A study of 4-chlorophenol continuous adsorption on nano graphene oxide column: model comparison and breakthrough behaviors
Akbar Eslami, Mohammad Mehralian and Ahmad Moheb

ABSTRACT
Removal of 4-chlorophenol in a continuous fixed-bed column was investigated by using nano graphene oxide (NGO) adsorbent in this study. The adsorbent (NGO) was characterized by X-ray diffraction (XRD) analysis and scanning electron microscopy analysis. Variables in the adsorption process were bed depths (5, 10 and 15 cm), flow rate (1, 2 and 4 mL/min), influent 4-chlorophenol concentrations (5, 10, 15, 20 and 30 mg/L) and influent solution pH (6–7). The enhancement of adsorption is favored by decreasing 4-chlorophenol concentration and flow rate and increasing bed depth. Indeed, the best result obtained in this study was 145.2 mg/g of adsorption capacity under 4-chlorophenol concentration of 5 mg/L at a flow rate of 1 mL/min toward a bed depth of 15 cm. The results of the study showed that the ideal 4-chlorophenol adsorption followed well the Thomas and Yoon–Nelson models for predicting breakthrough behavior at different flow rates and bed depths. Finally, increasing flow rate, decreasing bed depth and increasing influent 4-chlorophenol concentration resulted in the breakthrough time and exhaustion time decreasing.

Key words | adsorption, breakthrough behavior, nano graphene oxide, 4-chlorophenol

INTRODUCTION
Some of the priority pollutants according to the Environment Protection Agency (EPA) and Agency for Toxic Substances and Disease Registry (ATSDR), because of their toxicity and possible accumulation in the environment, are chlorophenols (ATSDR 1999; Xiao et al. 2013). Phenolic compounds are generated by different industries including coal conversion, petrochemical industry and phenol producing industries (phenolic resins, polyamide and adhesives) (Johnson et al. 1999; Hamdaoui & Naffrechoux 2009). Presence of this compound in wastewater is a major challenge for human societies, particularly in developing countries, concerning the provision of safe water in terms of microbial, physical and chemical characteristics (Penttinen 1995; Al-Rasheed 2005; Igbinosa et al. 2013). 4-chlorophenol as a toxic and corrosive compound enters the body via the skin, and respiratory and gastrointestinal systems causing increased irritation of the eyes, skin, throat and nose, and coughing and breathing problems (Zhou et al. 2014). So, in order to protect the health of people and the environment and ensure economical use of available water resources, changes need to be made to reduce water pollution (Hamdaoui & Naffrechoux 2009). Responsible agencies, such as the EPA, recommended a maximum contaminant level of phenol in water of 0.3 mg/L and for other halogenated phenols, such as pentachlorophenol, 0.001 mg/L (Johnson et al. 1999). Thus, the achievement of maximum concentration levels of phenols has become a major environmental problem. In the literature, different techniques like chemical oxidation, electrocoagulation, solvent extraction and membrane separation have been developed for removal of 4-chlorophenol from wastewater (Monsalvo et al. 2012). These techniques are expensive but among physicochemical processes, adsorption is a well-established and
effective technique for the removal of organic matter from water, wastewater, etc. (Akar et al. 2008). Nano material like graphene oxide can be effectively employed in water and wastewater treatment. In fact, it is able to retain organic matters, which are resistant to physicochemical and biological treatments, and removes a large proportion of pollutants. Furthermore, nano materials exhibit high adsorption capacity, rapid uptake and selectivity as well as being inexpensive (Nishiyama et al. 2015). Graphene oxides for adsorption of organic compounds have been investigated by researchers but studies related to the granular form of nano powder are unheard of. So, the role of graphene oxide in 4-chlorophenol adsorption is investigated in the present study. The results of continuous systems are important for obtaining basic engineering data, as batch studies of adsorption with undetermined factors may not provide accurate scale-up information concerning the column operation system (Benfield et al. 1982).

The objectives were to: (1) perform batch and continues studies to examine 4-chlorophenol adsorption using nano graphene oxide (NGO) (effect of concentration, flow rate, time and bed depth) and (2) perform modeling studies to investigate the breakthrough behavior and exhaustion time of granular NGO and analyze using Adams–Bohart, Thomas and Yoon–Nelson models.

**MATERIAL AND METHODS**

**Characterization of adsorbent**

Scanning electron microscopy (SEM) photomicrography of the granular NGO was carried out using an electronic microscope (Philips XI-30 ESEM-FEG Company, USA). X-ray diffraction (XRD) analysis on the adsorbent was carried out by means of a Philips PW1710/00 (Ireland) model.

**Graphene oxide granules preparation**

The sorbent was prepared at a concentration of 20 wt% and converted to granulated form in order to maintain the nano characteristics. A total of 2.5 g of the NGO powder (Nanosav Company, Iran) was mixed with 1,000 mL of water using a mechanical stirrer at 1,000 rpm for 2 hours. Due to the nano size of the graphene oxide powder, the particle tended to agglomerate, especially when dispersed in water. Next, a measured amount of sodium alginate powder was added to the graphene oxide powder solution to obtain 1% (w/v) alginate solution. The suspension was stirred for 4–6 hours in order to ensure dispersion of the sodium alginate. Then 100 mL of 1 molar chloride calcium, CaCl₂ (Merck, Germany) was prepared and set on a mechanical stirrer at 100 rpm. The suspension (mixture of nano powder and sodium alginate) was added to chloride calcium solution by using a dropping-tube to form granules (Smirnova & Arlt 2004). Granulation occurred due to ion exchange of calcium to sodium. For complete ion exchange, granules were kept in the chloride calcium solution for 2 hours. After this time, granules were washed with distilled water and were dried in an oven (65–75 °C). After drying, granules were kept in a container.

**Batch and continuous adsorption system studies**

Batch system experiments were carried out at 25 C using 50 mL of 4-chlorophenol (Merck, Germany) solution in a stirrer, with an agitation speed of 200 rpm. The experiments were performed in a beaker with a volume of 100 mL. Adsorbent doses of 2, 4, 6 and 8 g/L were used to obtain the optimal dose. The pH of the solution was 4 to 9 with concentrations of 0.1, 0.2, 0.3, 0.4, 0.5, 1, 10, 20 and 30 mg/L of 4-chlorophenol. Analysis of effluent 4-chlorophenol concentration was carried out spectrophotometrically (HACH DR 5000™ UV-Vis Spectrophotometer). Experiments conducted in a continuous mode used a glass column with an internal diameter of 5 cm and a height of 40 cm which had three separate outputs at heights of 5, 10 and 15 cm. 4-chlorophenol solution (5, 10, 15, 20, 25 mg/L) was pumped into the column by a peristaltic pump (BT100-2J model, Langer Company, USA) at a constant feeding speed (1, 2, 4 mL/min). Solution was withdrawn from the bottom of the column at selected intervals for spectrophotometric analysis. The absorption capacity was calculated from Equation (1):

\[
q_m = \frac{(t_e - t^* - \int_0^{t_e} f(t)dt)QC_0}{w}
\]

where \(q_m\) is the amount of metal ions adsorbed per unit weight of adsorbents (mg/g), \(Q\) is the flow rate (mL/min) and \(w\) is the dry weight of the adsorbent packed in the column (g), \(C_0\) is the
initial influent concentration (mg/mL), \( t_e \) is the time to adsorbent exhaustion (min), \( t_b \) is the time to constituent breakthrough (min), \( f(t) \) is the function of the effluent curves obtained from column testing, \( t_e - \int_{t_b}^{t_e} f(t) dt \) is the area of the breakthrough curve under exhaustion conditions, which can be estimated through integration.

### Analysis procedure

The concentration of 4-chlorophenol at 500 nm in a UV-visible spectrophotometer was determined by the 5530 D standard methods spectrophotometer (Li 2008). The breakthrough behavior of the adsorption of 4-chlorophenol solution was modeled using the Adams–Bohart, Thomas, and Yoon–Nelson models (Baral 2007; Baral et al. 2009). The equation of breakthrough curve models and the parameters are given in Table 1.

### RESULTS AND DISCUSSION

#### Adsorbent characteristics

In this study, NGO granules were characterized by XRD, see Figure 1. Diffraction peaks in XRD represent the corresponding inter-planar spacing where peak positions may actually indicate elemental presence. XRD of the graphene oxide structure (002) showed the highest intensity of peak at about 25 degrees. After oxidation, a peak (about 14°) of graphene structure (001) was observed corresponding to the structure (001). This is because of the increase in d-spacing due to the exchange properties and presence of functional groups by oxidation. Oxidation leads to an increase in d-spacing that can be attributed to the presence of functional groups and exchange properties of them. Subsequently, atomic-scale unevenness on the adsorbent surface can be caused by the functional groups. So, these factors together result in the high adsorption capacity of granules. Also, use of a scanning electron microscope at 500× magnification confirmed that NGO granules have a mean pore diameter. Indeed, after granulation of graphene powder for 4-chlorophenol adsorption, the surface changed and became porous, with globular and polyene structures. The porous structure of the graphene oxide was significantly altered after granulation. The graphene oxide granules, depicted in Figure 2, contain small pores of approximately 7 nm with 514 m²/g of specific surface area implying short diffusion paths. This indicates that NGO granules can be more porous in 4-chlorophenol removal.

#### Batch experiment description

Figure 3 shows the absorption of 4-chlorophenol with varying pH and contact time, indicating that absorption in the first few minutes was fast and then declined (5.75 to 3 mg/g) with contact time (3 to 30 min). Indeed, pH, which changes the number of active sites, plays an important role. So, the maximum adsorption of 4-chlorophenol occurred at a pH value of 7. Reduction of efficiency due to ionization between absorbent and adsorbate will occur at pH > 7 (Zhang et al. 2010, 2015). Huang et al. (2011) supported that 85% of absorption using adsorbent occurs in the first 5 minutes of the reaction. Determination of the adsorption mechanism in the batch experiment is also important for design purposes. In a solid–liquid adsorption process, the transfer of

### Table 1 | Breakthrough curve models and the parameters

<table>
<thead>
<tr>
<th>Models</th>
<th>Parameters</th>
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<tbody>
<tr>
<td>Adams–Bohart</td>
<td>( \ln \left( \frac{C_t}{C_0} \right) = K_{AB} C_0 t - K_{AB} N_0 Z U_0 )</td>
</tr>
<tr>
<td></td>
<td>( C_0 ) mg/L of influent concentration</td>
</tr>
<tr>
<td></td>
<td>( C_t ) mg/L of effluent concentration</td>
</tr>
<tr>
<td>Thomas</td>
<td>( \ln \left( \frac{C_t}{C_f} \right) = \frac{K_{th} q_0 m}{Q} - \frac{K_{th} C_0 V_{ eff}}{Q} )</td>
</tr>
<tr>
<td></td>
<td>( K_{AB} ) kinetic constant, L/mg min</td>
</tr>
<tr>
<td></td>
<td>( t ) time required for 50% adsorbate breakthrough, min</td>
</tr>
<tr>
<td>Yoon–Nelson</td>
<td>( \ln \left( \frac{C_t}{C_0 - C_f} \right) = K_{YN} t - t K_{YN} )</td>
</tr>
<tr>
<td></td>
<td>( N_0 ) mg/L of saturation concentration</td>
</tr>
<tr>
<td></td>
<td>( Z ) bed depth of the column, cm</td>
</tr>
<tr>
<td></td>
<td>( U_0 ) superficial velocity, cm/min</td>
</tr>
<tr>
<td></td>
<td>( V_{ eff} ) effluent volume, mL</td>
</tr>
<tr>
<td></td>
<td>( Q ) volumetric flow rate, cm³/min</td>
</tr>
<tr>
<td></td>
<td>( K_{yn} ) rate constant, min⁻¹</td>
</tr>
<tr>
<td></td>
<td>( K_{th} ) Thomas constant, mL/min mg</td>
</tr>
<tr>
<td></td>
<td>( q_0 ) adsorption capacity, mg/g</td>
</tr>
</tbody>
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the adsorbate is controlled by either boundary layer diffusion (external mass transfer) or intraparticle diffusion (mass transfer through the pores), or by both (Hamdaoui & Naffrechoux 2009). Generally, the adsorption mechanism is reported to consist of three stages: (1) diffusion of 4-chlorophenol to the external surface of the NGO through the liquid boundary layer, (2) diffusion of 4-chlorophenol through the pores of the NGO, and (3) internal diffusion on the adsorbent surface. Among these steps, internal diffusion is usually very rapid in comparison to the others. Therefore, the adsorption process is controlled by a combination of mechanisms. Mechanisms of the adsorption process have specified that the rate controlling step, i.e. boundary layer diffusion, is characterized via the concentration dilution of the adsorbate, small pores of NGO and poor mixing. Although, sufficient mixing, and the adequate amount of adsorbent toward a high concentration of 4-chlorophenol causes the intraparticle diffusion, which
means that the rate of diffusion after the early stages of the adsorption increased (Mohan & Singh 2004). Generally, after NGO granule synthesis, the highly crystal structure was altered, self-aggregation of graphene layers was evidently relieved, and more single to few layer graphene nanosheets were created with folds and wrinkles meaning that the micro pore volume and specific surface area of the NGO granules increased relative to before granulation. So, due to the more porous surface of the graphene and strong electron charge transfer, the adsorption rate was gradually promoted.

Comparison of breakthrough curve modeling

For industrial applications and successful design of a column adsorption process, breakthrough curve modeling is required (Han et al. 2009). To describe the laboratory-scale column studies, mathematical models have been developed. In this study Adams–Bohart, Thomas, and Yoon–Nelson models were used for determination of the best model in the column dynamic behavior prediction. Linear regression analysis and correlation coefficients ($R^2$) were calculated and are shown in Figure 4 (Optimization Results). It is shown from Figure 4 that the Thomas model ($R^2 = 0.724$) provided a better fitting compared to the Adams–Bohart model. Among the models for adsorption, the best fitness of the Thomas model demonstrates that the external and internal diffusions were not the limiting step (Bohart & Adams 1920). One of the assumptions regarding the Yoon–Nelson model for each adsorbate molecule is that the rate of decrease in the probability of adsorption is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. Noticeably the $R^2$ value of 0.72 showed the Yoon–Nelson model validity for the system. This model is also based on the surface reaction theory established by Bohart and Adams. There is a relationship between $C_t/C_0$ and $t$ in a continuous system by the assumption that equilibrium is not instantaneous (Sharma et al. 2013; Li et al. 2015). This model is provided for description of the initial part of the breakthrough curve (Bohart & Adams 1920; Baral et al. 2009). Comparison between models presented in this study with consideration of $R^2$ values, indicated both the Thomas and Yoon–Nelson models can be used to predict 4-chlorophenol adsorption performance.

Modeling of flow rate based breakthrough equations

The results given in Figure 4(a)–4(c) showed that the breakthrough of 4-chlorophenol gradually decreases with increasing flow rate (1, 2 and 4 mL/min). When increasing the flow rate from 1 to 2 mL/min, the exhaust time (corresponding to 98% of influent concentration) decreased from 420 to 150 min and at a flow rate of 4 mL/min, 160 min was obtained. This may be attributed to the fact that at a high rate of influent, the adsorbate did not have enough time to contact the NGO, which resulted in a lower removal of 4-chlorophenol in the column (Kulkarni 2014; Nourmoradi et al. 2016). Chen et al. (2015) showed the same result attaining higher removal of 4-chlorophenol at a low rate of influent because the 4-chlorophenol had more time to contact with the adsorbent. When the flow rate increased, the external film mass resistance at the surface of the NGO tended to decrease and the residence time declined. This could be attributed to the saturation time declining, giving the lower 4-chlorophenol adsorption efficiency. Similar results have been reported in other research (Yoon & Nelson 1984; Zhang et al. 2010, 2015). In addition, insufficient contact time results in decreasing of the bonding capacity of the 4-chlorophenol onto the graphene oxide. The best absorption rate was achieved at 1 mL/min with $q_e = 145.9$ mg/g and adsorbent saturation at the time of 500 min.

Modeling of influent 4-chlorophenol concentration based breakthrough equations

Model comparison and breakthrough behaviors of 4-chlorophenol absorption are shown in Figure 4(d)–4(f). Figure 4 illustrates that the graphene oxide time to reach saturation and breakthrough time decreased with increasing influent 4-chlorophenol concentration, except at 5 and 15 mg/L. With increasing influent 4-chlorophenol concentration, adsorption capacity decreased such that initial concentration variation from 5 to 25 mg/L resulted in increasing absorption capacity of the adsorbent from 116.84 to 449.98 mg/g but as expected the removal percentage decreased (from 48.34 to 38.7), see Figure 4. This can be explained by the fact that at the increasing gradient, the concentration of the adsorbate caused faster transport due to an increased diffusion coefficient or mass transfer coefficient.
Figure 4 | Model comparison and breakthrough behaviors of 4-chlorophenol absorption in different flow rate (a–c), initial concentration (d–f), bed depth (g–i) and optimization results.
The prepared NGO was highly efficient in 4-chlorophenol removal due to the presence of nanometer pores on the adsorbent surface. To predict the breakthrough curves, Thomas and Yoon-Nelson models for 4-chlorophenol removal were used, which indicated they were very suitable for NGO column design. 4-chlorophenol absorption by graphene oxide was dependent on three factors: influent 4-chlorophenol concentration, bed depth and flow rate. The adsorption capacity increased with increasing bed depth, but decreased with increasing the influent concentration and flow rate. The column sorption process was found to perform better at lower influent 4-chlorophenol concentration, lower flow rate and higher bed depth. NGO can transfer a 4-chlorophenol contamination problem of aqueous solution, being an effective adsorbent which can subsequently be cement stabilized or vitrified.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found in the online version.

REFERENCES


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