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A study on removal characteristics of *o*-, *m*-, and *p*-nitrophenol from aqueous solutions by organically modified diatomaceous earth

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ABSTRACT

The natural diatomaceous earth (DAT) was modified with surfactant of hexadecyltrimethylammonium bromide (HDTMABr) to form organic-modified diatomaceous earth (DAT-HDTMABr). The DAT and DAT-HDTMABr were characterized by X-ray fluorescence, X-ray diffraction, FT-IR and DTA-TG. The surface area was determined using Brunauer, Emmett, and Teller adsorption method. Cation exchange capacity was estimated using an ethylenediamine complex of copper method, and the modifier loading was calculated from the total carbon analysis. The ability of raw and organomodified diatomaceous earth to remove *o*-nitrophenol (ONP), *m*-nitrophenol (MNP), and *p*-nitrophenol (PNP) from aqueous solutions has been carried out at predetermined equilibration time, adsorbent amount, pH, and temperatures using a batch technique. The removal of ONP, MNP, and PNP from aqueous solutions by modified clay seems to be more effective than unmodified sample. The experimental equilibrium adsorption data were analyzed by four widely used two parameters, Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) isotherm equations. Kinetic studies showed that pseudo-second-order described the adsorption experimental data better than the pseudo-first-order kinetic model. Based on the calculated thermodynamic parameters, such as enthalpy (ΔH), entropy (ΔS), and Gibb's free energy changes (ΔG), it is noticeable that the adsorption of ONP, MNP, and PNP by DAT and DAT-HDTMABr adsorbents was carried out spontaneously, and the process was exothermic in nature.

Keywords: Adsorption; Diatomaceous earth; Surfactant; Nitrophenols

1. Introduction

Phenols, particularly nitrophenols, are classified to be extremely toxic for human beings and for all aquatic life. These compounds exist in wastewater from petrochemical, olive mill, photographic developer, oil refineries, plastics, leather, paint, pharmaceutical, and steel industries, and must be removed to satisfy the actual environmental regulations [1–4].

Phenolic compounds are pollutants of great concern because of the high toxicity and possible accumulation

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in the environment; they are listed on US Environmental Protection Agency's (EPA) list of toxic pollutants [5]. Most of them are recognized carcinogens and are known to be: harmful to organisms at low concentrations, impart toxicity to aquatic life, and are damaging the aesthetic nature of environment [6,7]. Nitrophenolic compounds, which are toxic components in chemical industrial wastewater, cause serious pollution because their biological degradation is difficult [8]. Furthermore, *o*-nitrophenol (ONP) and *p*-nitrophenol (PNP) have been prescribed as priority pollutants by the EPA [9]. The presence of substituted groups in phenols increases the toxic effects exerted on the environmental life, on the human health, and their characteristics of persistence in the environment [10]. *p*-Nitrophenol, for instance, which is used in the manufacturing of analgesics, pesticides and dyes, and in processing of leather, has been identified as a carcinogen mutagen, cytotoxic and embryotoxic to mammals, and is found in 10% of the hazardous compounds [11]. Therefore, it is necessary to remove nitrophenols from wastewaters before they are discharged [12].

Different new water treatment technologies are being constantly researched and developed to remove phenolic pollutants. Such technologies include biological degradation [13], chemical oxidation [14], and recuperative process such as adsorption into porous solids [15] and membrane separation [16]. Among these methods, adsorption is an attractive process due to its high rate, high uptake capacity, and effective treatment in dilute solution, low cost, and regeneration [17–20]. The use of activated carbons as adsorbents for the removal of phenolic compounds has been studied extensively [21–23]. The major disadvantages of using these carbons are their high price and regeneration cost. However, this subject remains highly controversial as described in a recent review by Radovic et al. [24].

Diatomite clay is abundant in many areas in the world and has unique physicochemical characteristics. Diatomite's highly porous structure, low density, and high surface area resulted in a number of industrial applications as filtration media for various beverages and inorganic and organic chemicals as well as an adsorbent for oil spills. The properties of diatomite's surface, such as hydrophobia, solubility, charge, acidity, ion exchange, and adsorption capabilities, are highly governed by the presence of water, which is partially structurally connected to the crystal mesh of diatomite, forming active hydroxyl groups on it [25]. Although diatomite has a unique combination of physical and chemical properties, its use as an adsorbent in wastewater treatment has not been greatly investigated [26,27]. To increase the ability of mineral clays to remove non-polar and anion water pollutants, it is necessary to modify their surfaces. Organic modification of diatomite clay has been shown to significantly increase the attenuation of some organic and inorganic pollutants [28–37]. Limited numbers for the adsorption of *o*-, *m*-, and *p*-nitrophenols have been reported [37–40]. For example, Koyuncu et al. [38] reported that organically modified bentonite was used as an adsorbent for the removal of *o*-, *m*-, and *p*-nitrophenols from an aqueous solution. The adsorption of *o*-, *m*-, and *p*-nitrophenols on activated carbon under various experimental conditions was investigated by Gokturk and Kaluc [39]. The adsorption of *o*-, *m*-, and *p*-nitrophenols on clinoptilolite-type natural zeolite has been studied as a function of the solution concentration and temperature [40]. Qiu et al. [41] reported the comparative adsorption of ONP, *m*-nitrophenol (MNP), and PNP onto a macroporous polymeric and hypercrosslinked polymeric adsorbents. To the best of our knowledge, there have been no reports on the adsorption of nitrophenols by diatomaceous earth and its organomodified form.

It was therefore decided in this study to explore the feasibility of using diatomaceous earth and its organically modified form as an adsorbent for the removal of ONP, MNP, and PNP from aqueous solutions. Herein, the diatomaceous earth had been organically modified using a cationic surfactant, hexadecyltrimethylammonium bromide (HDTMABr). Thus, this work examined the effects of factors such as initial nitrophenol concentration, pH, and amount of adsorbent and temperature on adsorption rate of ONP, MNP, and PNP, and evaluating the usefulness of pseudo-first-order and pseudo-second-order models for analyzing the adsorption system. In addition, this paper further evaluated the applicability of common isotherm models, i.e. the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) and differences in using diatomaceous earth and its organomodified form adsorbent for the adsorption of ONP, MNP, and PNP from an aqueous system at different temperatures.

2. Experimental

2.1. Materials

Reagents grade of *o*-nitrophenol (ONP), *m*-nitrophenol (MNP), *p*-nitrophenols (PNP), HDTMABr, and sodium chloride (NaCl) were obtained from Sigma–Aldrich chemical company, where their purity is higher than 99% and used without further purification. The diatomaceous earth (DAT) sample was supplied by Sigma–Aldrich.

2.2. Preparation of organomodified diatomaceous earth

Organically modified diatomaceous earth was prepared by ion exchange reaction. The amount of HDTMABr (8.5 g) equal to the cation exchange capacity (CEC) of diatomaceous earth (78 meq^{-1}100 g) was dissolved in 1 L distilled water and 30 g of diatomaceous earth was added and stirred with mechanical stirrer (Boeco Germany, OSD-20) for 24 h at 1,000 rpm. The organomodified clay was separated from the mixture by filtration, washed about five times with distilled water, and dried at 110˚C for three hours until constant mass. The organomodified diatomaceous earth is labeled as DAT-HDTMABr.

2.3. Analysis

Quantitative analysis of nitrophenols in aqueous solutions was carried out by a UV-Cary 100 Varian. Elemental analysis (C, H, N) was carried out using a Perkin-Elmer model 2400 C instrument.

DAT and DAT-HDTMABr were characterized by X-ray diffraction (XRD) (7000 Shimadzu 2 kW model X-ray spectrophotometer with a nickel-filtered copper X-ray radiation (Cu Kα 1.5418 Å)), X-ray fluorescence (XRF) (1800 Shimadzu PW 1404 X-ray spectrometer wave length-dispersive), and FT-IR spectroscopic analysis (Thermo Nicolet Nexus 870 FTIR spectrophotometer).

The surface area of the powdered diatomaceous earth was determined using the Brunauer, Emmett, and Teller (BET) method [42]. The method involves liquid nitrogen physisorption on the surface of the sample at 77 K. The measurements were performed with a Micrometrics Gemini (V) (USA) apparatus.

The CEC was estimated using the ethylenediamine copper complex method. The adsorption of bis(ethylenediaminecopper(II)) complex, ($\mathrm{Cu(EDA)_2^{2+}}$) on clay minerals was successfully used as a method for determining CEC of clay minerals [43]. The CEC of the samples was calculated from the difference between the initial ($\mathrm{Cu(EDA)_2^{2+}}$) concentration and that remaining in solution after equilibration was attained. The calculated value was found to be 79 meq $(100\mathrm{g})^{-1}$ diatomaceous earth.

Effect of temperature on the morphology of the original and organomodified DAT were evaluated by DTA-TG analysis (DTA STA 409 PC, Netzsch).

2.4. Adsorption experiments

The stock solutions were prepared in 0.01 M NaCl in order to promote the flocculation and to have a constant background electrolyte concentration. pH was adjusted by adding small amount of 0.1 M HCl or NaOH solutions. A batch equilibration method was used to determine the adsorption of ONP, MNP, and PNP by DAT or DAT-HDTMABr. In a typical adsorption run, 0.2 g of DAT or DAT-HDTMABr was equilibrated with 100 mL of nitrophenol solutions in a stoppered polyethylene plastic bottle in a thermostatic water bath. The stirring speed was 350 rpm with a constant temperature of 25˚C. The pH of solution was adjusted until the equilibrium was achieved. At the end of the desired equilibrium period, the contents of the bottles were filtered, centrifuged for 10 min at 3,500 rpm using a mLw T5 (Germany) centrifuge, and the supernatant was subsequently analyzed for residual concentration of nitrophenols. The concentration of nitrophenols in solutions was typically in the range of 10–100 mg L^{-1}. The batch test was conducted by combining 100 mL of nitrophenols solutions with 0.20 g of DAT or DAT-HDTMABr. The narrow-neck darkly brown colored bottles were used to prevent photo-oxidation. The bottles were consequently capped with screw caps fitted with Teflon liners and placed on a temperature-controlled JSSB-30T (Germany) orbital shaker and agitated at a constant speed of 350 rpm. The equilibrium concentrations of nitrophenols were measured spectrophotometrically on a UV spectrophotometer at wavelengths 279, 274, and 317 nm for ONP, MNP, and PNP, respectively. The calibration curve at these wavelengths was established as a function of nitrophenols concentration. The reproducibility of the data varied in the range of ±1.5%. The capacity or the amount of nitrophenols taken up by the material (q_e mg g^{-1}) was calculated by Eq. (1):

$$q_\mathrm{e} = \frac{(C_\mathrm{i} - C_\mathrm{eq})V}{m} \tag{1}$$

where q_e is the quantity of the nitrophenols in mg held by 1 g of the adsorbent, C_i is the initial concentration (mg L^{-1}), C_eq is the equilibrium concentration (mg L^{-1}) of the nitrophenols in the aqueous phase, V is the volume of solution (L), and m is the mass of the material (g).

The removal efficiency (%R) values were calculated as a percentage using the Eq. (2):

$$\%R = \frac{(C_\mathrm{i} - C_\mathrm{eq})}{C_\mathrm{i}} \times 100 \tag{2}$$

The effect of adsorbent dose on nitrophenols removal was studied by agitating 100 mL of 60 mg L^{-1} solution of nitrophenols containing 0.20 g DAT or DAT-HDTMABr for a period of 210 min. The effect of pH on nitrophenols removal was studied using 100 mL of 60 mg L^{-1} solution of nitrophenols, and agitated with 0.20 g of adsorbents for 210 min.

The thermodynamic effect was studied by agitating 60 mg L^{-1} solution of nitrophenols solution with 0.20 g of adsorbents at 25, 30, and 45℃ for a time period of 210 min.

For adsorption kinetics, set of experiments was carried out in which 100 mL of 60 mg L^{-1} solution of nitrophenols was adsorbed on 0.20 g of DAT or DAT-HDTMABr over a time period of 0–210 min following the procedure of batch experiment.

Adsorption of nitrophenols on the walls of glass flasks and centrifuge tubes, which was found negligible, was determined by running blank experiments. Each experiment was carried out in triplicate and the average results are presented in this work.

3. Results and discussion

3.1. Characterization of adsorbents

The structure of DAT and DAT-HDTMABr, characterized by FT-IR spectra, are shown in Fig. 1. Both DAT and DAT-HDTMABr show characteristic bands of DAT. The absorption band at 3,623 cm^{-1} is due to stretching vibrations of structural OH groups of diatomaceous earth. A large broadband at 1,086 cm^{-1} is related to stretching vibrations of Si–O groups. The H_2O-stretching vibration was observed as a broadband at 3,431 cm^{-1}. For the organomodified diatomaceous earth, two new absorption bands at 2,920 and 2,851 cm^{-1} appeared which represented the stretching vibrations of $–CH_3$ and $–CH_2$, respectively. These two characteristic bands confirmed the cationic exchange reaction between organic cation of quaternary ammonium salt of surfactant and cations of DAT.

To check the amount of cationic surfactant loaded on the surface of diatomaceous earth sample, the total carbon analysis technique has been selected since it gives accurate results for the real surfactant coverage on the samples. The difference in carbon content between the unmodified sample and the modified sample was considered to be entirely due to the exchanged modifier. The total carbon content before $\%C_N$ and after $\%C_M$ modification was related to the modifier loading, L_M, by the following formula [44]:

$$L_M = \frac{1}{\%C_{mW_{mod}}}\left[\frac{\%C_M - \%C_N}{1-\left(\%C_M\,\frac{mW_{mod}}{mW_{C_{mod}}}\right)}\right] \times V_{mod} \times \frac{100}{1000} \tag{3}$$

where L_M is modifier loading in milliequivalents per 100 g of unmodified clay, $\%C_N$ is the carbon fraction of the unmodified clay, $\%C_M$ is the carbon fraction of the modified clay, mWC_{mod} is the molecular weight of carbon in the modifying cation, mW_{mod} is the molecular weight of the modifying cation, and V_{mod} is the valency of the modifying cation, (1 for HDTMABr). According to Eq. (3), the modifier loading in meq $(100g)^{-1}$ DAT was calculated as 67.04 meq $(100g)^{-1}$ diatomaceous earth.

The specific surface areas of the samples were calculated from nitrogen adsorption isotherms by the BET method. The DAT-HDTMABr had lower surface area (23.71 $m^2 g^{-1}$) than the original sample DAT (49.78 $m^2 g^{-1}$). The relatively low surface area of the DAT-HDTMABr indicates that only the external surface was accessible to nitrogen gas [45].

The XRD pattern for DAT and DAT-HDTMABr looks identical as shown in Fig. 2. However, the extra peaks (3.20°, 6.68°, 16.92° 18.14°, 23.54°, 24.68°, and 25.52°) appeared after the addition of organic HDTMABr. This is a strong evidence of the modification which is carried out on the surface of diatomite. It could be explained that during the ion exchange mechanism, an amount of HBr was produced and then reacted with Na, Ca, Fe, and Mg ions forming minority phases. The chemical elemental composition of DAT and DAT-HDTMABr as determined by XRF technique (wt%) are found as follows: DAT, Si: 88.14; Fe: 5.96; Na: 2.55; Al: 1.63; Ca: 0.98; Mg: 0.57; and K: 0.19. DAT-HDTMABr, Si: 74.24; Br: 16.80; Fe: 4.06; Al: 2.12; Na: 1.66; Ca: 0.67; Mg: 0.30; and K: 0.17. It seems from the chemical elemental compositions of the raw sample that the predominant exchangeable cations were sodium and calcium.

The DTA-TG pattern of DAT and DAT-HDTMABr were shown in Fig. 3. These patterns demonstrate that the inorganic cation in DAT was replaced by an organic cation. The DTA patterns of DAT-HDTMABr exhibit exothermic peaks at about 250–300℃ due to combustion of the organic carbon.

3.2. Effect of adsorbent dose

The effect of DAT or DAT-HDTMABr dosages on the percentage removal (%*R*) and adsorption quantity q_e (mg g^{-1}) of ONP (as a representative example) were illustrated in Fig. 4. As the adsorbent dose was increased from 0.05 to 0.50 g $(100\,mL)^{-1}$, for DAT or DAT-HDTMABr, the percentage ONP removal increased from 13.03 to 31.37% and 37.12 to 87.42%. Whereas, the equilibrium adsorption amount, q_e, decreased from 9.01 to 1.13 mg g^{-1} and 37.79 to 7.48 mg

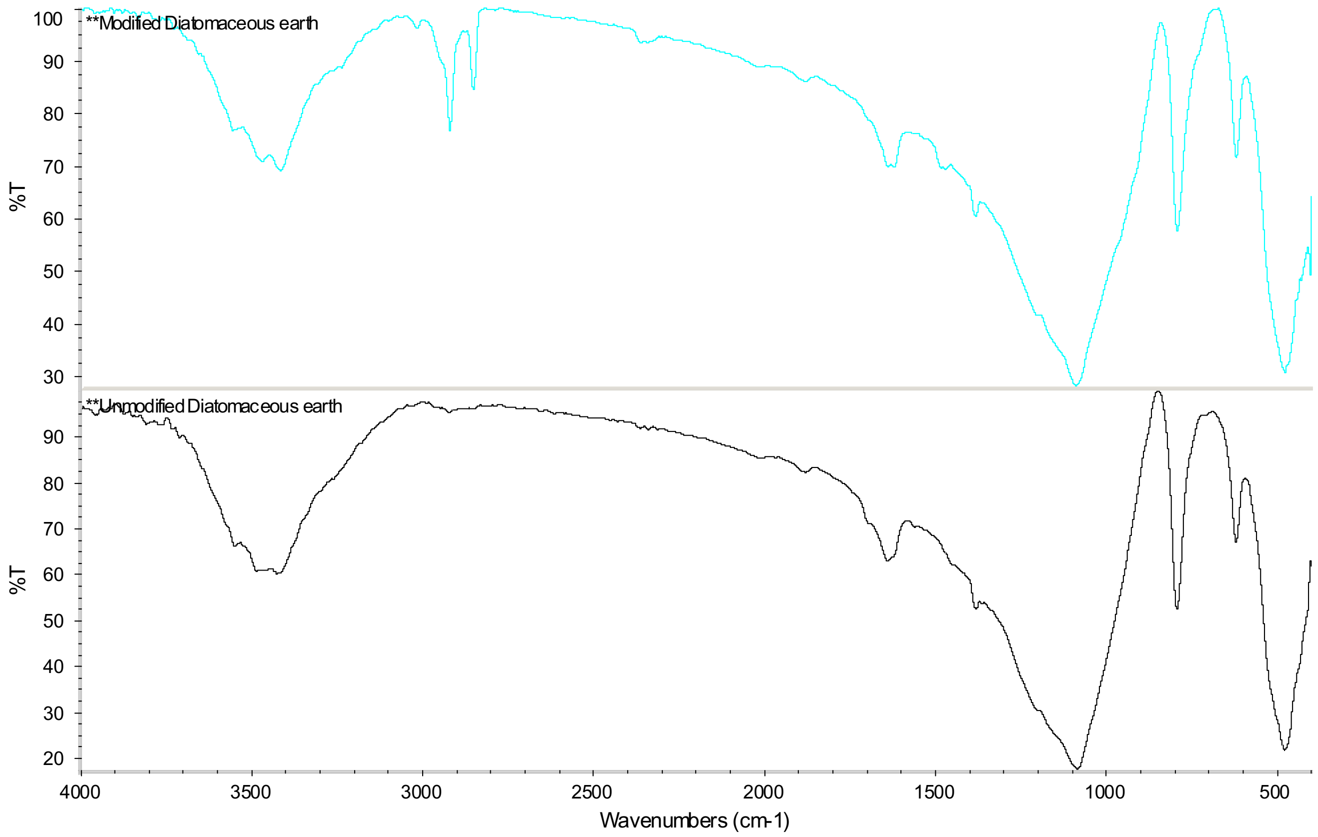

Fig. 1. FT-IR spectra of raw DAT and organomodified DAT-HDTMABr diatomaceous earth.

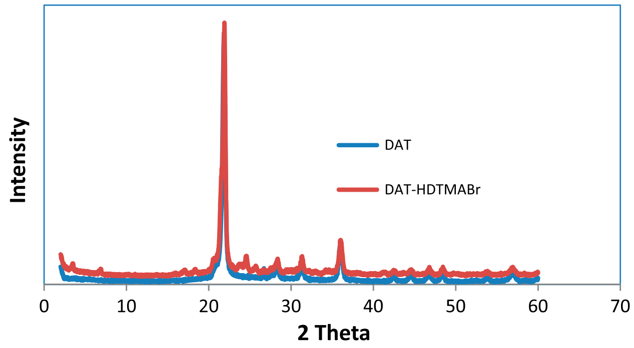

Fig. 2. XRD pattern of the raw DAT and organomodified DAT-HDTMABr diatomaceous earth.

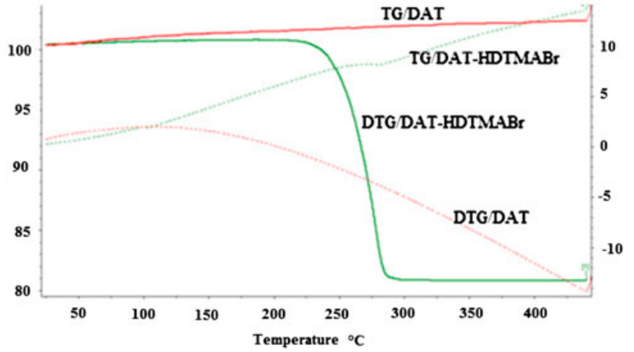

Fig. 3. Thermograms of the raw DAT and the organomodified DAT-HDTMABr diatomaceous earth.

g^{-1}, respectively. The increase in the percentage of ONP removal with increasing DAT dose could be attributed to an increase in the absolute adsorption surface. However, the decrease in q_e for DAT for ONP could be due to two reasons. Firstly, with increasing adsorbent dose, there was a decrease in total surface area of the adsorbent and increase in diffusion path length, which was the result of aggregation of adsorbent particles. The aggregation becomes increasingly significant as the weight of the adsorbent is increased [46]. Secondly, the increase in adsorbent dose at constant ONP concentration and volume will lead to unsaturation of adsorption sites through the adsorption process.

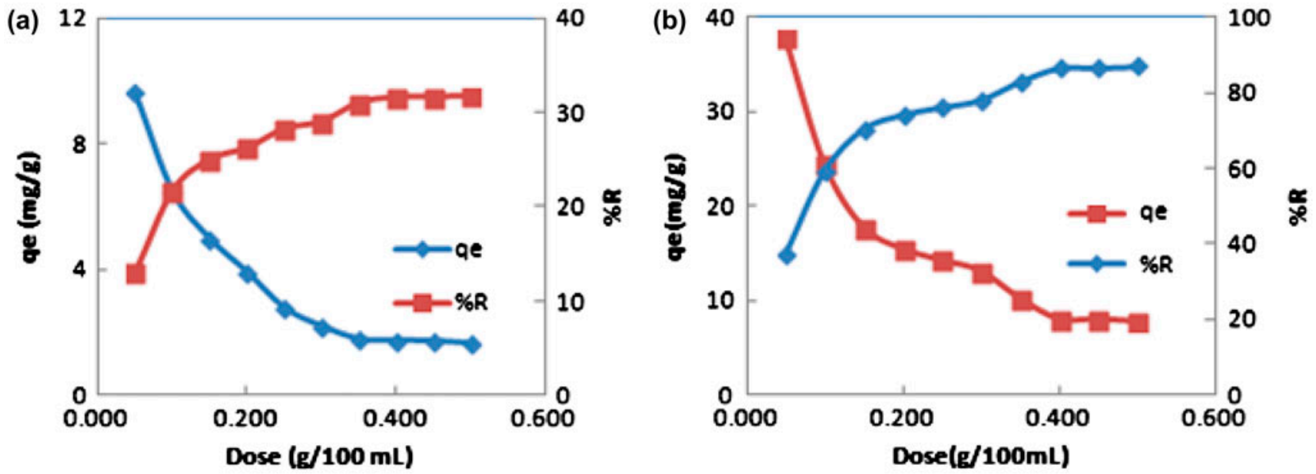

Fig. 4. The effect of adsorbent dose for the adsorption of ONP on: (a) DAT, and (b) DAT-HDTMABr. Initial concentration is 60 mg L^{-1} and temperature is 25˚C.

3.3. Effect of contact time

The effects of contact time of ONP, MNP, and PNP on the adsorption process were studied in the time range between 5 and 210 min at 25˚C with a fixed DAT and DAT-HDTMABr adsorbent dose. Fig. 5 shows that the equilibrium time required for the adsorption of ONP, MNP, and PNP on DAT is almost 2.5 h. HDTMABr modification covered the DAT surface and increased molecular interaction between nitrophenol molecules and the DAT surface. Therefore, adsorption capacities for ONP, MNP, and PNP increased from 6.035, 8.139, and 20.486 mg g^{-1} on raw DAT clay to 11.175, 19.717, and 26.802 for DAT-HDTMABr, respectively. The modification of DAT clay by HDTMABr increased the adsorption capacities for nitrophenols and reached equilibrium after 90–120 min of contact time. Adsorption first followed linear rising in which fast initial uptake takes place, and then a stationary state was observed. The fast initial uptake was due to accumulation of nitrophenols on surfaces of DAT and DAT-HDTMABr adsorbents, which is a rapid step [47]. For all systems and in all subsequent investigations, a shaking time of 240 min was conveniently adopted followed by the standing overnight in the thermostatic bath.

3.4. Effect of initial pH

The pH of the nitrophenol solutions was left free during adsorption experiments and, therefore, these solutions were slightly acidic (pH 5.5–6.5). Consequently, ONP, MNP, and PNP that have pK_a equal to 7.17, 8.28, and 7.15, respectively, were virtually not ionized in the solutions used. It was then decided to conduct all the detailed investigations at the actual pH value of the aqueous solution of the nitrophenols at its initial concentration.

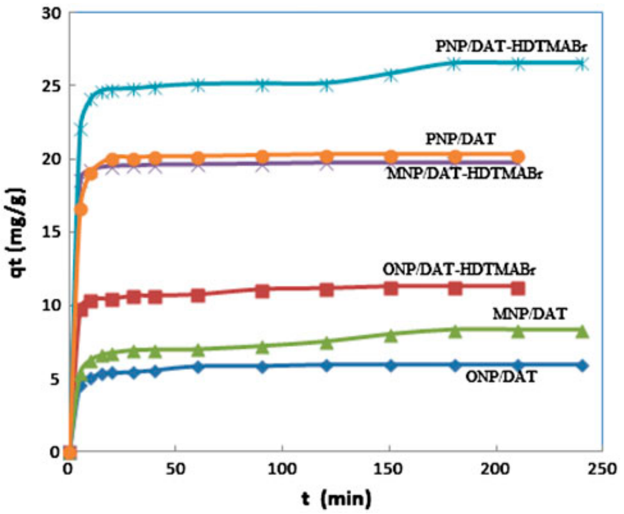

Fig. 5. The effect of equilibrium time on the adsorption of nitrophenols on DAT and DAT-HDTMABr. Initial concentration, adsorbent dosage, and temperature are: 60 mg L^{-1}; 0.02 g L^{-1}, and 25˚C, respectively.

3.5. Adsorption isotherms modeling

Adsorption equilibrium data are generally described by adsorption isotherms, which are very important to optimize the design parameters of an adsorption system. They are also helpful to provide sufficient physicochemical information to understand the mechanism of adsorption. These isotherms relate the amount of solute adsorbed at equilibrium per weight of adsorbent, q_e, to the adsorbate concentration at equilibrium C_{eq}.

In the present study, four of the most commonly used models, namely the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) isotherms were used to fit the experimental data.

The non-linear form of the Langmuir isotherm model [48] is given

$$q_e = \frac{q_{max} K_L C_{eq}}{1 + K_L C_{eq}} \tag{4}$$

where K_L (L mg^{-1}) is the Langmuir adsorption constant related to the energy of adsorption and q_{max} and q_e (mg g^{-1}) are the maximum and equilibrium adsorption capacity, respectively. Langmuir constants generated from adsorption data plot of q_e against C_{eq} (Figs. S1–S3, see the Supplementary data) are summarized in Tables 1 and 2.

One of the essential characteristics of the Langmuir equation could be expressed by dimensionless constant called equilibrium parameter R_L which is defined as [49]:

$$R_L = \frac{1}{(1 + K_L C_\circ)} \tag{5}$$

where $C_\circ$ is the highest initial concentration (mg L^{-1}). The value of R_L indicates the type of isotherm to be irreversible adsorption ($R_L = 0$), favorable adsorption ($0 < R_L < 1$), unfavorable adsorption ($R_L > 1$), and linear adsorption ($R_L = 1$). As seen from Tables 1 and 2, the adsorption of ONP, MNP, and PNP on modified and unmodified diatomaceous is favorable [50].

The Freundlich isotherm is based on the premise that adsorption occurs on rare heterogeneous surface sites with different energy of adsorption, and are also non-identical. The non-linear form of the Freundlich isotherm was used to investigate the adsorption process adherence to the model [51].

$$q_e = K_F C_{eq}^{1/n} \tag{6}$$

K_F can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. $1/n$ is the heterogeneity factor and n is a measure of the deviation from linearity of adsorption. Its

Table 1
Constants parameters and correlation coefficients calculated for various adsorption isotherm models at different temperatures for ONP, MNP, and PNP onto DAT

Adsorbate	ONP			MNP			PNP		
T/℃	25℃	35℃	45℃	25℃	35℃	45℃	25℃	35℃	45℃
Langmuir									
q_{max} (mg g^{-1})	6.035	5.913	3.580	8.139	4.195	3.566	20.486	10.467	10.191
K_L (L mg^{-1})	0.088	0.138	0.015	0.038	0.180	0.051	0.020	0.029	0.056
R^2	0.8978	0.9782	0.8953	0.9862	0.9757	0.9778	0.9841	0.9844	0.9879
R_L	0.102	0.068	0.401	0.208	0.051	0.164	0.333	0.256	0.152
Freundlich									
K_L (L g^{-1})	2.648	0.245	1.226	0.770	1.676	0.643	0.895	1.031	1.534
n	5.848	1.701	4.630	2.066	4.950	2.899	1.651	1.642	2.268
R^2	0.9410	0.9844	0.9625	0.9902	0.9117	0.8988	0.9716	0.9649	0.9757
Temkin									
B_T (J mol^{-1})	9.623	0.132	2.528	1.724	5.351	0.808	0.256	0.415	0.632
K_T	0.841	1.365	0.594	0.435	0.667	0.456	4.970	3.365	2.444
R^2	0.9257	0.9807	0.9483	0.9869	0.9488	0.9563	0.9844	0.9548	0.9814
D–R									
q_{max} (mg g^{-1})	1.576	7.185	8.020	8.980	8.281	3.004	10.176	11.359	5.929
E (kJ mol^{-1})	1.851	3.061	4.179	4.041	4.002	3.693	3.841	4.134	5.671
R^2	0.9055	0.9568	0.9712	0.8812	0.9825	0.8722	0.9206	0.9503	0.8945

Table 2
Constant parameters and correlation coefficients calculated for various adsorption isotherm models at different temperatures for ONP, MNP, and PNP onto DAT-HDTMABr

Adsorbate	ONP			MNP			PNP		
T/℃	25℃	35℃	45℃	25℃	35℃	45℃	25℃	35℃	45℃
Langmuir									
q_{max} (mg g^{-1})	11.175	6.285	4.393	19.717	13.014	6.480	26.802	18.093	11.674
K_L (L mg^{-1})	0.017	0.034	0.146	0.020	0.021	0.038	0.022	0.457	0.831
R^2	0.9784	0.9641	0.8913	0.9728	0.9860	0.9721	0.9489	0.9550	0.9517
R_L	0.370	0.227	0.064	0.333	0.323	0.208	0.313	0.021	0.012
Freundlich									
K_L (L g^{-1})	0.465	0.624	1.913	0.874	0.627	0.787	1.203	7.506	0.743
n	1.645	2.155	6.082	1.618	1.667	2.364	1.812	3.889	1.873
R^2	0.9815	0.8918	0.9496	0.9435	0.9542	0.9018	0.9028	0.9646	0.9446
Temkin									
B_T (J mol^{-1})	0.203	0.263	0.830	1.724	0.204	0.305	0.163	3.239	0.328
K_T	2.228	1.521	0.612	0.435	2.877	1.552	5.091	0.696	2.206
R^2	0.9543	0.9624	0.9290	0.9869	0.9880	0.9649	0.9599	0.9694	0.9687
D–R									
q_{max} (mg g^{-1})	1.407	2.638	6.987	5.474	3.819	4.137	5.641	3.004	3.155
E (kJ mol^{-1})	5.631	6.911	7.453	7.813	6.932	6.172	3.962	4.065	4.873
R^2	0.9342	0.9630	0.8989	0.9063	0.9513	0.8779	0.9118	0.8047	0.8701

value indicates the degree of non-linearity between solution concentration and adsorption as follows: if the value of n is equal to unity, the adsorption is linear; if the value is below unity, this implies that adsorption process is chemical; and if the value is above unity, adsorption is a favorable physical process [52]. The values of the model parameters obtained from the plot of q_e against C_{eq} (Figs. S1–S3, see Supplementary data) are presented in Tables 1 and 2.

Temkin isotherm equation [53] assumes that the heat of biosorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions and that the adsorption is characterized by a uniform distribution of the binding energies up to some maximum binding energy. The Temkin isotherm has been used in the linear form as follows:

$$q_e = \frac{RT}{B_T}\ln K_T + \frac{RT}{B_T}\ln C_{eq} \tag{7}$$

where B_T is the Temkin constant related to the heat of adsorption (kJ mol^{-1}), R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the Temperature (K), and K_T is the empirical Temkin constant related to the equilibrium binding constant related to the maximum binding energy (L mg^{-1}), (L mol^{-1}), respectively.

A plot of q_e vs. $\ln C_e$ enables the determination of the isotherm constants B_T and K_T from the slope and the intercept (Tables 1 and 2). The Temkin isotherm takes into account the effects of the interaction of the adsorbate and the adsorbing species. By ignoring the extremely low and large concentration values, the model assumes that the heat of adsorption (a function of temperature) of all of the molecules in the layer would decrease linearly rather than logarithmically with coverage due to adsorbate–adsorbent interactions [54].

Langmuir, Freundlich, and Temkin isotherms are limited in their scope to explain the physical and chemical characteristics of the sorption process. Therefore, the D–R isotherm is commonly used to describe the sorption isotherms of a single solute system. The D–R isotherm, apart from being analogous to the Langmuir isotherm, is more general than the latter as it does not assume the homogeneity of the surface or constant adsorption potential.

The D–R equation is given by [55]:

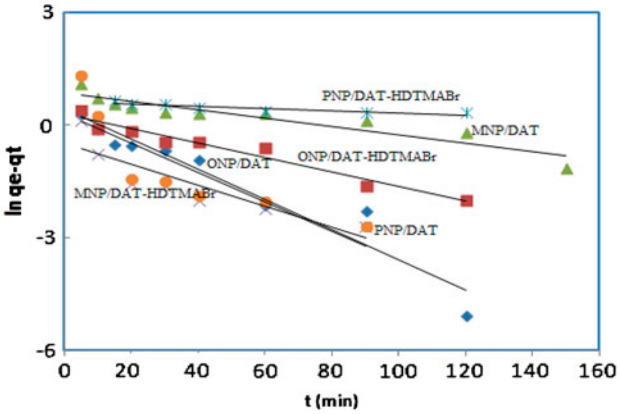

Fig. 6. Pseudo-first-order reaction kinetics for the adsorption of nitrophenols on DAT and DAT-HDTMABr. Initial concentration, adsorbent dosage, and temperature are: 60 mg L^{-1}, 0.02 g L^{-1}, and 25°C, respectively.

$$\ln q_e = \ln q_{\max} - \beta\varepsilon^2 \tag{8}$$

In this equation, q_e is the amount of nitrophenols taken up by the DAT and DAT-HDTMABr at equilibrium (mg g^{-1}), $q_{\max}$ is the D–R monolayer capacity (mg g^{-1}), β is the constant related to the adsorption energy (mol^2/kJ^2), and ε is the Polanyi potential which is related to the equilibrium concentration as Eq. (9):

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_{eq}}\right) \tag{9}$$

The main energy of adsorption (E) is calculated using the following expression [56].

$$E = \frac{1}{\sqrt{2\beta}} \tag{10}$$

Adsorption capacities $q_{\max}$ and the main adsorption energies E are calculated for the two adsorbents. The results obtained for the four isotherm equations are listed in Tables 1 and 2. Based on Langmuir isotherm, the highest value of maximum adsorption capacity of adsorption, $q_{\max}$, of ONP, MNP, and PNP by DAT was calculated at 25°C; 6.035, 8.139, and 20.486 mg g^{-1}, respectively. Whereby DAT-HDTMABr were 11.175, 19.717, and 26.802 mg g^{-1}, respectively. The n value as indicated by Freundlich model was greater than unity, suggesting a favorable adsorption process. The maximum E values determined for D–R isotherm are 5.671 and 7.813 kJ mol^{-1} for DAT and DAT-HDTMABr, respectively. They are the orders of physisorption mechanism, in which the sorption energy <16 kJ mol^{-1} [57]. Hence, the results obtained in this study indicate that the adsorption has low potential barrier and is assigned to physisorption.

Table 3
Pseudo-first-order and pseudo-second-order adsorption rate constant and calculated $q_{e.clcd.}$ and experimental $q_{e.Exp.}$ values for the adsorption of nitrophenols on DAT and DAT-HDTMABr

	Pseudo-first-order			Pseudo-second-order		
$q_{e.Exp.}$ (mg g^{-1})	k_1 min^{-1}	$q_{e.calcd.}$ (mg g^{-1})	R^2	k_2 (g. mg^{-1}. min^{-1})	$q_{e.calcd}$ (mg g^{-1})	R^2
ONP/DAT						
6.035	0.040	1.534	0.9285	0.086	6.061	0.9999
ONP/DAT-HDTMABr						
11.175	0.019	1.319	0.9515	0.055	11.363	0.9998
MNP/DAT						
8.139	0.011	2.371	0.8632	0.019	8.475	0.9965
MNP/T-HDTMABr						
19.717	0.066	1.150	0.7990	0.014	19.608	1.0000
PNP/DAT						
20.486	0.013	1.878	0.8265	0.018	26.316	0.9994
PNP/DAT-HDTMABr						
26.486	0.039	1.326	0.7899	0.103	20.408	1.0000

3.6. Adsorption kinetic modeling

The mechanism of adsorption depends on the physical and/or chemical characteristics of adsorbents as well as on the mass transport process [58]. In order to analyze the rate of adsorption and possible adsorption mechanism of ONP, MNP, and PNP onto DAT and DAT-HDTMABr, the pseudo-first-order of Lagergren and pseudo-second-order models were applied to adsorption data. The pseudo-first-order model is given as [59]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{11}$$

where q_t is the amount of nitrophenols adsorbed at time t (mg g^{-1}) and k_1 is the pseudo-first-order rate constant (min^{-1}) for the first-order adsorption. The pseudo-first-order plots are shown in Fig. 6 and their constants are given in Table 3.

Based on Table 3, the correlation coefficient R^2 was found to be low and the values of calculated adsorption capacities ($q_{e.calc.}$) were far much lower than experimental ones ($q_{e.expt.}$), suggesting that adsorption process did not fit the pseudo-first-order model.

The pseudo-second-order model can be expressed as [60]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{12}$$

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}). Values of k_2 and q_e were calculated from the slopes and intercepts of the linear plot of t/q_t against t (Fig. 7). The regression coefficients R^2 are found to be 0.9965–1.0000, and the calculated maximum adsorption capacity values of $q_{e.calc.}$ are quite close to the experimental values, $q_{e.expt.}$ for adsorption of ONP, MNP, and PNP onto DAT and DAT-HDTMABr indicates that the pseudo-second-order model fits with the kinetic data very well. The values of $q_{e.calc.}$ and k_2 are listed in Table 3.

3.7. Thermodynamic parameters

The thermodynamic parameters including change in the Gibbs free energy ΔG, enthalpyΔH, and entropy ΔS are calculated from the variation of thermodynamic equilibrium constant K_d with changes in temperature. K_d for the adsorption reaction can be defined [61]:

$$K_d = \frac{q_e}{C_e} \tag{13}$$

Values of K_d are obtained by plotting $\ln q_e/C_e$ vs. q_e and extrapolating q_e to zero.

Gibbs free energy changes ΔG for interactions are calculated from the relationship:

$$\Delta G = -RT \ln K_d \tag{14}$$

The enthalpy changes ΔH and entropy changes ΔS are then determined from the slope and intercept of the following Eq. (15) plot of $\ln K_d$ vs. $1/T$.

$$\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{15}$$

The values obtained are shown in Table 4. The negative Gibbs free energy changes ΔG confirm that the

Table 4
Thermodynamic parameters for the adsorption of nitrophenols on DAT and DAT-HDTMABr

T/℃	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
ONP/DAT			
25	−7.211	−88.968	286.991
35	−5.832		
45	−4.691		
ONP/DAT-HDTMABr			
25	−11.866	−135.385	413.156
35	−8.788		
45	−3.556		
MNP/DAT			
25	−4.725	−61.506	190.108
35	−3.148		
45	−1.908		
MNP/DAT-HDTMABr			
25	−2.751	−19.413	56.535
35	−2.122		
45	−1.637		
PNP/DAT			
25	−1.570	−8.912	24.643
35	−1.312		
45	−1.078		
PNP/DAT-HDTMABr			
25	−5.137	−30.529	85.634
35	−4.238		
45	−3.434		

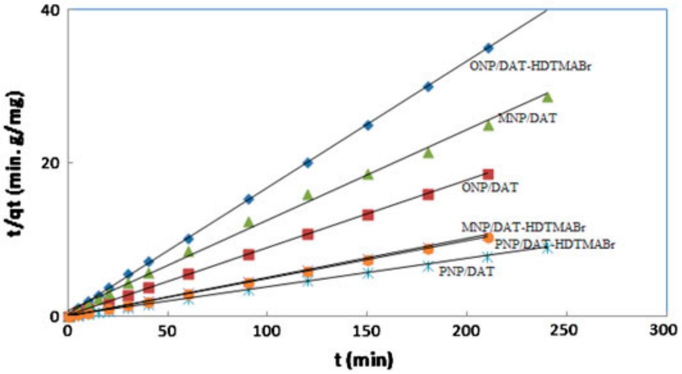

Fig. 7. Pseudo-second-order reaction kinetics for the adsorption of nitro phenols on DAT and DAT-HDTMABr. Initial concentration, adsorbent dosage and temperature are: 60 mg L^{-1}, 0.02 g L^{-1}, and 25℃, respectively.

adsorption process has a natural tendency to proceed spontaneously. The values of the ΔG also confirm that maximum adsorption is obtained with the ONP, MNP, and PNP onto DAT-HDTMABr higher than that of DAT. Generally, the change of free energy for physisorption is between −20 and 0 kJ mol^{-1}, but chemisorption is at the range from −80 to −400 kJ mol^{-1} [62]. The overall free energy change during the adsorption process was negative for the experimental range of temperature (see Table 4), corresponding to a spontaneous physical process of ONP, MNP, and PNP adsorption and that the system does not gain energy from an external source.

It is clear from these results that overall enthalpy change ΔH of the adsorption of ONP, MNP, and PNP onto DAT and DAT-HDTMABr is negative which indicates that the adsorption is exothermic and the products are energetically stable with high binding of ONP, MNP, and PNP to the available sites. The positive values of ΔS show the increased randomness of the solid–solution interface during the adsorption of ONP, MNP, and PNP onto DAT and DAT-HDTMABr.

4. Conclusions

The experimental investigation concluded that DAT and DAT-HDTMABr could be used as potential adsorbents for the removal of ONP, MNP, and PNP from aqueous solutions. The batch adsorption parameters: adsorbent dose, contact time, and temperature were found to be effective on the adsorption process. The kinetic studies revealed that the adsorption process followed the pseudo-second-order kinetic model. The experimental extraction data at different temperatures (25, 35, and 45℃) for ONP, MNP, and PNP by DAT and DAT-HDTMABr fitted to the Langmuir, the Freundlich, the Temkin, and the D–R isotherm models. The maximum adsorption capacity of ONP, MNP, and PNP were found to be at 25℃ onto DAT: 6.035, 8.139, and 20.486 mg g^{-1}, respectively, and onto DAT-HDTMABr: 11.175, 19.717, and 26.802 mg g^{-1}, respectively. Thermodynamic parameters ΔH, ΔS, and ΔG, showed the exothermic and spontaneous nature of the adsorption of ONP, MNP, and PNP onto DAT and DAT-HDTMABr. The thermodynamic parameters, although apparent, are useful if the present results are to be utilized on large-scale of industrial processes.

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Supplementary data

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