novel nanocomposite as adsorbent for formaldehyde removal from aqueous solution

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Abstract. In order to develop a new adsorbent for removal of formaldehyde from aqueous solution, surface modification of TiO_2 nanoparticles was performed with 2,4-Dinitrophenylhydrazine (DNPH) that have a strong affinity to the formaldehyde. Sodium dodecyl sulfate (SDS) surfactant was used to improve the DNPH grafting to TiO_2 surface. Modified adsorbents were characterized by SEM, TEM, XRD, EDX and FTIR. Since the COD level in wastewaters including formaldehyde is considerable, it is necessary to determine the COD content of the synthetic wastewater. In order to determine the optimal removal conditions, the effect of contact time (60-210 min), pH (4-10) and adsorbent dosage (0.5-1.5 g/L) on adsorption and COD removal efficiencies were studied, using response surface method. EDX and FTIR analysis confirmed the presence of nitrogen-containing functional groups on the modified TiO_2 surface. The maximum formaldehyde adsorption and COD removal efficiencies by modified TiO_2 were about 15.65 and 7.35% higher than the unmodified nanoparticles respectively. Therefore, the grafting of nano-TiO_2 with DNPH would greatly improve its formaldehyde adsorption efficiency. The optimum conditions determined for a maximum formaldehyde removal of 99.904% and a COD reduction of 94.815% by TiO_2/SDS/DNPH nanocomposites were: adsorbent dosage 1.100 g/L, pH 7.424 and the contact time 183.290 min.

Keywords: titanium dioxide nanoparticles; DNPH; formaldehyde; aqueous solution; adsorption; COD

1. Introduction

Formaldehyde (HCHO), whose scientific name is methanal, is one of the most harmful compounds for humans and the environment. Because of more electronegativity of oxygen relative to carbon in its carbonyl functional group (C = O), formaldehyde is a polar molecule. The dipole attractions between this molecule and other materials cause formaldehyde to be dissolved in polar solvents such as water and ethanol. Formaldehyde has properties like other aldehydes, but it is usually more reactive than most of them and is widely used due to its high reactivity, colorless nature, stability, purity in commercial forms and low cost. Industries such as synthetic resins, adhesives, detergents, preservatives, explosives, paper production, wood processing, chemical and petrochemical industries, plastics and polymers are formaldehyde consumers (Afkhami *et al.* 2011, Krishnamurthy *et al.* 2018, Su *et al.* 2018, Szczurek *et al.* 2018). It is also used in formalin as a disinfectant in hospitals. All of these applications can lead to the considerable entrance of formaldehyde within environment. Exposure to this reactive organic compound can cause central nervous system damage; blood, immune system and growth disorders; blindness and respiratory disease (Moteleb *et al.* 2002, Li *et al.* 2007, Afkhami *et al.* 2011, Kowalik 2011, Khanmohammadi *et al.* 2012, Teiri *et al.* 2018). Also, the International Agency for Research on Cancer (IARC) has classified formaldehyde as a human carcinogen and the US Environmental Protection Agency (EPA) has classified it as a probable human carcinogen (Afkhami *et al.* 2011). Therefore, formaldehyde should be removed effectively from water.

Due to the presence of formic acid and methanol, COD content of formaldehyde contaminated wastewaters is high (Osada *et al.* 2004). Conventional removal technologies include reverse osmosis, advanced oxidation processes (Kowalik 2011), biological (Hidalgo *et al.* 2002, Priya *et al.* 2009, Ebrahimi and Borghei 2011, Veenagayathri and Vasudevan 2017) and chemical methods (Moussavi *et al.* 2009) are often costly and complex with low efficiency and by-products. Moteleb et al. had examined the biological treatment of a formaldehyde simulating wastewater from a resin production facility and achieved a removal rate of up to 99.99% under continuous loading (Moteleb *et al.* 2002). Ebrahimi et al. investigated formaldehyde degradation in a bioreactor with pumice stone as a support. The average formaldehyde and COD removal efficiencies obtained were 97.1% and 88%, respectively (Ebrahimi and Borghei 2011). Veenagayathri *et al.* studied the biodegradation of formaldehyde under saline conditions by a moderately halophilic bacterial consortium; A maximum degradation (up to 90%) was obtained in the presence of 5% salt content (Veenagayathri and Vasudevan 2017). Moussavi *et al.* removed formaldehyde from concentrated synthetic wastewater using $O_3/MgO/H_2O_2$ process integrated with the biological treatment. The formaldehyde and COD

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concentrations were reduced 79 and 65.6%, respectively (Moussavi *et al*. 2009).

Adsorption is an attractive pollutant removal method due to its process simplicity, low cost; selectivity and reusability of the adsorbent (Al-Rashdi *et al*. 2012, Jafari *et al*. 2012, Li *et al*. 2018a, b, Huang *et al*. 2019). Nowadays, nano-adsorbents are widely used in separating pollutants from water due to high surface-to-volume ratio, easy synthesis and rapid absorption. However, most of the used adsorbents have not succeeded in effectively formaldehyde removal, especially in high concentrations (Afkhami *et al*. 2011). Song *et al*. had reported the breakthrough time and formaldehyde adsorption capacity 361 min and 0.478 mmol/g, respectively for removal of formaldehyde at low concentration from air using various activated carbon fibers (Song *et al*. 2007). Afkhami *et al*. had used alumina nanoparticles grafted with functional groups as adsorbent in removal of formaldehyde from water and had obtained a high removal efficiency (Afkhami *et al*. 2011). Rong et al. removed formaldehyde by activated carbon fibers modified by P-aminobenzoic acid. They observed much higher adsorption capacity because of the presence of nitrogen-containing functional groups on the surface of modified adsorbent (Rong *et al*. 2010). Krishnamurthy et al. had focused on evaluating the dynamic adsorption of formaldehyde over binary mixed-metal oxides such as ZrO_2/SiO_2 and TiO_2/SiO_2 (Krishnamurthy *et al*. 2018). Ghasemi et al. had eliminated Hg (II) ions (more than 96%), by TiO_2 nanocrystals from aqueous solution (Ghasemi *et al*. 2012).

Titanium dioxide is a nontoxic material and has been applied in environmental treatments such as water and air disinfection because of relatively low price, corrosion resistance and its unique properties such as strong photocatalytic activity and high physical and chemical stability (Ghasemi *et al*. 2012, Hejri *et al*. 2013, Lu *et al*. 2014, Petala *et al*. 2016, Safavila *et al*. 2017). Also, researches have shown that TiO_2 can be recovered from various effluents and it can be reused as a sorbent in the elimination of contaminants from water (Mehta and Patel 1951, Khezri and Bloorchian 2009, Ahmed 2015, Lim and Shon 2015). Anatase nanoparticles has higher sorption capacity relative to other phases of TiO_2 (Xie and Gao 2009, Suriyaraj *et al*. 2014). In recent years, TiO_2 nanoparticles have been used to removal of some pollutants by adsorption because of its considerable adsorption capacity (Visa *et al*. 2009, Xie and Gao 2009, Parshetti and Doong 2010, Al-Rashdi *et al*. 2012, Ghasemi *et al*. 2012, Parida *et al*. 2012, Jiang *et al*. 2013, Lu *et al*. 2014), but to the best of our knowledge, any research focused on formaldehyde removal from water by adsorption on TiO_2 nanoparticles has not yet been reported. Compounds containing amine groups that can react with aldehydes are used as adsorbents for the formaldehyde separation (Rong *et al*. 2010). It is anticipated that impregnation of TiO_2 with amino-containing compounds can enhance its removal capacity for formaldehyde because of the cooperation of physical adsorption and the increased chemical interaction between amino groups on the surface of adsorbent and formaldehyde molecules. In this research, grafting of nanoparticles with 2,4-Dinitrophenylhydrazine ($C_6H_6N_4O_4$) as a source of amine groups on TiO_2 surface was conducted and formaldehyde removal optimum conditions were determined.

2. Materials and methods

2.1 Materials

Nano-TiO_2 powder (anatase-phase crystal structure with average particle size of about 25 nm) was supplied by Nanolin, Germany. Formaldehyde solution (37 wt. % in H_2O with density 1.09 g/cm^3), ammonium acetate (98% purity, molecular weight 77.0825 g/mol and density 1.17 g/cm^3), acetic acid (96% purity, molecular weight 60.05 g/mol and density 1.05 g/cm^3); acetylacetone (99% purity, molecular weight 100.12 g/mol and density 0.97 g/cm^3), 2,4-Dinitrophenylhydrazine (99% purity, molecular weight 198.1 g/mol and density 0.97 g/cm^3) and sodium dodecyl sulfate (SDS) were purchased from Merck, Germany.

2.2 Preparation of TiO_2/DNPH nano-adsorbent

To improve the formaldehyde adsorption rate by TiO_2, grafting of the nanoparticles with DPNH which has a strong affinity to bonding with formaldehyde, was performed according to the method of Afkhami *et al*. (2011). DPNH was used as an agent to form amine groups on TiO_2 surface. Anionic Sodium Dodecyl Sulfate (SDS) surfactant was used as grafting agent between TiO_2 and DPNH. For this purpose, 2 g TiO_2 nanoparticles were suspended in 50 mL deionized water and 100 mg SDS was poured. Then 20 mL DNPH solution (0.9 g DNPH in concentrated solution of hydrochloric acid and acetonitrile) was added. The solution was stirred at 60°C for 3 h, and then the solvent evaporated under vacuum. The remaining solid phase was washed with deionized water; after drying, it was kept in a sealed container for absorption tests.

2.3 Characterization of adsorbent

The morphology of unmodified and modified nanoparticles was studied using Cambridge S360 scanning electron microscope (SEM) equipped with an Oxford EDX. All images were taken with an operating voltage 30 kV and 200, 500, 1000 and 2000 magnifications. Specimens were sputter-coated with gold in a Quorum sputter coater model Q 150R ES. A closer look at the shape, size, and arrangement of the nanostructure adsorbent was carried out by Philips transmission electron microscope (TEM) model CM120. The X-ray diffraction analysis (XRD) was performed at an angular range of 5°-70° (2θ) with a step size of 2θ = 0.02° in Philips Analytical X-Ray diffractometer model X’ Pert PW 3040/60 using a CuK_α radiation (λ = 1.5406 nm), 40 kV, and 30 mA. The diffractometer was equipped with 1° divergence slit and a 0.1 mm receiving slit. Fourier transform infrared spectroscopy (FTIR) was carried out by the Thermo Nicolet apparatus model Avatar 370, made in USA. All of the peaks were obtained in the range of 4000 to 400 cm^{-1} for modified and unmodified nano-adsorbent.

2.4 Design of experiments

Response Surface Method (RSM), Central Composite Design (CCD) type has been employed to design of experiments, analyze resulted data and to determine the effect of various process parameters namely “contact time”, “pH” and “adsorbent dosage” with three levels for each one, on “adsorption efficiency” and “COD removal efficiency” responses (20 runs containing 8 factorial points, 6 central points and 6 axial points). The levels of factors have been selected according to preliminary tests. Design expert software version 10 was applied for analysis of variance (ANOVA). The 0.05 significance level was used. The optimal value for each of the three parameters was determined according to the obtained responses. Factors under study along with their levels are summarized in Table 1.

Table 1 Factors under study along with their levels

Factor	Level	
	Low	High
A : Contact Time (min)	60	210
B : pH	4	10
C : Adsorbent Dosage (g/L)	0.5	1.5

2.5 Adsorption experiments

Experiments were conducted discontinuously in presence of nitrogen (to prevent oxidation), to evaluate the amount of formaldehyde adsorption. Certain concentrations of formaldehyde at specific contact times and pHs were subjected to different amounts of adsorbent, based on the relevant experiments design. Aqueous formaldehyde solution was stirred on a magnetic stirrer at 1000 rpm to allow transfer of the pollutant onto the adsorbent. Finally the adsorbent was separated by centrifuge at 15000 rpm for 15 min.

2.6 Determination of COD and formaldehyde content

Proposed methods for determining the formaldehyde content often include spectrophotometric techniques, based on the formaldehyde reaction with organic or inorganic reagents. In this study, the formaldehyde reaction with Hantzsch reagent was used based on Nash method (Nash 1953). To prepare Hantzsch reagent, 150 g ammonium acetate (2 M), 3 mL acetic acid (0.05 M) and 2 mL acetylacetone (0.02 M) were dissolved in 1000 mL water. To determine the formaldehyde content of aqueous solutions, 5 mL of the solution was transferred to another

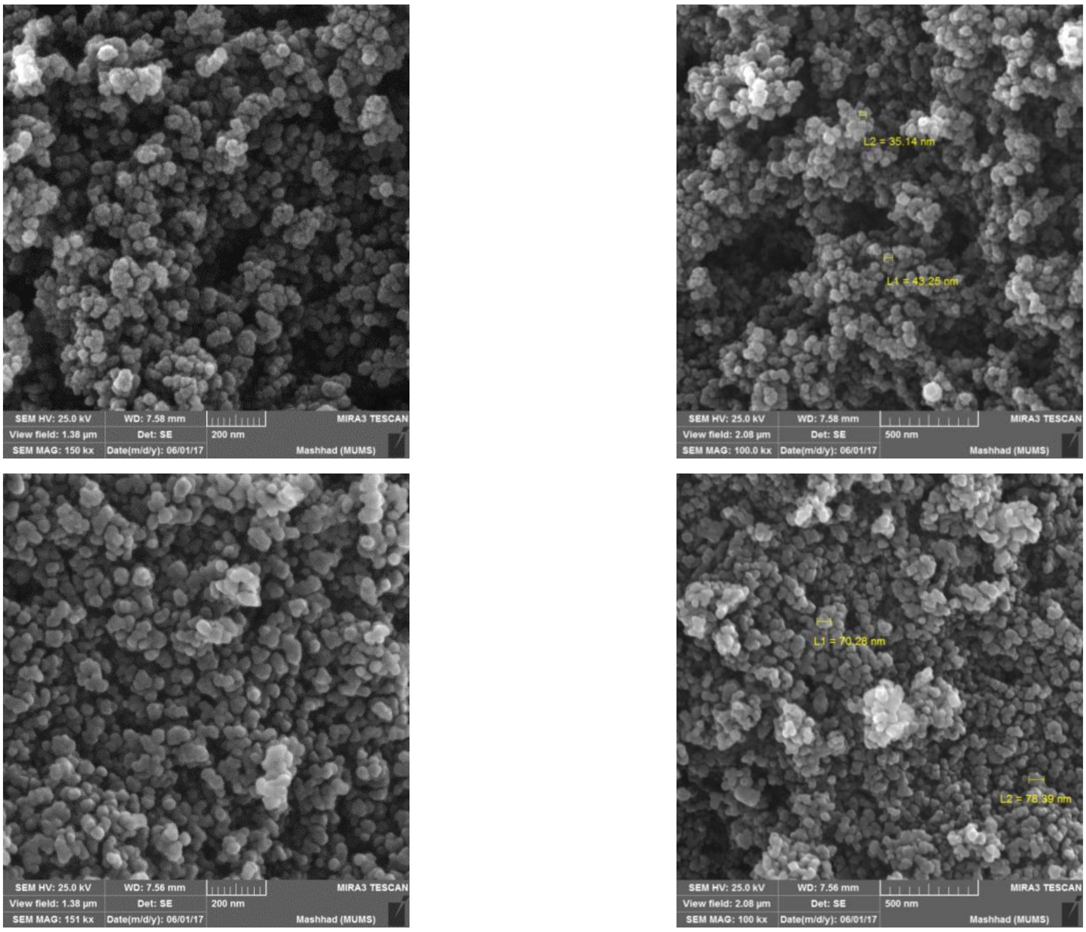

Fig. 1 SEM images of: (a), (b) titanium dioxide nanoparticles; (c), (d) TiO_2/SDS/DNPH nanocomposites

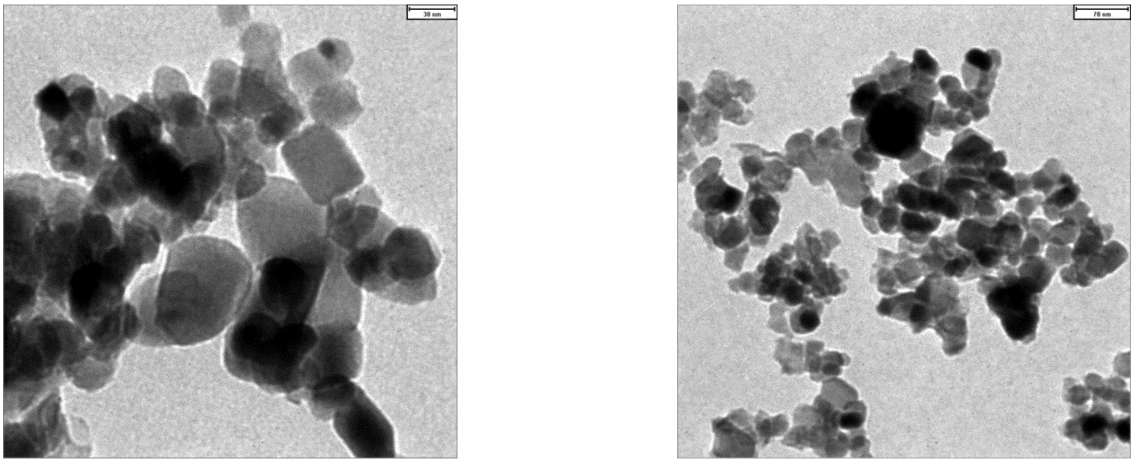

Fig. 2 TEM images of TiO_2/SDS/DNPH nanocomposite

tube and an equal amount of the Hantzsch reagent was added. Solution was placed in the incubator at 60°C for 10 minutes. Then, absorbance of the sample was determined at 412 nm by spectrophotometer. To assess the reduction rate of COD (caused by formaldehyde in water), an Aqualytic COD meter (Germany) and vials (HACH, USA) with an operating range of 0-15000 ppm were applied.

The formaldehyde adsorption efficiency in defined times on TiO_2 and TiO_2/SDS/DNPH nanocomposite was obtained by following formula

$$\text{Adsorption Efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \qquad (1)$$

Where, C_0 is the initial formaldehyde concentration in the aqueous solution; C_t is the concentration of formaldehyde in the aqueous solution at t min.

The COD removal efficiency was calculated in the same way.

3. Results and discussion

3.1 Morphological properties

SEM micrographs of titanium dioxide nanoparticles and their modified form with different magnifications are shown in Figs. 1(a) to (d). The micrographs, taken from the surface of samples, illustrate that particles are largely spherical and the modified particles are slightly larger than the unmodified particles.

Based on the results of SEM analysis, the average diameter of the modified particles was 70-80 nm. The larger size of TiO_2/SDS/DNPH nanoparticles indicates a good grafting of TiO_2 nanoparticles with the modifier factor (Figs. 1(c) and (d)). As it is seen, the resulting nanocomposites are spherical with no agglomeration between them.

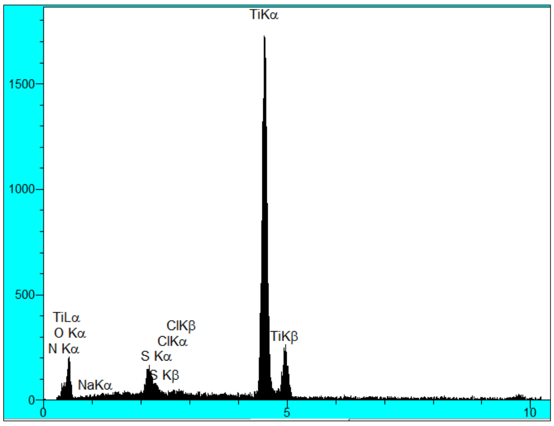

Fig. 3 EDX spectrum analysis of TiO_2/SDS/DNPH nanocomposites

Table 2 EDX analysis of TiO_2/SDS/DNPH nanocomposites

Element	Int	Chi2	K	Kr	W%	A%	ZAf	Pk/Bg
C	1.11	1.3536	0.0034	0.0019	0.56	1.09	0.3301	4.59
N	23.86	1.3760	0.0934	0.0515	9.07	15.12	0.5676	6.77
O	44.74	0.1163	58.76	40.25	0.0468	0.0858	1.3983	67.02
Na	2.09	0.2764	0.08	0.08	0.0002	0.0004	0.3352	1.03
S	4.01	0.8794	1.59	2.18	0.0192	0.0351	1.8362	82.41
Cl	2.20	0.8835	0.09	0.13	0.0012	0.0022	1.8622	4.70
Ti	71.09	0.8903	23.27	47.73	0.4249	0.7788	1.8149	1148.06
Total			100	100	0.5456	1.0000		

TEM images taken from SDS-coated TiO_2 modified with DNPH as shown in Fig. 2, revealed that the average diameter of prepared nanoparticles was below 100 nm. Furthermore the coated core is visible that suggests a good coating of TiO_2 nanoparticles with SDS and grafting with DNPH.

3.2 Structural properties

The element composition of the prepared TiO_2/SDS/DNPH nanocomposite was identified by an energy dispersive X-ray spectroscopy system (EDX) coupled to the SEM (Fig. 3 and Table 2). EDX analysis of nanocomposites confirmed the presence of carbon, titanium, oxygen, sodium, nitrogen, sulfur and chlorine elements in the composition of the compound. The presence of some oxygen in the composition is not surprising, since the occurrence of partial oxidation is inevitable. Presence of some nitrogen was expected to improve the absorption capacity of TiO_2 for formaldehyde removal from water.

-ray diffraction patterns of TiO_2 nanoparticles and TiO_2/SDS/DNPH nanocomposites at $2\theta = 5° - 70^{\circ}$ are shown in Fig. 4. As it is seen, TiO_2 exhibits a sharp peak at 2θ = 25.402° corresponding to the plane spacing (*d*-spacing) of 0.351 nm (Hejri *et al*. 2013, Lu *et al*. 2014). Furthermore, it can be seen that the main diffraction peaks at (101), (103), (004), (112), (200), and (204) by comparison with Joint Committee on Powder Diffraction Standards (JCPDS card, file No. 21–1272), are indexed to TiO_2 anatase phase. Since the compounds grafted with TiO_2 are organic, the X-ray diffraction pattern of TiO_2/SDS/ DNPH nanocomposite has the same pattern as for TiO_2.

Fourier transformation spectrums (FTIR) of TiO_2 and its modified form (before and after adsorption) are shown in Fig. 5. In the nano-TiO_2 spectrum, a strong and broad absorption band at 3430.52 cm^{-1} shows a large amount of -OH at the nano-TiO_2 surface. Absorption band at 1629.16 cm^{-1} is related to Ti-OH bending vibration and the absorption band at 713.06 cm^{-1} indicates the Ti –O–Ti stretching vibration (Bagheri *et al*. 2012, León *et al*. 2017).

Comparison between FTIR spectra of TiO_2/SDS/DNPH nanocomposite with the spectra of TiO_2 nanoparticles indicates that surface-modified TiO_2 nanoparticles contained N-H functional group as a result of the immobilization procedure. In TiO_2/SDS/DNPH spectrum, the broad band at 3200-3500 cm^{-1} is due to stretching vibrations of –OH (which should be in the range of 3200-3500 cm^{-1}) or symmetric stretching vibrations of N-H (which should be in the range of 3100-3500 cm^{-1}) (Devi *et al*. 2010, Sobhanardakani and Zandipak 2015). Comparison between this absorption band in TiO_2 and TiO_2/SDS/DNPH spectrums, indicates the absorption of N-H in this area which is largely overlapping with the absorption of OH. Also the absorption bands at 1345-1640 cm^{-1} are corresponding to the bending vibration of N–H group (Afkhami *et al*. 2011, Sobhanardakani and Zandipak 2015). Also the NH_2 and N–H bands around 1430 to 1470 cm$^{–1}$, illustrate the existence of amine ligands on surface-modified adsorbent (Srisuda and Virote 2008, Bernabe *et al*. 2015). This proved that TiO_2 was successfully modified with DNPH. Shifting the Ti-O absorption band from 713.06 cm^{-1} to 514.84-652.57 cm^{-1} is also indicative of Ti-O composition with other elements during the surface modification process (Afkhami *et al*. 2011).

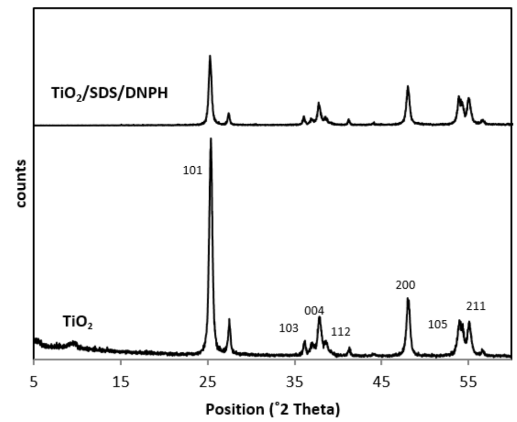

Fig. 4 X-ray diffraction patterns of TiO_2 and TiO_2/ SDS/DNPH nanoparticles

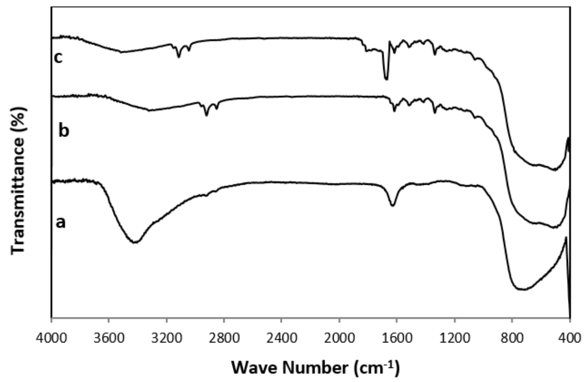

Fig. 5 FT-IR spectra of: (a) TiO_2; (b) TiO_2/SDS/DNPH before adsorption; (c) TiO_2/SDS/DNPH after adsorption

On the other hand, NH_2 and N–H bands which illustrate the existence of amine ligands on surface of adsorbent are clearly changed after formaldehyde adsorption and a peak of imine appears subsequently (Bernabe *et al*. 2015) (Fig. 5(c)). The imine (–N = C =) is the product of reaction between amine and formaldehyde that its band displays around 1640–1690 cm^{-1} (Srisuda and Virote 2008).

3.3 Suggested mechanism

Amine groups have been proven to improve the adsorption of formaldehyde through their reaction that produces imine (Bernabe *et al*. 2015). Carbonyl groups in the formaldehyde molecule can react with primary amine to produce imines, according to the following reaction mechanism (Rong *et al*. 2010, Afkhami *et al*. 2011, Le *et al*. 2013)

$$>C{=}O + R{-}NH_2 \longrightarrow -\overset{|}{\underset{|}{C}}-NH-R \longrightarrow >C{=}N-R + H_2O \quad (2)$$

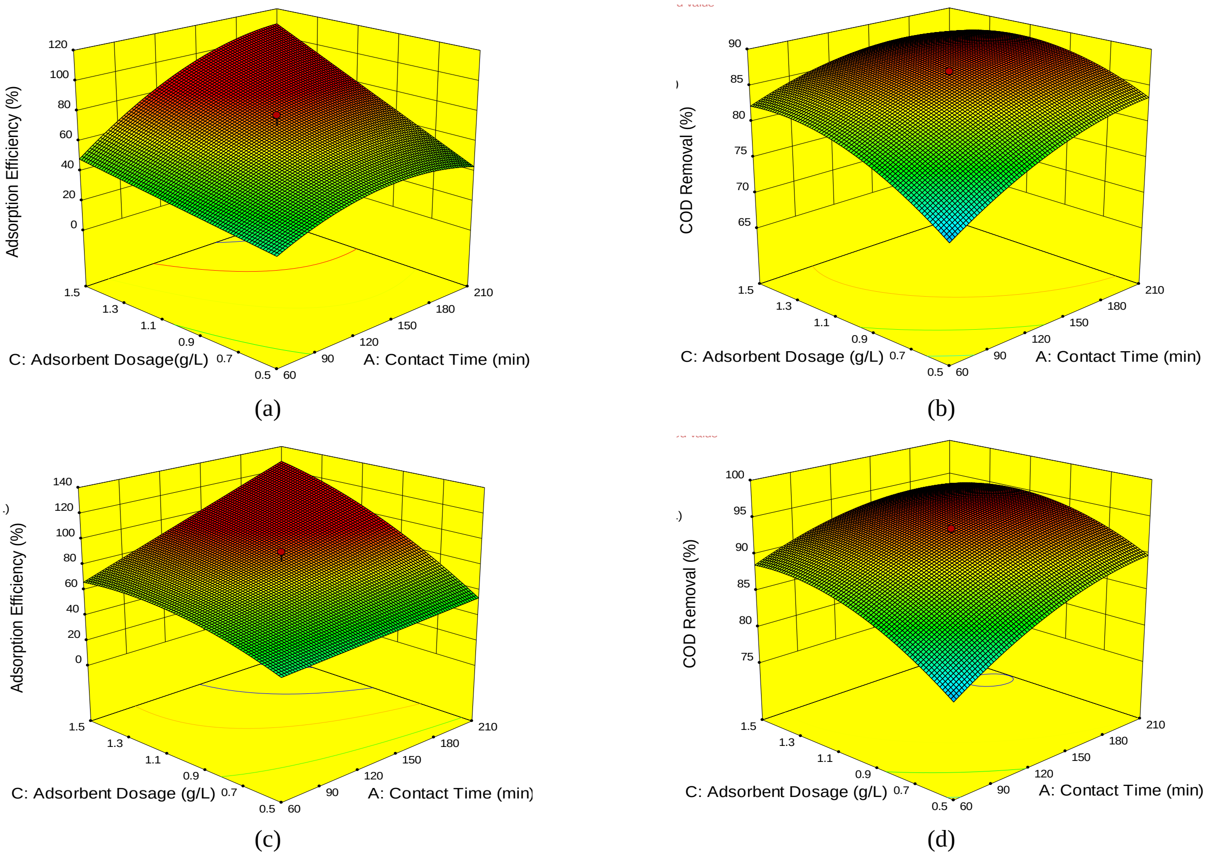

Fig. 6 Interaction between contact time and adsorbent dosage for: (a) adsorption efficiency by TiO_2 nanoparticles; (b) COD removal by TiO_2 nanoparticles; (c) adsorption efficiency by TiO_2/SDS/DNPH nanocomposites; (d) COD removal by TiO_2/SDS/DNPH nanocomposites

According to Eq. (2), if formaldehyde reacts with the amino groups on the surface of the TiO_2, the amount of formaldehyde adsorbed onto the modified nano-TiO_2 could increase significantly (Rong *et al*. 2010). The reasons that might be effective in efficient removal of formaldehyde are as follows: (1) the active hydrogen atom of adsorbent might react with formaldehyde to form alcohol; (2) the nitrogen atoms in the TiO_2/SDS/DNPH structure possess partly negative charge for its strong electronegativity, while carbon atom of formaldehyde shows slightly positive charge for its weaker electronegativity than oxygen atom. So the nitrogen atoms in the TiO_2/SDS/DNPH structure and carbon atom in the carbonyl of formaldehyde will attract each other for the electrostatic gravitation, which will lead to better formaldehyde adsorption capacity over TiO_2 (Afkhami *et al*. 2011). Comparison between FTIR spectra of TiO_2/SDS/DNPH nanocomposite before and after adsorption, confirmed the evidence of the reaction between formaldehyde molecules and amine groups on surface of modified adsorbents. We proposed that the improvement of formaldehyde removal by TiO_2/SDS/DNPH nanocomposites was attributed to the combined effects of physisorption and chemisorption contributed by the N-containing functional groups, whereas there was only physisorption between the TiO_2 nanoparticles and formaldehyde molecules.

3.4 Effects of factors

In order to determine the optimal removal conditions, the effect of contact time (60-210 min), pH (4-10) and adsorbent dosage (0.5-1.5 g/L) were studied. For this reason, the specific concentration of formaldehyde, under controlled pH conditions was contacted with different amounts of adsorbent during certain contact times.

3.4.1 Effect of contact time

Statistical analysis indicated that the contact time and the adsorbent dosage have interactive effects. The effect of contact time and adsorbent dosage on formaldehyde adsorption and COD removal efficiencies by modified and unmodified TiO_2 are shown in Figs. 6(a)-(d). As expected, increasing the contact time has improved the efficiency of formaldehyde adsorption and COD removal (Figs. 6(a) and (b)). The main reason for increasing the amount of adsorption over time is increasing the collision chance of formaldehyde with active sites on the adsorbent. The maximum adsorption and COD removal efficiencies achieved by unmodified TiO_2 nanoparticles were 81.8095% at 135 min and 88.3117% at 240 min, respectively. By increasing the contact time and approaching the equilibrium, no other increase in adsorption efficiency occurred; this is due to the adsorbent saturation over time. Figs. 6(c) and (d) illustrate the elimination efficiencies have obtained using coated TiO_2. Comparison of the obtained results showed that the maximum adsorption (94.6191% at 135 min.) and COD removal (94.8052 % at 240 min.) efficiencies obtained by modified TiO_2 were about 15.66% and 7.35% higher than the unmodified nanoparticle. This is due to the increased adsorbent surface and the high tendency of the nitrogen agent integrated with TiO_2 to absorb formaldehyde. As it is clear from the figure, the efficiency of COD removal initially has improved by increasing the amount of adsorbent and then remained constant. This is because of adsorbent saturation and decreasing of formaldehyde concentration in the solution. Afkhami *et al*. had obtained the same result for the removal of formaldehyde from water through adsorption on modified alumina nanoparticles. They also observed more reduction by modified alumina (Afkhami *et al*. 2011).

3.4.2 Effect of pH value

The role of pH is important, as it may influence both the reactivity with the pollutants and the actual composition of adsorbent (Suriyaraj *et al*. 2014). The dependency of formaldehyde adsorption and COD removal efficiencies on pH was studied by changing pH from 4.0 to 10.0 and also 2.8 and 11.2 as axial points in CCD design, using either 0.01–0.1 M NaOH or HCl, (shown in Figs. 7(a)-(d)). The experimental results showed that the maximum formaldehyde adsorption and COD removal efficiencies by nano-TiO_2 were 81.8095 and 88.3117% at pH 7 respectively. At low pHs, formaldehyde removal was decreased because of competition between formaldehyde that is a strong electrophile, and H^+ ions for sitting on TiO_2 nanoparticles active sites. When using modified TiO_2, in acidic conditions, hydrogen ions (H^+) protonated the nitrogen-containing functional groups of TiO_2/SDS/DNPH nanocomposites and as a result, formaldehyde adsorption by these functional groups was decreased (Afkhami *et al*. 2011); Therefore, the COD value was high too. In alkaline conditions, some aldehydes such as formaldehyde react with hydroxide anions (OH^-) and produce alkoxide; This alkoxide lost its proton and converts to another intermediate

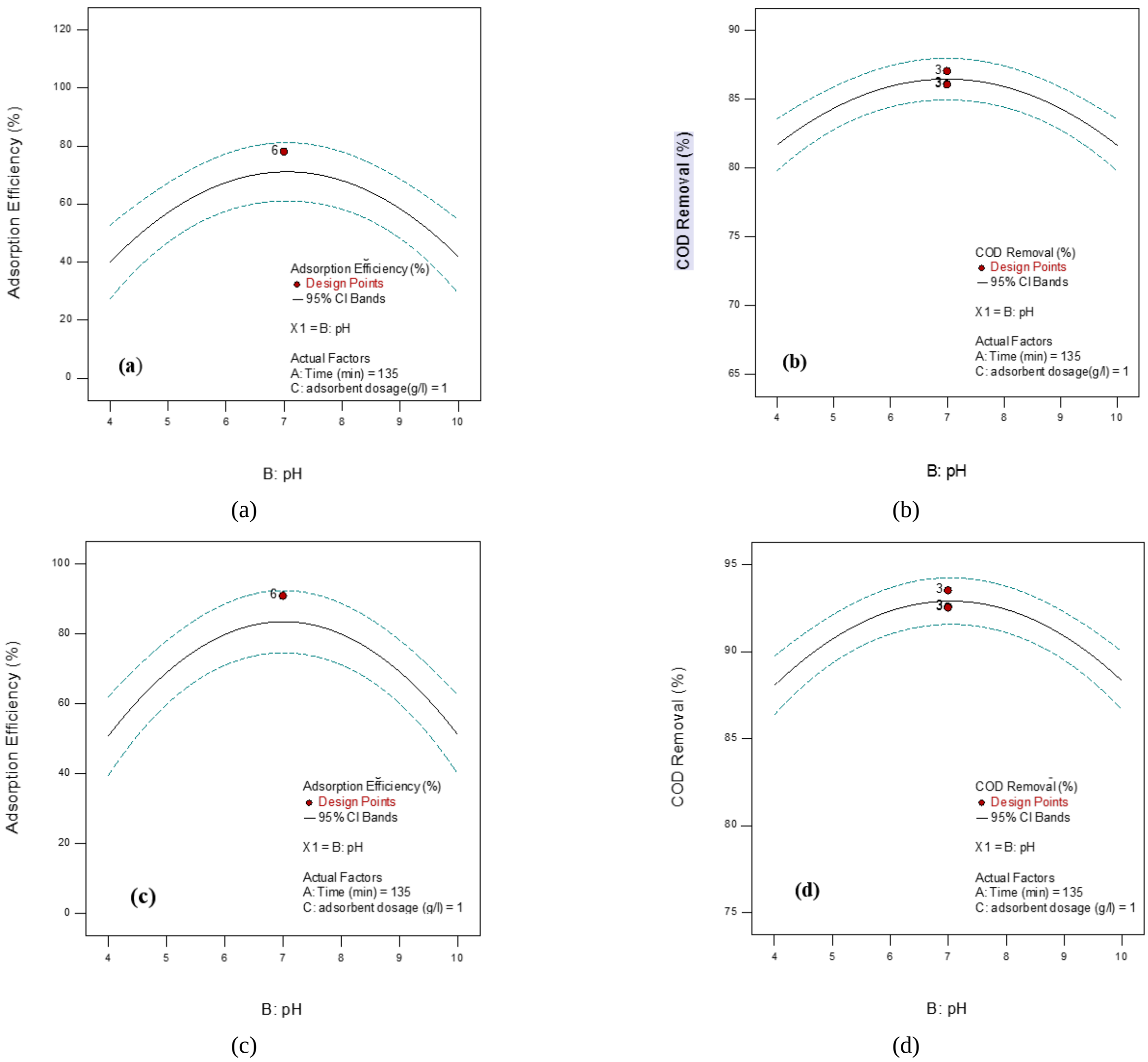

Fig. 7 Effect of pH on: (a) formaldehyde adsorption by TiO_2 nanoparticles; (b) COD removal by TiO_2 nanoparticles; (c) formaldehyde adsorption by TiO_2/SDS/DNPH nanocomposites; (d) COD removal by TiO_2/SDS/DNPH nanocomposites

products (Afkhami *et al*. 2011). We think that these compounds probably have some absorption in the spectrophotometry analysis. Therefore, in high pHs we did not face with a significant reduction in COD. Comparison of the obtained results showed that at pH 7 the maximum adsorption (94.6191%) and COD removal (94.8052 %) efficiencies by modified TiO_2 were about 15.66% and 7.35% higher than the unmodified nanoparticles respectively (Figs. 7(c) and (d)). This result is similar to what proposed by Afkhami et al. in their research on formaldehyde removal from water by nano-alumina. They investigated the effect of pH in the range of 2 to 10 and reported the best pH in the range of 4.5 to 8.5 (Afkhami *et al*. 2011).

3.4.3 Effect of adsorbent dosage

The dependence of formaldehyde adsorption and COD removal efficiencies by nano-TiO_2 and TiO_2/SDS/DNPH nanocomposites on the adsorbent dosage and its interaction with time is observable in Figs. 6(a)-(d). As it is clear from these figures, both adsorption efficiency and COD removal performance have improved by increasing the adsorbent dosage. Since the adsorption efficiency changes with adsorbent dosage is incremental (Figs. 6(a) and (c)), achieving to higher adsorption efficiencies is possible by utilizing more amounts of adsorbent. When using unmodified nano-TiO_2, the highest adsorption and COD removal efficiencies were 81.8095% with 1.7 g/L and 88.3117% with 1 g/L of adsorbent respectively. It is noteworthy that due to the high surface-to-volume ratio, nanoparticles have a high adsorption capacity; so, favorable results can be achieved in pollutant elimination using very low amounts of nano-adsorbents. As it is seen in the Fig. 6, adsorbent dosage and time have an incremental effect on adsorption efficiency. However, according to the F-values obtained in the statistical analysis, the effect of adsorbent dosage on the adsorption performance was much higher than that of time. With saturation of the adsorbent surface and reduction of formaldehyde in the solution, increasing the amount of adsorbent to more than 1 g/L did not increase COD removal efficiency significantly. The maximum formaldehyde adsorption and COD removal efficiency by TiO_2/SDS/DNPH nanocomposites were 94.6191% and 94.8052%, which were higher than the unmodified TiO_2 with the same adsorbent dosage. We attribute this removal performance improvement to formaldehyde reaction with nitrogen-containing functional groups on the surface of modified TiO_2. As shown in the Fig. 6, adsorption efficiency changes are not yet constant, that means formaldehyde adsorption process on TiO_2/SDS/DNPH has not reached equilibrium and with greater amounts of adsorbent, more elimination can be achieved. Salman et al. had reported that the maximum removal of formaldehyde from aqueous solution was 83.76% and 89.48% for 1.0 g/25 mL kaolin and 0.8 g/25 mL bentonite, respectively (Salman *et al*. 2012). Bagheri et al. had obtained an elimination percentage of 70%w/w for rice bran, 83%w/w for carbon-300 and 90%w/w for carbon-500 in best adsorption conditions (Bagheri *et al*. 2018). Also the determined sorption efficiency after 8-12 hours applying 2 mg/l chemically modified zeolite was 95.0% in Paliulis' research on removal of formaldehyde from synthetic wastewater (Paliulis 2016).

3.5 Statistical results

Analysis of the results by Design Expert software showed that the quadratic model was statistically well matched to the obtained data for formaldehyde removal by TiO_2 nanoparticles before and after grafting with DNPH. The obtained equations for formaldehyde adsorption and COD reduction efficiencies by unmodified TiO_2 nanoparticles based on the real factors were

$$\begin{aligned}&\text{Adsorption Efficiency (\%)} =\\&-169.13632+0.54682*\text{Time (min)}+47.27428\\&*\text{pH}-1.14898*\text{adsorbent dosage (g/L)}+0.31747\\&*\text{Time (min)}*\text{adsorbent dosage (g/L)}-2.29590\text{E-}003\\&*\text{Time (min)}^2-3.35409*\text{pH}^2\end{aligned}\tag{3}$$

$$\begin{aligned}&\text{COD Removal (\%)} =\\&+22.68168+0.19509*\text{Time (min)}+7.44605\\&*\text{pH}+36.26409*\text{adsorbent dosage (g/L)}-0.042981\\&*\text{Time (min)}*\text{adsorbent dosage (g/L)}-3.80682\text{E-}004\\&*\text{Time (min)}^2-0.53242*\text{pH}^2-12.12448\\&*\text{adsorbent dosage(g/L)}^2\end{aligned}\tag{4}$$

The obtained equations for formaldehyde adsorption efficiency and COD reduction by modified TiO_2 nanoparticles based on the real factors were

$$\begin{aligned}&\text{Adsorption Efficiency (\%)} =\\&-163.85201-0.11347*\text{Time (min)}+50.59950\\&*\text{pH}+77.17113*\text{adsorbent dosage (g/L)}+0.34403\\&*\text{Time (min)}*\text{adsorbent dosage (g/L)}-3.61059\\&*\text{pH}^2-38.29769*\text{adsorbent dosage (g/L)}^2\end{aligned}\tag{5}$$

$$\begin{aligned}&\text{COD Removal (\%)} =\\&+29.93577+0.18752*\text{Time (min)}+7.38550\\&*\text{pH}+35.16228*\text{adsorbent dosage (g/L)}-0.036797\\&*\text{Time (min)}*\text{adsorbent dosage (g/L)}-3.67833\text{E-}004\\&*\text{Time (min)}^2-0.52439*\text{pH}^2-11.83536\\&*\text{adsorbent dosage (g/L)}^2\end{aligned}\tag{6}$$

Above equations reveal how the individual variables or double interactions affected formaldehyde removal from aqueous solution by nano-TiO_2 and TiO_2/SDS/DNPH nanocomposites.

Design Expert software has been used to determine the optimal elimination conditions within the tested range. Predicted and experimental optimum conditions for formaldehyde removal by TiO_2/SDS/DNPH along with the maximum adsorption value have illustrated in Table 2.

3.6 Effect of ionic strength

The effect of ionic strength on formaldehyde removal efficiency was determined by addition of NaCl. For this purpose, the salt content of feed solution was adjusted for the optimized conditions (adsorbent dosage 1.100 g/L, pH

Table 3 Predicted and experimental optimum conditions for formaldehyde removal by TiO_2/SDS/DNPH

Contact time (min)	pH	Absorbent dosage (g/L)	Adsorption efficiency (%): predicted	Adsorption efficiency (%): experimental	Error (%)	COD removal efficiency (%): predicted	COD removal efficiency (%): experimental	Error (%)
183.290	7.424	1.100	99.904	97.191	2.715	94.815	94.70	0.121

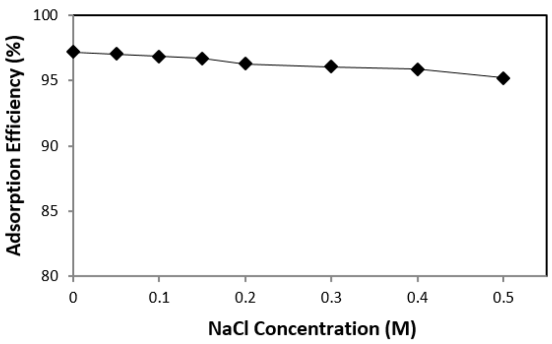

Fig. 8 Effect of ionic strength on formaldehyde adsorption efficiency

7.424 and the contact time 183.290 min). Obtained results illustrated that the presence of NaCl had no considerable effect on adsorption of formaldehyde by TiO_2/SDS/DNPH nanocomposites (Fig. 8); the reason was that the modified adsorbent surface had a negative charge due to the presence of the amine group, so the Cl^- negative ions had no tendency to sit on the adsorbent surface and therefore had no effect on the formaldehyde removal efficiency. On the other hand, the tendency of formaldehyde carbonyl groups to react with the amine group on the adsorbent surface was so high that positive Na^+ ions had no chance of sitting on the adsorbent surface. Afkhami *et al*. also had reported that the presence of large amounts of Na^+ and Ca^{2+} ions did not substantially reduce the sorption capacities of amine grafted nanoparticles for formaldehyde. It means that the co-existed competitive cations only have slight influence on the sorption ability of the nano- sorbent (Afkhami *et al*. 2011).

4. Conclusions

The present work has demonstrated formaldehyde removal from water through adsorption on modified TiO_2 nanoparticles. To improve the morphological characteristics of titanium dioxide nanoparticles and increasing its capability to absorb formaldehyde, DNPH as a source of nitrogen-containing group was grafted on the surface of TiO_2 nanoparticles with the aid of sodium dodecyl sulfate surfactant.

- The developed functionalized TiO_2/SDS/DNPH nanocomposites were effective for formaldehyde elimination from water and very few amounts of adsorbent could remove up to 97.191 % of formaldehyde at optimum conditions.
- On the basis of SEM and TEM analysis, the prepared nanocomposites were spherical with no agglomeration between them and the coated core was visible.
- EDX and FTIR analysis confirmed the formation of TiO_2/SDS/DNPH and the presence of N-H functional groups on the adsorbent surface.
- The adsorption capacity of modified TiO_2 for formaldehyde was found to be 15.65 % higher than that of unmodified TiO_2. Impregnation of nano-TiO_2 with amino-containing compounds enhanced their removal capacity for formaldehyde because of the cooperation of physical adsorption and the increased chemical interaction between amino groups on the surface of functionalized TiO_2 and formaldehyde molecules.
- The optimum conditions predicted for maximum formaldehyde removal and COD reduction by TiO_2/SDS/DNPH nanocomposites were: adsorbent dosage 1.100 g/L, pH 7.424 and the contact time 183.290 min.

Therefore, the combination of nano-TiO_2 with DNPH would greatly improve formaldehyde adsorption efficiency and surface-modified nano-TiO_2 has a high potential in remediation of wastewaters containing formaldehyde.

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