Modeling of the adsorption breakthrough behaviors of 4-chlorophenol in a fixed bed of nano graphene oxide adsorbent

Maryam Khashij, Ahmad Moheb, Mohammad Mehralian and Mostafa Gharloghi

ABSTRACT

Continuous fixed-bed column studies were carried out using nano graphene oxide adsorbent for the removal of 4-chlorophenol in a contaminated aquatic solution. The adsorbents were characterized by X-ray diffraction analysis and scanning electron microscope 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 column sorption process was found to perform better at lower influent 4-chlorophenol concentration, lower flow rate and higher bed depth. The highest adsorption capacity (145.2 mg/g) on a 5 mg/l 4-chlorophenol solution was achieved within a flow rate of 1 ml/min and a bed depth of 15 cm. The results of this study have shown that 4-chlorophenol can be effectively adsorbed on nano graphene oxide. Thomas and Yoon–Nelson models were successfully used for predicting breakthrough curves for 4-chlorophenol removal by a fixed bed of nano graphene oxide using different flow rates and bed depths. The breakthrough time and exhaustion time decreased with increasing flow rate, decreasing bed depth and increasing influent 4-chlorophenol concentration.

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

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INTRODUCTION

One of the major challenges of societies in developing countries is the provision of safe water that is free of microbial, physical and chemical pollutants. Distribution of unsafe or non-standard water will have irreparable short-term and, more importantly, long-term effects on the health of consumers in these societies (Al-Rasheed 2005). In order to protect people's health, environment and to make economical use of available water resources, water pollution should be prevented to speed up development (Hamdaoui & Naffrechoux 2009). Chlorophenols are pollutants that need prioritized consideration because of their toxicity and possible accumulation in the environment, and are considered as primary pollutants by the United States Environmental Protection Agency (USEPA) (Xiao *et al.* 2013; Chen *et al.* 2015). The group of phenol compounds, petrochemicals, coal conversion and phenol producing industries are common contaminants in wastewater. Phenols are widely used for the production of commercial products such as phenol resins, which are used as manufacturing materials for automobiles and appliances, and for the production of epoxy resins, adhesives and polyamides in various applications (Johnson *et al.* 1999; Hamdaoui & Naffrechoux 2009). 4-Chlorophenol enters the body as a toxic and corrosive substance through the skin, respiratory and gastrointestinal systems, and may cause irritation in the eyes, skin, throat and nose, as well as coughing and breathing problems (Sharma *et al.* 2013). The recommended maximum contaminant level of phenol in water resources determined by the USEPA is 0.3 mg/l, and for other halogenated phenols such as pentachlorophenol, it is

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0.001 mg/l in drinking water (Johnson *et al.* 1999). To remove phenol from wastewater, different techniques including chemical oxidation, electrocoagulation, solvent extraction and membrane separation were developed (Hamdaoui & Naffrechoux 2009). Among physicochemical processes, adsorption, due to its cheapness and high quality, is an effective process when used in water treatment, particularly in phenol compounds' removal (Wu & Yu 2007; Akar *et al.* 2008). Due to their broad spectrum of adsorption capacity, better selectivity in treatment, rapid uptake and inexpensiveness, the use of nano materials such as graphene oxide is common in water treatment systems (Park & Ruoff 2009). Several researchers have studied the role of graphene oxide on the adsorption of organic compounds by various adsorbents. Tan *et al.* (2009) have explored the adsorption of aqueous phenol compounds onto a fixed-bed column of activated carbon. The effects of 2,4,6-trichlorophenol inlet concentration, feed flow rate and activated carbon bed height on the breakthrough characteristics of the adsorption system were determined. They showed, through ethanol desorption, 96.25% of the adsorption sites could be recovered from the regenerated activated carbon. Lim *et al.* (2013), who studied simultaneous 4-chlorophenol and nitrogen removal in moving bed sequencing batch reactors packed with polyurethane foam cubes of various sizes, also showed that the complete 4-chlorophenol removal within the reaction period could be achieved by increasing the packing volume to 20%. Because of the importance and necessity of removing 4-chlorophenol, the aim of this study was to remove the 4-chlorophenol using granular nano graphene oxide. The effects of design parameters, such as time, influent 4-chlorophenol concentration, flow rate and pH were investigated using a laboratory scale fixed-bed column. The breakthrough curves for the adsorption of 4-chlorophenol were analyzed using Adams–Bohart, Thomas and Yoon–Nelson models.

MATERIAL AND METHODS

Characterization of adsorbent

Scanning electron microscope (SEM) photomicrography of the nano graphene oxide and manganese oxide was taken using an electronic microscope (Philips XI-30 ESEM-FEG Company, USA). X-ray diffraction (XRD) analysis was performed on the nano graphene oxide with a Philips PW171/00, Ireland model.

Preparation of graphene oxide granules

To prepare the adsorbent at a concentration of 20%, 2.5 g of the nano graphene oxide powder (Nanosav Company, Iran) was mixed with 250 ml of water using a mechanical stirrer at 1,200 rpm for 2 hours. After dispersion of the graphene nano powder in the water, sodium silicate (Na_2SiO_3) solution (Merck, Germany) was added to reach 1 liter. Then 200 ml of 65% hydrochloric acid (Merck, Germany) was added to a specific amount of suspension in a container made of polyethylene to form granules (Smirnova & Arlt 2004).

Adsorption tests carried out in batch system

Adsorption of 4-chlorophenol onto nano graphene oxide was studied in a batch reactor. Various concentrations of C_6H_5CLO solution stock (Merck, Germany) (0.1, 0.2, 0.3, 0.4, 0.5, 1, 10, 20, 30 mg/l) were placed in a capped volumetric flask (100 ml), and a fixed amount of nano graphene oxide (2, 4, 6, 8 g) was added into the solution under stirring (180 rpm) at various times (3, 5, 10, 20, 30 minutes). The effects of pH on the adsorption process in the range of 4, 5, 6, 7, 8 and 9 were evaluated, and to adjust the pH, 0.1 normal H_2SO_4 and NaOH were used. Aliquots were withdrawn from the reactor at intervals in the course of the run for spectrophotometric analysis (by HACH DR 5000™ UV-Vis spectrophotometer).

Continuous adsorption tests

The adsorption test was carried out in a continuous mode using nano graphene oxide as the fixed-bed adsorbent. In order to do the experiments, we used a column of glass with 5 cm internal diameter and 40 cm height. It 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 fixed-bed column at constant feeding speed (1, 2, 4 ml/min) by a peristaltic pump (BT100-2J model, Langer Company, USA). The solution was withdrawn from the bottom of the column at selected intervals for spectrophotometric analysis. The adsorption capacity for the nano graphene

oxide in these column studies was calculated by the use of the following equation:

$$q_m = \frac{(t_e - \int_{t_b}^{t_e} f(t)d_t)\ Q\ C_0}{w} \quad (1)$$

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 and $t_e - \int_{t_b}^{t_e} f(t)d_t$ is the area of the breakthrough curve under exhaustion conditions, which can be estimated through integration.

Analysis procedure

The concentration of 4-chlorophenol is determined by the 5530 D standard methods spectrophotometer method (Li 2008). The samples were measured at 500 nm in a UV-visible spectrophotometer. The breakthrough curves for the adsorption of 4-chlorophenol were analyzed using Adams–Bohart, Thomas and Yoon–Nelson models (Baral *et al.* 2009). The equations of the breakthrough curves models are given in Table 1 and the description of parameters is given in Table 2.

Table 1 | Equations of breakthrough curves models

Model	Equation	References
Adams–Bohart	$ln\frac{C_t}{C_0} = K_{AB}C_0t - K_{AB}N_0\frac{Z}{U_0}$	Baral *et al.* (2009)
Yoon–Nelson	$\ln\left(\frac{c_t}{C_0 - c_t}\right) = K_{YN}t - \tau K_{YN}$	Baral *et al.* (2009)
Thomas	$\ln\left(\frac{c_0}{c_t} - 1\right) = \frac{K_{th}q_0m}{Q} - \frac{K_{th}C_0V_{eff}}{Q}$	Baral *et al.* (2009)

Table 2 | Parameters of breakthrough curves model equations

C_0	the influent concentration, mg/l	K_{YN}	the rate constant, min^{-1}
C_t	the effluent concentration, mg/l	τ	the time required for 50% adsorbate breakthrough, min
K_{AB}	the kinetic constant, l/mg min	K_{th}	the Thomas model constant, ml/min mg
t	the total flow time, min	q_0	the adsorption capacity, mg/g
N_0	the saturation concentration, mg/l	m	total amount of metal ion sent to column, g
Z	the bed depth of the fixed-bed column, cm	V_{eff}	the effluent volume, ml
U_0	the superficial velocity, cm/min	Q	the volumetric flow rate, cm^3/min

RESULTS AND DISCUSSION

Characteristics of adsorbent

Figure 1 indicates XRD patterns of the graphene oxide. It was found that pure graphene oxide has the highest peak intensity, at about 25 °, corresponding to the graphene structure (002). This peak disappeared after oxidation and a peak (about 14 °) corresponding to the structure (001) was observed. Oxidation leads to an increase in d-spacing that can be attributed to the presence of functional groups and their exchange properties. Furthermore, the preparation of graphene powder as an adsorbent due to their exchange and surface oxidation, can cause atomic-scale unevenness or peaks, with this reaction being conducted by functional groups on the surface. The micrographs shown in Figure 2 were taken at × 500 magnification to observe nano graphene oxide morphology. With analysis, the mean pore diameter was approximately obtained as 7 nm and also the specific surface area was 514 m^2/g. Also, the image shows that the adsorbent surface is porous and allows for good sorption between 4-chlorophenol and nano graphene oxide.

Batch experiment description

The pH solution plays an important role due to the change in the number of active sites during the adsorption process. As shown in Figure 3, the maximum adsorption of 4-chlorophenol occurred at pH = 7, which is suitable for practical application. Ionization between adsorbent and adsorbate causes a repulsion force and this will lead to a reduction of efficiency at pH > 7 (Zhang *et al.* 2010). An increase in

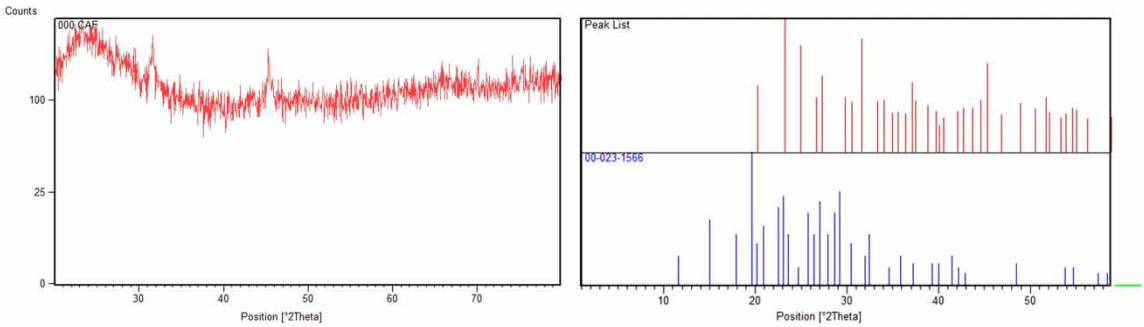

Figure 1 | X-ray diffraction of nano graphene oxide.

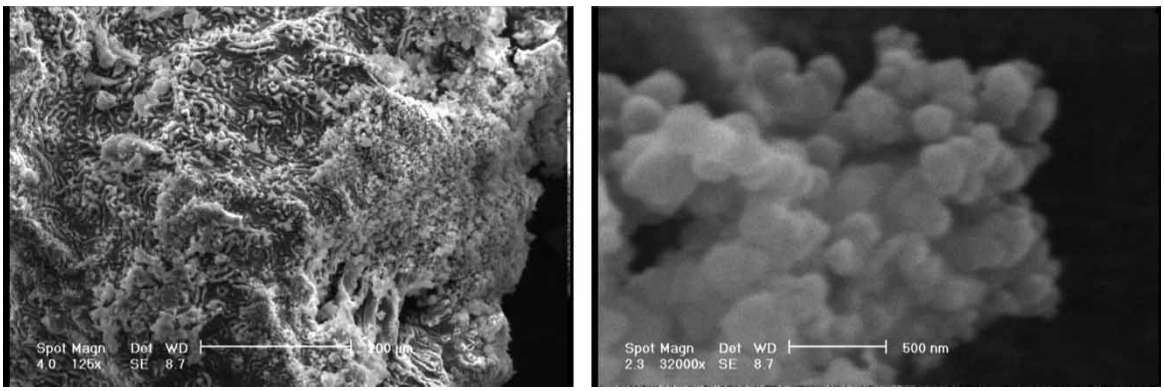

Figure 2 | SEM of nano graphene oxide.

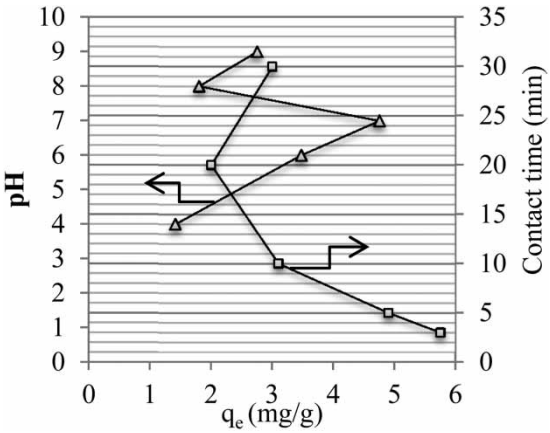

Figure 3 | Effect of pH and contact time on 4-chlorophenol adsorption rate.

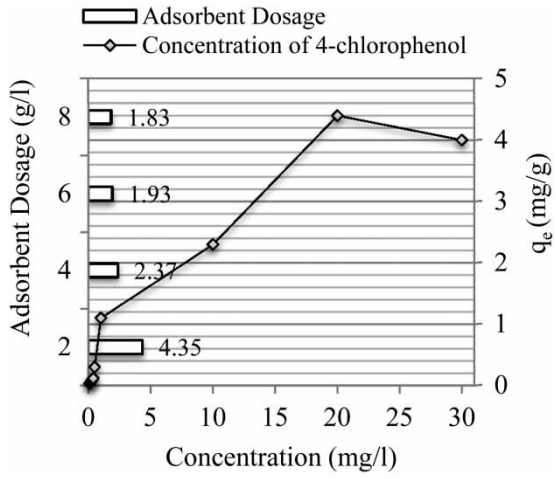

Figure 4 | Effect of dosage and initial concentration of 4-chlorophenol on adsorption.

the amount of adsorbent was associated with an increase in the number of active sites (Figure 4), and subsequently increasing elimination of 4-chlorophenol will follow (Kuleyin 2007). As displayed in Figure 4, the highest removal, with an efficiency of 78%, was obtained for a concentration of 20 mg/l. Gradually, with further increase in concentration, removal performance decreased. This phenomenon can be due to saturation of adsorbent and electrostatic repulsion caused by the positive charge (Huang

et al. 2011). Figure 3 shows that the adsorption of 4-chlorophenol in the first few minutes was fast and declined with time (5.75 to 3 mg/g with 3 to 30 min) of contact. In the early stage, adsorption of the active sites is available; then with the passage of time, they get occupied by molecules of 4-chlorophenol. This result is supported by Huang *et al.* who reported 85% of lead adsorption using nano graphene oxide occurs in the 5 minutes following the start of the reaction (Huang *et al.* 2011).

Effect of flow rate on breakthrough curve

The breakthrough curves at various flow rates (1, 2 and 4 ml/min) of 4-chlorophenol are shown in Figures 5 and 6. Figure 5 shows that the breakthrough occurred significantly faster with the decrease in the flow rate. As the flow rate increased from 1 to 2 ml/min, the exhaust time (corresponding to 98% of influent concentration) was found to be decreasing from 420 to 150 min, and at flow rate of 4 ml/min, 160 min was obtained. This was because at a high rate of influent, 4-chlorophenol did not have enough time to contact with the nano graphene oxide, which resulted in a lower removal of 4-chlorophenol in the column (Kulkarni & Kaware 2014). Indeed this means at a low rate of influent, 4-chlorophenol had more time to contact with the nano graphene oxide, which resulted in a higher removal of 4-chlorophenol in the column (Chen *et al.* 2011). When at higher flow rate, the external film mass resistance at the surface of the adsorbent tends to decrease and the residence

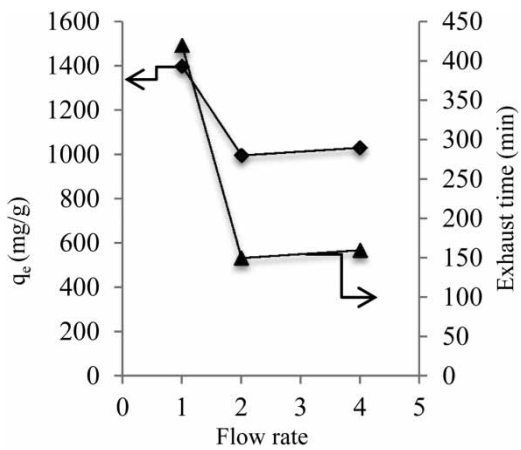

Figure 5 | Effect of flow rate on time to exhaustion and adsorption capacity.

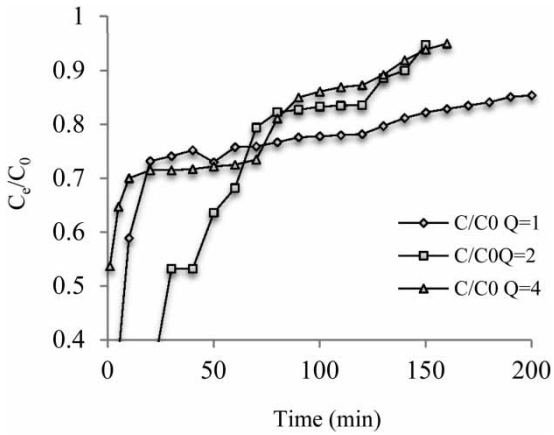

Figure 6 | Effect of flow rate on 4-chlorophenol adsorption.

time decreases, hence the saturation time decreases, and in turn, it gives a lower removal efficiency. A similar tendency has been found by other studies (Baral *et al.* 2009). The insufficient time reduced the bonding capacity of the 4-chlorophenol onto the adsorbent. Then the best adsorption rate was at 1 ml/min with the $q_e = 145.9$ mg/g. Also, according to Figure 3, saturation of the adsorbent will happen at the time of 300 min.

Effect of influent 4-chlorophenol concentration on breakthrough curve

The effect of influent 4-chlorophenol concentration on the breakthrough curves is shown in Figure 7. It is illustrated that the adsorption process reached saturation faster and

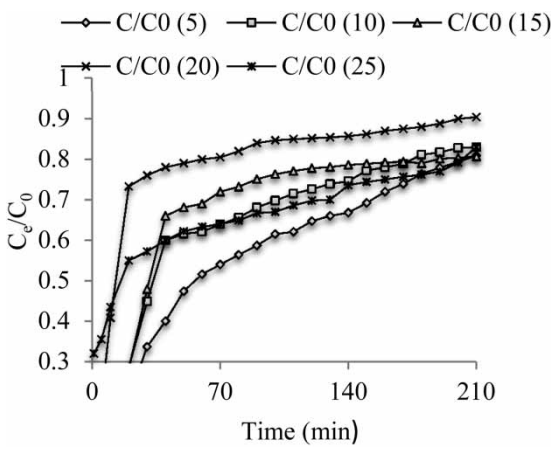

Figure 7 | Effect of initial concentration on time to exhaustion and adsorption capacity.

the breakthrough time decreased with the increase in influent 4-chlorophenol concentration, except at 5 and 15 mg/l. As expected, adsorption capacity decreased with increasing of influent 4-chlorophenol concentration. With increasing initial concentrations of 5 to 25 mg/l, adsorption capacity on the adsorbent increased from 116.84 to 449.98 mg/g, but the removal percentage decreased from 48.34 to 38.7 (see Figures 7 and 8). This can be explained by the fact that at the greater concentration, the gradient caused a faster transport due to an increased diffusion coefficient or mass transfer coefficient (Baral 2007). The maximum adsorption capacity of nano graphene oxide was 145.9 mg/g at 5 mg/l influent 4-chlorophenol concentration, 15 cm bed depth and 1 ml/min flow rate. This may be attributed to high influent 4-chlorophenol concentration providing a higher driving force for the transfer process to overcome the mass transfer resistance (Baral *et al.* 2009). Furthermore, when the concentration rose from 5 to 25 mg/l, saturation time decreased from 400 to 280 minutes for adsorption. Colin *et al.* studied the breakthrough in relation to organic matter. Input initial concentration can be set from 5 to 25 mg/l, and the best breakthrough is 5% of the input initial concentration, which is determined depending on the initial concentration and flow rate (Poole & Poole 2000). In fact, the smallness of adsorbent pore sizes brings down the breakthrough to be considered, which means that the adsorbent is saturated. On the other hand, an increase in concentration (5 to 25 mg/l) causes a reduction in the saturation time (Simpson 2000). In order to remove the 4-chlorophenol using a multilayer adsorption process, Sze and McKay activated carbon columns and used the Homogeneous Surface Diffusion Model for prediction of breakthrough. In these experiments, breakthrough was in the range of 10, 20 and 30% of the initial concentration and the point of exhaustion was equal to the breakthrough point (Sze & McKay 2012).

Effect of different bed depths on breakthrough curve

The breakthrough curves at different bed depths are shown in Figures 9 and 10. It is clear that as the bed depth increased, both the exhaustion time and effluent volume increased. With the increase in bed depth, the effluent volume increased, which might be due to the greater contact time. Figure 9 shows that the removal efficiency of 4-chlorophenol had an increasing trend in the column with the

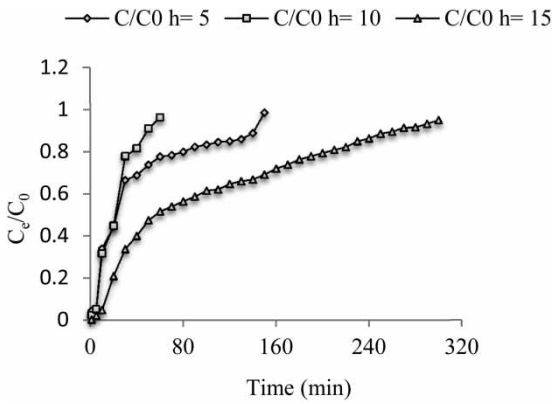

Figure 9 | Effect of bed depth on time to exhaustion and adsorption capacity.

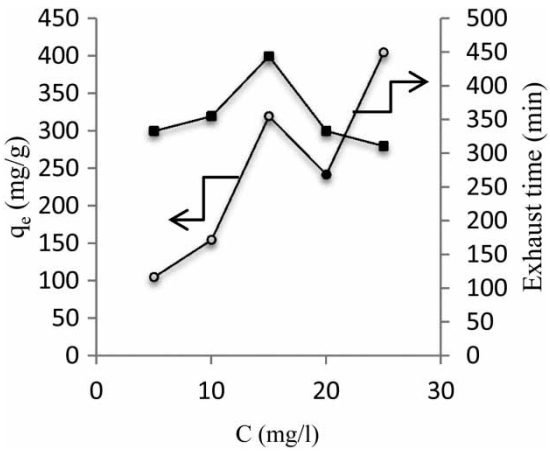

Figure 8 | Effect of initial concentration on 4-chlorophenol adsorption.

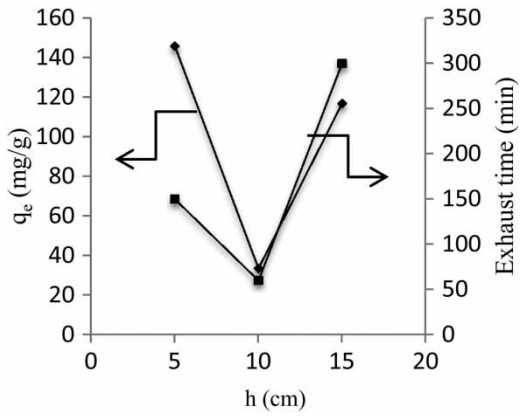

Figure 10 | Effect of bed depth on 4-chlorophenol adsorption.

increase in the mass of the adsorbent. The slope of the breakthrough curve decreased with increasing bed depth, which resulted in a broadened mass transfer zone (Baral 2007). As shown in Figure 10, the bed depth strongly influenced the 4-chlorophenol uptake capacity of 145.9 mg/g, 33.54 mg/g and 116.84 mg/g, which were recorded at 5 cm, 10 cm and 15 cm, respectively. The increase in 4-chlorophenol uptake capacity will occur with the increasing bed depth in the fixed-bed column. This issue may be due to increased adsorbent surface area, providing more binding sites for the column adsorption (Kumar & Chakraborty 2009; Gupta *et al.* 2010).

Breakthrough curve modeling

Successful design of a column adsorption process requires prediction of the breakthrough curve for the effluent (Han *et al.* 2009). Over the years, several simple mathematical models have been developed for describing and analyzing the laboratory-scale column studies for the purpose of industrial applications. So in this study, Adams–Bohart and Thomas–Yoon models were developed to identify the best model for predicting the dynamic behavior of the column. All breakthrough curves were calculated and are presented in Table 3 using linear regression analysis and the correlation coefficients (R^2). It was shown that the Thomas model ($R^2 = 0.724$) provided better fitting compared to the Adams–Bohart model. The Thomas model was suitable for the adsorption process, which indicated that the external and internal diffusions were not the limiting step (Baral *et al.* 2009). The Yoon–Nelson model is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. The R^2 value of 0.72 indicated the validity of the Yoon–Nelson model for the present system. On the basis of surface reaction theory, Bohart and Adams established a fundamental equation which describes the relationship between Ct/C_0 and t in a continuous system. This model assumes that equilibrium is not instantaneous (Cruz-Olivares *et al.* 2013; Sharma & Singh 2013; Wang *et al.* 2015). It is used for describing the initial part of the breakthrough curve (Bohart & Adams 1920). In a comparison of values of R^2, both Thomas and Yoon–Nelson models can be used to predict adsorption performance for adsorption of 4-chlorophenol in a fixed-bed column.

Table 3 | Parameters of models under different conditions using linear regression analysis

R^2

Parameter	Value	Adams–Bohart	Thomas	Yoon–Nelson
Q (ml/min)	1	0.221	0.612	0.616
C_0 (mg/l)	5	0.421	0.724	0.724
h (cm)	15	0.421	0.724	0.724

CONCLUSION

This study identified nano graphene oxide as an effective adsorbent for the removal of 4-chlorophenol from aqueous solution. Uptake of 4-chlorophenol through a fixed-bed column was dependent on the bed depth, influent 4-chlorophenol concentration and flow rate. The adsorption capacity increased with increasing bed depth, but decreased with an increase in 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. The Thomas and Yoon–Nelson models were both successfully used to predict the breakthrough curves, indicating that they were very suitable for nano graphene oxide column design.

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