Introduction

Phenol and its compounds are one of the major materials commonly used in the petrochemical, coking, coal refining, chemical, and pharmaceutical industries [1, 2]. The harmful effects due to the presence of phenols in industrial wastewaters have been confirmed [3, 4]. Thus, development of suitable methods for the decontamination of phenols is necessary. Research has studied the removal of phenol from aqueous solutions, including advanced oxidation processes [5, 6], biological degradation [7, 8], ozonation [9, 10], adsorption [11-14], etc. Among these methods, adsorption has been developed as a simple and cheap method to treat phenolic compounds. Various adsorbents such as bentonite [15], sawdust [16], activated carbon [17], nano-titanium dioxide [18], and carbon nanotubes [19] have been tested for adsorption of phenol and its compounds from aqueous solutions. Among them, carbon materials show significant adsorption yields. This may be because of their large surface area and good distribution of pore size. Therefore, using new carbonaceous materials as adsorbents is interesting for scientists. An example of a new carbonaceous material is graphene, whose atoms are arranged in a 2D honeycomb structure [20]. As literature results show, graphene has a high adsorption capacity for removal of aqueous pollutants [21-25].

In the present study, the potential application of graphene for 4-chloro-2-nitrophenol (4C2NP) adsorption
from aqueous solutions was investigated. Adsorption kinetics, isotherms, and thermodynamics were deduced from the experimental results.

### Materials and Methods

#### Materials

Graphene nanopowder was supplied by Supermarket, USA. Average particle (lateral) size, average flake thickness, and specific surface area of nanopowders were about 10 microns, 1 nm (less than 3 monolayers), and 510 m$^2$/g, respectively. 4C2NP (C$_6$H$_4$ClNO$_3$, M$_w$ = 173.56 g/mol) was purchased from Fluka, Germany.

#### Adsorption Experiments

Batch adsorption experiments of 4C2NP onto graphene were carried out to obtain equilibrium data. A stock solution (1000 mg/L) was prepared by dissolving 4C2NP in ethanol and then diluting with distilled water (pH of this solution was almost 4.5). The effects of main parameters such as contact time, graphene doses (0.2-0.8 g/L), pH (3-10), initial 4C2NP concentrations (2-10 mg/L), and temperatures (298-328 K) were studied. Solution pH was adjusted by HCl or NaOH. Experiments were done in an Erlenmeyer flask on a hot plate stirrer (300 rpm) by adding 250 mL of 4C2NP solution and the desired amount of graphene. At predetermined time intervals, samples were drawn and were filtered using 0.22 µm membrane filters. The concentration of 4C2NP in the filtrate was measured by a UV-Vis spectrophotometer (SPEKOL 1500, analytikjena Co., Germany) at maximum wavelength ($\lambda_{max}$=219 nm for acidic pHs or 234 nm for neutral and alkaline pHs).

The amount of adsorbed 4C2NP at various and equilibrium times were obtained from equations (1) and (2), respectively:

\[
q_t = \frac{(C_0 - C_t)}{m} \times V \tag{1}
\]

\[
q_e = \frac{(C_0 - C_e)}{m} \times V \tag{2}
\]

...where $C_0$, $C_t$, and $C_e$ represent the initial various time $t$ and equilibrium concentrations of 4C2NP (mg/L), respectively. $V$ is the solution volume (L) and $m$ is the adsorbent mass (g).

Zeta potential of graphene was measured by a Dynamic light scattering (DLS) instrument (Nanotrac Wave, Microtrac Co.).

#### Results and Discussion

**Effect of Contact Time and Graphene Dosage**

The amount of 4C2NP adsorption onto graphene versus contact time and adsorbent dose is illustrated in Fig. 1. The adsorption capacity of graphene decreased with increasing dosage. This decline can be due to the aggregation of graphene and an increase in diffusion path length of 4C2NP molecules [26]. As shown in Fig. 1, the adsorption of 4C2NP by graphene increased rapidly in the first 10 min and then achieved equilibrium gradually at about 60 min. Thus, one hour was selected as the contact time. The fast adsorption at the initial period can be related to the special one-atom-thick layered structure of graphene, which makes 4C2NP contact immediately with the active vacant sites on the graphene surface [27].

![Fig. 1. Effect of contact time and graphene dosage ([$4C2NP_0$]=10 mg/L, pH=4.5, T=298 K).](image1)

**Effect of pH**

The pH of solution affects the ionization of adsorbate and the adsorbent’s surface charge [28]. As shown in the zeta potential analysis (Fig. 2), the pH of the zero point of charge (pH$_{ZPC}$) for graphene is 6. This indicated that graphene sheets possess a positive charge at pH<6 and negative charge at pH>6. The experimental results (Fig. 3) demonstrate that the adsorption of 4C2NP by graphene decreases with increases in pH. The decrease in adsorption until pH=7 is gradual, and then it drops significantly at pH>7. In fact, there is not a repulsive electrostatic interaction between the non-ionized 4C2NP and graphene surfaces at pH<7 (4C2NP, pKa= 6.46, 25ºC) and the adsorption is higher. As pH>pK$_a$, 4C2NP dissociates and forms...
C₆H₃ClNO₃⁻ anions, while graphene’s surface contains a negative charge, the repulsive electrostatic interactions cause a decrease in sorption. Such observations were also reported by other researchers [29].

Effect of Initial Concentration

As shown in Fig. 4, by increasing the initial 4C2NP concentration, adsorption of 4C2NP onto graphene was increased. In fact, the initial concentration can provide a driving force to overcome the resistances to the mass transfer of 4C2NP from aqueous to solid phase. In addition, this may be due to higher interaction between 4C2NP and graphene [30].

Effect of Temperature

To evaluate the temperature effect on the adsorption process, four different temperatures were selected (298 to 328 K). Fig. 5 shows that the 4C2NP adsorption by graphene was decreased by increasing the temperature from 298 to 328 K. It may be due to this fact that at low temperatures, more active sites are available [31].

Adsorption Isotherm Studies

Isotherm studies were conducted with various initial concentrations of 4C2NP (2-10 mg/L), with 0.2 g/L of graphite at 25°C and pH=4.5. Non-linear forms of Langmuir, Freundlich, and Temkin models were fitted to adsorption equilibrium data (equations 3-5, respectively):

\[ q_e = \frac{q_m K_f C_e}{1 + K_f C_e} \]  
\[ q_e = K_f C_e^\frac{1}{n} \]  
\[ q_e = B_1 \ln(K_f C_e) \]

...where \( q_m \) is the maximum amount of adsorption (mg/g) and \( K_f \) is the affinity constant (L/mg). \( K_f \) and \( n \) are the Freundlich constants indicating adsorption capacity and adsorption strength, respectively. \( K_f \) and \( B_1 \) are the Temkin model constant [32-34].

The curves of experimental data and results obtained from different models are shown in Fig. 6.

Polymath software (version 6.10) was used to determine the isotherm constants. We have used correlation coefficient (R²) and adjusted correlation coefficient (R² adj.) parameters to predict which model correctly represents the data. If R² value was close to one and also close to R² adj., it could be concluded that the regression model is correct [35]. Root mean square error and average relative error

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(equations 6 and 7, respectively) were also used to determine the best-fit isotherm model. A model with smaller \(Rms\) and \(ARE\) shows the data accurately [36].

\[
Rms = \frac{1}{n} \left( \sum_{i=1}^{n} (q_{i,exp} - q_{i,cal})^2 \right)^{1/2}\]  
\[ARE = \frac{1}{100} \sum_{i=1}^{n} \left( \frac{q_{i,exp} - q_{i,cal}}{q_{i,exp}} \right)\]  

...where \(n\) is the number of experimental data points, \(q_{i,exp}\) is the experimental adsorption capacity, and \(q_{i,cal}\) is the theoretically calculated adsorption capacity.

The isotherm parameters and the error functions are listed in Table 1.

By comparing the values of \(R^2, R^2_{adj}\), and other error functions in Table 1, it is found that the Freundlich model is the most suitable model to satisfactorily describe the studied sorption phenomenon. In this isotherm, if the value of \(n\) is below unity, then the adsorption is chemical; otherwise, the adsorption is physical [37]. Thus, in this research the value of 1.624 for \(n\) indicates that the adsorption of 4C2NP onto graphene is a favorable physical process.

### Adsorption Kinetic Studies

The kinetic studies of 4C2NP adsorption by graphene were investigated by 250 mL of solution containing 10 mg/L 4C2NP in the range of 0-60 min. The adsorption kinetic data were described according to the non-linear rate equations of Lagergren’s pseudo-first and Ho’s pseudo-second order, respectively:

\[
q_t = q_e (1 - e^{-k_1t}) 
\]
\[
q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} 
\]

...where \(k_1\) (min\(^{-1}\)) and \(k_2\) (g/mg.min) are the Lagergren and Ho kinetic model rate constants, respectively [38, 39]. In Fig. 7, the plots of adsorption kinetic models are depicted. Similar to isotherm studies, parameters of these models were determined by non-liner trial and error method using Polymath 6.10 software and are given in Table 2.

Based on the results (Fig. 7 and Table 2), the pseudo-second-order model has a higher \(R^2\) value, lower \(Rms\) value, and its calculated equilibrium adsorption amount (\(q_{e,cal}\)) is closer to the experimental data (\(q_{e,exp}=26.737\) mg/g). On the other hand, the value of \(k_{2,f}(0.269\) min\(^{-1}\)) indicates that 4C2NP adsorption onto graphene is a fast
A similar phenomenon has been observed in adsorption of bisphenol by graphene [40].

**Adsorption Thermodynamic Studies**

Thermodynamic studies were performed in four different temperatures, at an initial 4C2NP concentration of 10 mg/L. Various thermodynamic parameters (standard Gibbs free energy, standard enthalpy, and entropy) were calculated by equations (10-12):

\[
\Delta G^o = -RT \ln K_C 
\]

\[
K_C = \frac{q_e}{C_e} 
\]

\[
\ln K_C = -\frac{\Delta H^o}{R} \left(\frac{1}{T}\right) + \frac{\Delta S^o}{R} 
\]

...where \(K_C\) is the equilibrium constant, \(T\) is the absolute temperature (K), and \(R\) is the universal gas constant (8.314 J/mol·K) [41]. \(\Delta H^o\) and \(\Delta S^o\) were calculated from the slope and intercept of the plot of \(\ln K_C\) vs. \(1/T\) using equation 12 (Fig. 8).

According to the results (Table 3), negative values of \(\Delta G^o\) indicate the spontaneity of the adsorption process. The decrease in \(\Delta G^o\) with the decrease of temperature reveals more efficient adsorption at lower temperature. The negative \(\Delta H^o\) value confirms the exothermic nature of the adsorption, which is also supported by the decline in the adsorption capacity of 4C2NP with the increase in temperature. The negative value of \(\Delta S^o\) reflects a decrease in freedom degree of the adsorbed species.

**Conclusions**

The findings demonstrated that the adsorption of 4C2NP by graphene increased rapidly in the first 10 min and then achieved equilibrium gradually at about one hour. The adsorption capacity of graphene increased by decreasing pH, temperature, and adsorbent dosage, and increasing the 4C2NP initial concentration. Adsorption isotherm and kinetic studies showed that the Freundlich isotherm equation and pseudo-second-order kinetic model provided the best correlation of the adsorption data. The negative sign of \(\Delta G^o\) and \(\Delta H^o\) indicates that the adsorption process is spontaneous and exothermic. In conclusion, adsorption by the graphene process is an appropriate method for reducing 4C2NP from aqueous solutions.

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**References**


