

# Biosorption of 4-chlorophenol by dried anaerobic digested sludge: artificial neural network modeling, equilibrium isotherm, and kinetic study

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Received: 4 June 2015/Revised: 1 March 2016/Accepted: 28 September 2016/Published online: 8 October 2016  
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**Abstract** In this study, dried anaerobic digested sludge (DADS) was utilized to remove 4-chlorophenol (4-CP) from aqueous solutions. Batch biosorption experiments were carried out to investigate the effects of physico-chemical parameters such as pH, contact time, biosorbent dosage, and initial concentration. Artificial neural network (ANN) was then used to predict the removal efficiency of the process. The comparison between predicted and experimental results provided a high degree of determination coefficient ( $R^2 = 0.98$ ), indicating that the model could predict the biosorption efficiency with reasonable accuracy. Biosorption data were successfully described by the Freundlich isotherm and pseudofirst-order model. The Weber–Morris kinetic model indicated that intraparticle diffusion was not the only rate-controlling step, and other mechanisms may be involved in the biosorption process. The optimum pH was detected to be 3 for DADS. By increasing contact time and biosorbent dosage, the removal efficiency of 4-CP increased. Also, a decreasing trend was observed when initial concentrations were increased. The findings suggested that the results predicted by ANN are very close to the experimental values, and DADS as an

available adsorbent can efficiently remove 4-CP from aqueous solutions.

**Keywords** Biosorption · 4-chlorophenol · Digested sludge · Kinetics · Isotherms

## Introduction

The fate of phenolic compounds in the environment is of great concern since they are very toxic and carcinogenic to humans (Aksu 2005; Aksu and Yener 2001). The main symptoms of long-term intake of excessive phenolic compounds concentration include loss of appetite, headache, rapid fatigue, and severe chronic insomnia (Denizli et al. 2005). Pesticide, pharmaceutical, wood-preserving chemicals, and cellulose pulp manufacturing industries are the primary sources of phenolic derivatives (Monsalvo et al. 2012). Different physical, chemical, and biological processes such as activated carbon adsorption, chemical oxidation, aerobic/anaerobic biological degradation, coagulation, solvent extraction, and liquid membrane permeation have been employed for the removal of chlorinated aromatics from wastewater (Aksu 2005; Bayramoglu et al. 2009; Demirak et al. 2011). Problems such as high cost, low efficiency, and generation of toxic by-products are limiting factors for the wide application of some of these remediation technologies (Aksu 2005; Nadavala et al. 2009). Among various physicochemical processes, adsorption technology has been extensively studied in recent years. However, due to economic limitations, there is a growing interest in the use of low-cost and abundant adsorbents. Biosorbents are considered as promising materials for the removal of chlorophenols. The special surface properties of biosorbents enable them to adsorb

Editorial responsibility: M. Abbaspour.

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different kinds of pollutants from solutions (Aksu 2005; Bayramoglu et al. 2009). The biosorption term refers to a number of metabolism-independent processes (e.g., physical and chemical adsorption, electrostatic interaction, ion exchange, complexation, chelation, and micro-precipitation) that occurs naturally in certain biomass which allows it to passively concentrate and bind contaminants onto its cellular structure (Lin and Juang 2009). The mechanism of biosorption is complex due to its nonlinear behavior and interaction of variables. Biosorption experiments are usually carried out in a way that one factor is used and analyzed, whereas the others remained constant. This procedure is called one variable at a time (OVAT) (Kumar et al. 2012; Wang et al. 2002). Commonly used models employed to describe equilibrium and kinetic studies such as Langmuir, Freundlich, and pseudosecond order may be insufficient in determining the connection between the factors and evaluating their impact on the biosorption process. To overcome this problem, multivariate statistical techniques have been used. Among these techniques, artificial neural network (ANN) is the most commonly used method in the biosorption literature (Giri et al. 2011). Neural networks are composed of simple elements operating in parallel. These elements are inspired by biological nervous systems which can be trained to perform a particular function by adjusting the values of connections (weights) between elements. ANN is a powerful data-modeling tool able to capture and represent complex nonlinear relationships between independent variables and responses of the system (Witek-Krowiak et al. 2014). Besides, with regard to aforementioned sentences, ANN as a mathematical tool cannot identify mechanisms of adsorption, whereas commonly used models can specify rate-controlling steps in kinetic studies and adsorption intensity or capacity in equilibrium studies. In the present study, dried anaerobic digested sludge (DADS) was selected as an abundant biosorbent. The objectives were (1) to investigate the sorption of 4-CP on DADS, (2) to investigate the effect of various parameters on the biosorption process, (3) to develop an ANN model, and (4) to study kinetic and equilibrium models of the biosorption process.

## Materials and methods

### Preparation of chemicals

All chemicals used in the biosorption experiments were supplied with a high grade of purity (99%). A stock solution of 1000 mg/L 4-CP was prepared by dissolving  $C_6H_5ClO$  (M: 128.56 g/mol,  $pK_a$ : 9.41, Merck) in deionized water. All working concentrations were obtained by

diluting the stock solution with deionized water, and the pH was adjusted to the desired values by adding 1 M HCl or NaOH.

### Preparation of DADS

The sludge was obtained from the anaerobic digester of the south municipal wastewater treatment plant (Isfahan, Iran). Digested sludge was dried at 105 °C to constant weight and then ground and sieved to obtain particle size <0.35 mm. Protonated sludge biomass was prepared by adding 50 g of the raw sludge biomass into 1 L of HCl solution (0.1 mol/L) and stirring the mixture at 55 rpm for 30 min at  $25 \pm 1$  °C. Thereafter, the acid-treated biomass was washed with deionized water several times until the pH did not change, and then it was dried at 105 °C. Elemental composition test (Elementar, Vario Max, Germany) has been done to specify elements of digested sludge which resulted in 27.49 % Carbon, 5.01 % Hydrogen, 10.39 % Nitrogen, and 7.8 % Oxygen.

### Experimental procedures

Batch experiments were performed in 250-mL conical flasks by mixing a desired amount of the sludge biomass with 100 mL of a 4-CP solution of known concentration. The effects of initial pH values, initial 4-CP concentration, and DADS dosage as well as contact time on the removal efficiency of 4-CP were studied as summarized in Table 1. In all experiments, the flasks were agitated on a shaker at 250 rpm at room temperature ( $25 \pm 1$  °C). After the adsorption period, the DADS was separated using filter papers (Whatman, No. 2, 8  $\mu$ m). The residual concentration of 4-CP was analyzed by measuring the absorbance of the red complex of 4-CP at 500 nm using a spectrophotometer (Milton Roy, 21d). The adsorption capacity at equilibrium,  $q$  (mg/g), was calculated as follows Eq. (1):

$$q = \frac{[(C_0 - C_e) \cdot V]}{m} \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium concentration of 4-CP (mg/L),  $V$  is the solution volume (L), and  $m$  is the mass of DADS (g).

### Artificial neural network

The MATLAB R (2012) neural network toolbox was used to simulate the biosorption process. A three-layer feed-forward network with a linear transfer function (purlin) at the output layer and a tangent sigmoid transfer function (tansig) at the hidden layer was developed to predict and simulate the sludge adsorption capacity for 4-CP removal. The Levenberg–Marquardt back-propagation algorithm

**Table 1** Experimental parameters for 4-CP removal

Tests	Biomass concentration (g/L)	Initial (4-CP) concentration (mg/L)	Initial pH	Time (min)
Biomass dosage	5–30	5–30	3	240
Initial concentration	5–30	5–30	3	240
pH	5–10	5–10	2–11	90
Time	20	20–40	3	5–360

(LMA) was used to train the network as the best algorithm (Ahmad et al. 2014; Ghaedi et al. 2014). Four neurons in the input layer [pH, concentration (mg/L), DADS dosage (g), and contact time (min)], 1–20 neurons in the hidden layer, and one neuron (removal percentage) in the output layer were used to design the network. The data were randomly divided into three groups (70 % for training, 15 % for validation, and 15 % for testing) and normalized in the 0.1–0.9 range to avoid the scaling effect of the parameter values (Giri et al. 2011; Yang et al. 2011). Therefore, all the data ( $X_i$ ) were converted to the normalized values ( $A_i$ ) as follows Eq. (2):

$$A_i = 0.8 \left( \frac{X_i - \min(X_i)}{\max(X_i) - \min(X_i)} \right) + 0.1 \tag{2}$$

where  $\min(X_i)$  and  $\max(X_i)$  are the extreme values of the variable  $X_i$ . The performance of the network was evaluated using the mean squared error (MSE) and the coefficient of determination ( $R^2$ ), which can be defined as follows (Eqs. 3 and 4):

$$MSE = \frac{1}{N} \sum_{L=1}^N (|y_{prd,l} - y_{exp,l}|)^2 \tag{3}$$

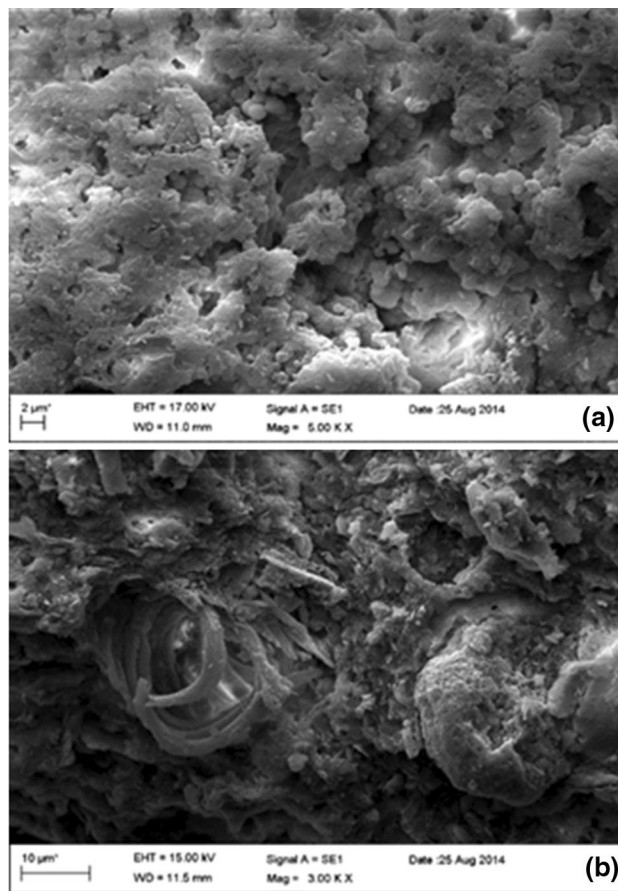
$$R^2 = 1 - \frac{\sum_{L=1}^N (|y_{prd,l} - y_{exp,l}|)}{\sum_{L=1}^N (y_{prd,l} - y_m)} \tag{4}$$

where  $y_{prd,l}$  is the value predicted by the ANN model,  $y_{exp,l}$  is the experimental value,  $N$  is the number of data, and  $y_m$  is the average of the experimental values (Giri et al. 2011; Bingöl et al. 2012; Yang et al. 2011).

## Results and discussion

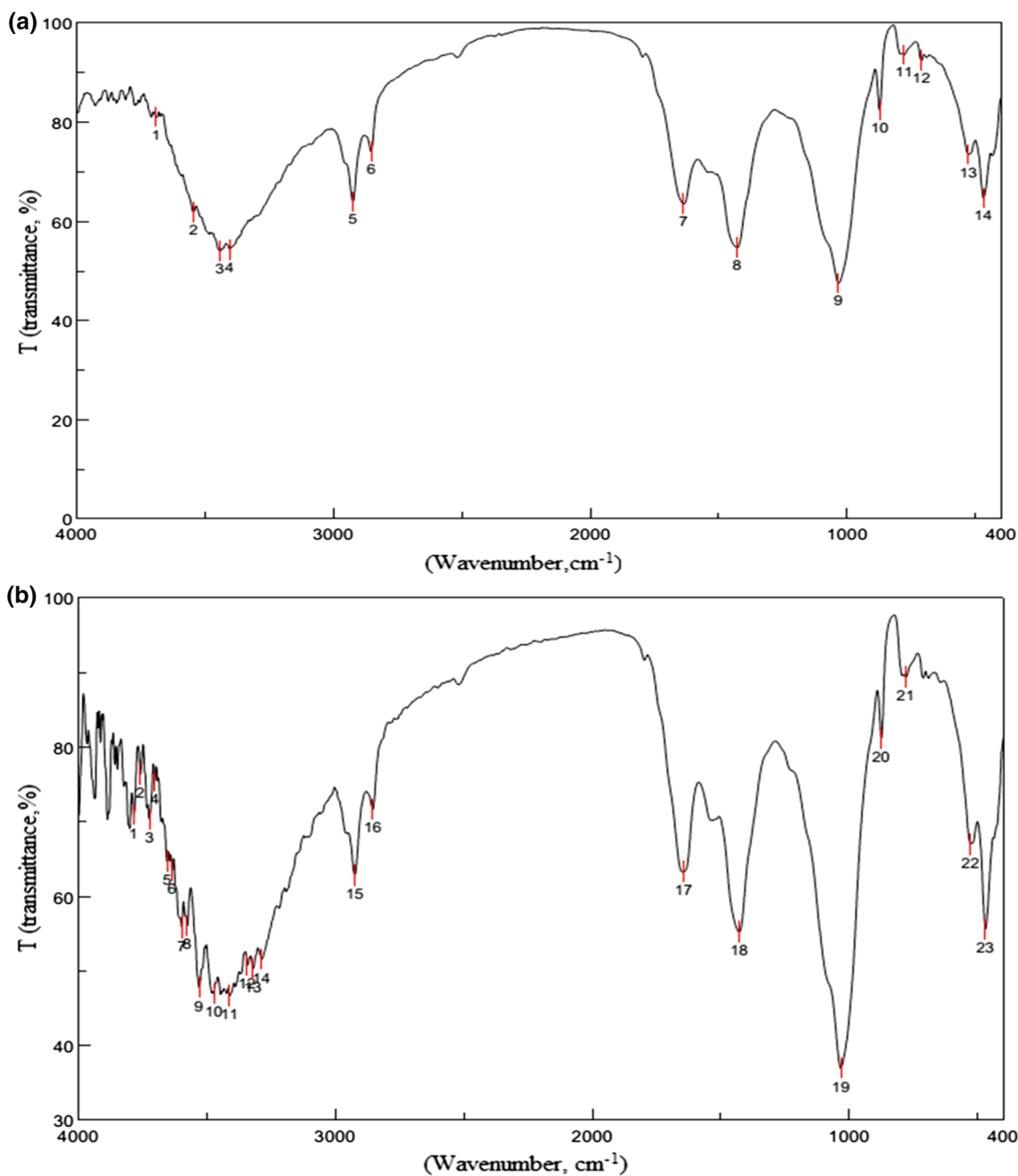
### Characterization of the adsorbent

Scanning electron microscopy (SEM) is widely used to study the morphological features and surface characteristics of biosorbent materials. The spatial properties of biosorbent surface influences initial stages of adsorption process.



**Fig. 1** SEM micrographs of DADS at a 5 k and b 3 k × magnification

In the present study, the SEM images in Fig. 1a, b show the surface texture and morphology of the DADS at two different magnifications, evidencing a structure with high porosity constituted by very small aggregated components. The Fourier transform infrared (FTIR) spectral analysis is important to identify the different functional groups on the biosorbent that are responsible for the biosorption of 4-CP. The FTIR spectra are shown in Fig. 2a, b in the overall range of 4000–400  $\text{cm}^{-1}$  for DADS before and after biosorption of 4-CP, respectively. The spectra display a number of adsorption peaks. The peaks at 470 and 528  $\text{cm}^{-1}$  can be assigned to O–P–O bending vibrations. The sharp adsorption peak at 875  $\text{cm}^{-1}$  is attributed to the C–Cl stretching vibration. The intense peak at 1032  $\text{cm}^{-1}$  is assigned to the stretching vibration of P–O bonds. The peaks at 1428 and 1643  $\text{cm}^{-1}$  are related to aromatic C–C bond vibrations. The two peaks at 2854 and 2923  $\text{cm}^{-1}$  are attributed to stretching vibrations of the aliphatic C–H bond. The small peaks at 3287, 3318, and 3342  $\text{cm}^{-1}$  are related to vibrations of aromatic C–H bonds. The peaks at



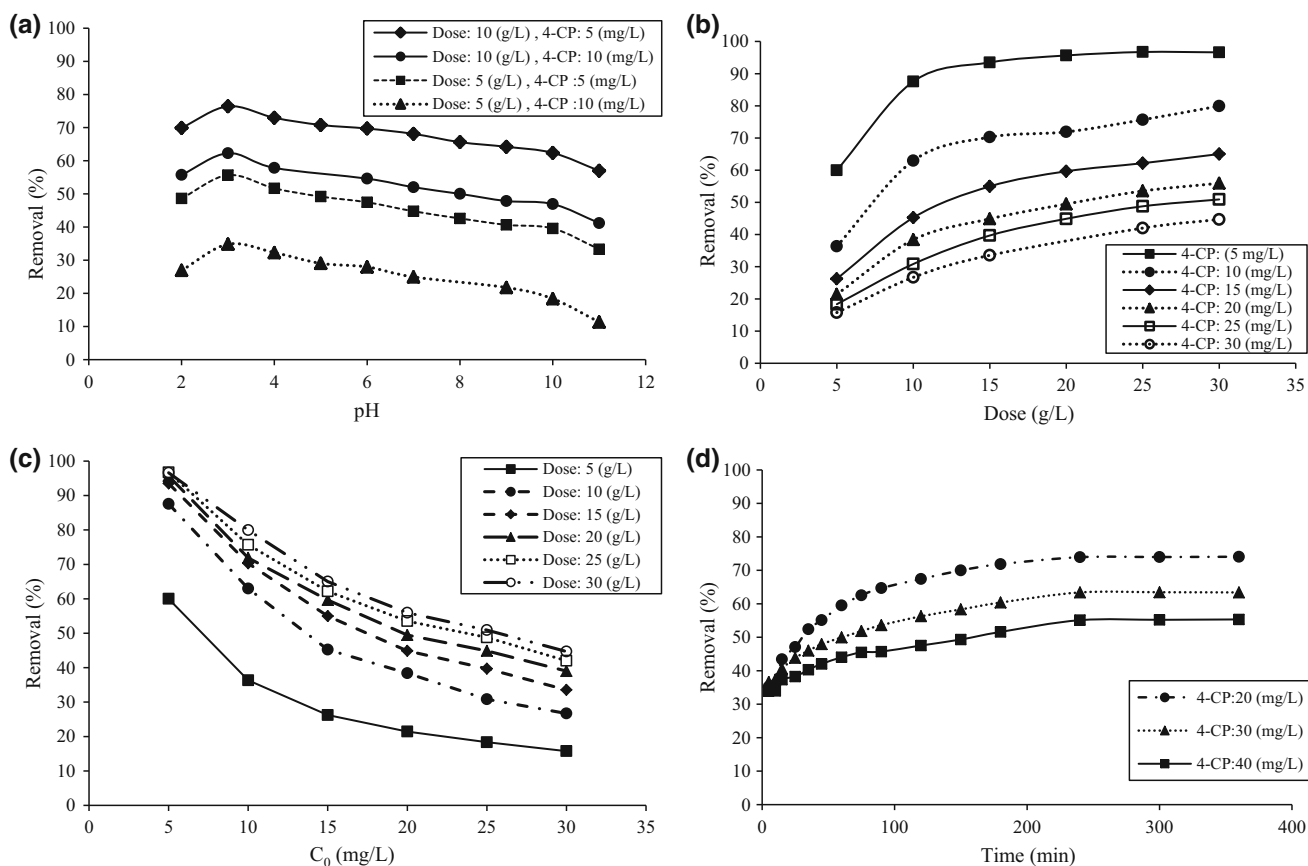
**Fig. 2** FTIR spectra of DADS **a** noninteracted DADS, **b** 4-CP interacted DADS

3411, 3473, and 3529  $\text{cm}^{-1}$  are assigned to the O–H bond of the sludge, and the peaks at 3575 and 3597 are attributed to the O–H bond of the aromatic ring. By the investigation and comparison of two FTIR spectra, it can be stated that O–P–O, C–CL, and O–H are three important functional bonds which are involved in the process of biosorption.

### Effect of the pH

The initial pH of the adsorption medium is one of the most important parameters affecting the adsorption process (Kamble et al. 2008) because pH primarily affects the surface properties of the biosorbent and the degree of ionization of phenolic compounds (Wang et al. 2002; Gao





**Fig. 3** Effect of **a** initial pH, **b** biosorbent dosage, **c** initial concentration of 4-CP, **d** contact time on sorption capacity of 4-CP by dried anaerobic sludge

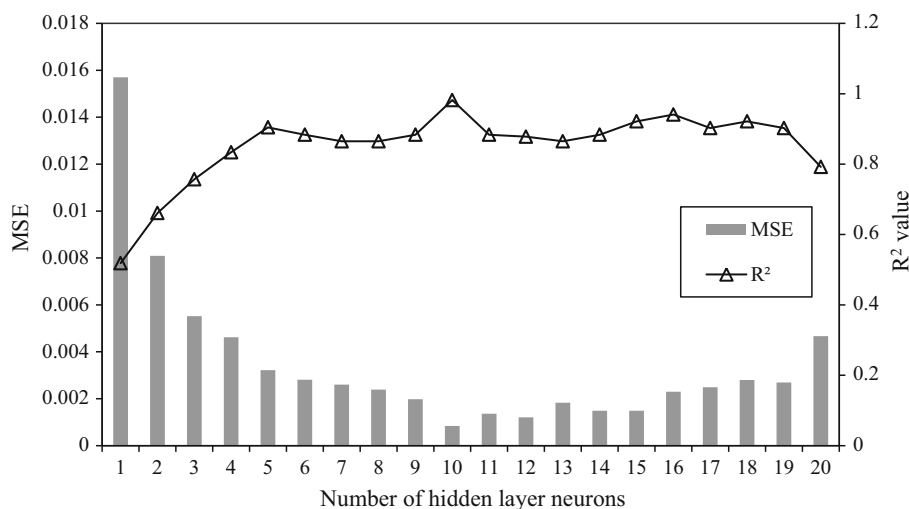
and Wang 2007; Wu and Yu 2006). A wide range of pH values (2–11) was used to examine the effect of the pH on the sorption capacity. Maximum removal of 4-CP was obtained at pH 3 (Fig. 3a). Increase or decrease of the pH from this optimum value resulted in the reduction of the biosorption capacity of 4-CP. The overall surface charge on the cells became positive when the pH was lower than the isoelectric point of the biomass. Since the isoelectric point of anaerobic sludge is usually between pH 1 and 3, this led to interactions between the aromatic ring of 4-CP activated by the  $\text{OH}^-$  and  $\text{Cl}^-$  and the groups on the biosorbent surface. As the pH increases, the overall surface charge on the cells becomes negative, and the biosorption between negatively charged phenolic compounds and binding sites of the biomass surface decreases (Wang et al. 2002; Gao and Wang 2007; Jianlong et al. 2000). The degree of ionization is another determining factor. When the pH is not more than one unit above the pKa values of 4-CP (9.41), nondissociated forms activated by  $\text{OH}^-$  and  $\text{Cl}^-$  dominated

the overall sorption of chlorinated phenols on organic sorbent. When the pH is greater than the pKa values of 4-CP, negatively charged ionized forms dominate in the solution (Gao and Wang 2007; Wu and Yu 2006). Optimum pH (i.e., 3.0) is well in agreement with previous studies carried out on granular anaerobic sludge (Gao and Wang 2007; Kennedy et al. 1992).

### DADS dosage

Different DADS dosages from 5 to 30 g/L were used to investigate the effect of DADS concentration on the sorption capacity. Maximum sorption capacity of 0.94 mg/g for 30 mg/L of 4-CP was observed when 5 g/L of DADS was used. With increasing biomass dosage from 5 to 30 g/L, a decreasing trend in sorption capacity was observed. The drop in adsorption capacity was due to the binding sites of the adsorbent remained unsaturated during the adsorption process. In Fig. 3b, it is apparent that the removal of 4-CP

**Fig. 4** Effect of number of hidden layer neurons on mean square error and regression coefficient values



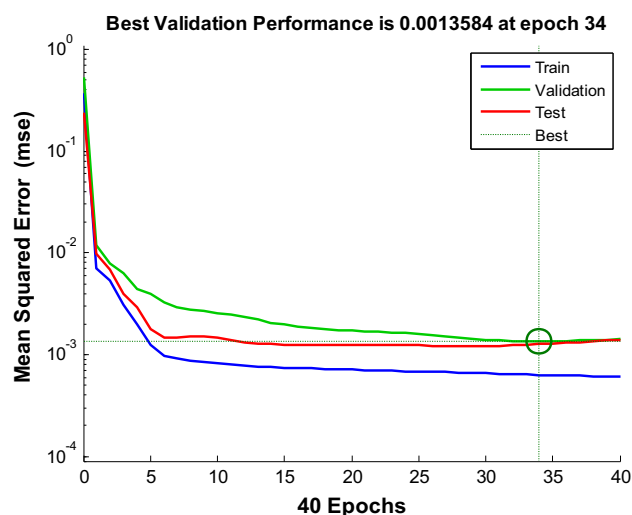
increases rapidly with the increase in the dosage of adsorbent due to greater availability of the binding sites on the biosorbent (Kumar and Min 2011). The maximum removal percent was 96.6 % with 5 mg/L 4-CP and 30 g/L of DADS. Adsorption studies carried out using different kinds of biosorbent showed a similar trend with change in biomass concentration (Gao and Wang 2007; Aksu et al. 1999).

#### Initial concentration

The initial concentration of 4-CP provides an important driving force to overcome all the mass transfer resistance of the adsorbate between the aqueous and solid phase interface and therefore increases the rate at which adsorbate molecules pass from the bulk solution to the adsorbent surface. Moreover, the high initial concentration of 4-CP would enhance the availability of 4-CP molecules increasing the chance of collision with biosorbent surfaces (Wu and Yu 2006; Paul et al. 2012). As shown in Fig. 3c, the removal percentage decreased with increasing initial 4-CP concentration from 5 to 30 mg/L. Similar results were observed by other researchers by changing the adsorbate concentration (Kamble et al. 2008).

#### Contact time

The relationship between contact time and 4-CP sorption on DADS (20 g/L) at different initial 4-CP concentrations (20, 30 and 40 mg/L) is presented in Fig. 3d. Biosorption rate of 4-CP was very high at the beginning of the process, and saturation level was gradually reached within 4 h. Adsorption rate had a marked upward trend due to the greater availability of functional groups in the initial stage



**Fig. 5** Neural network performance

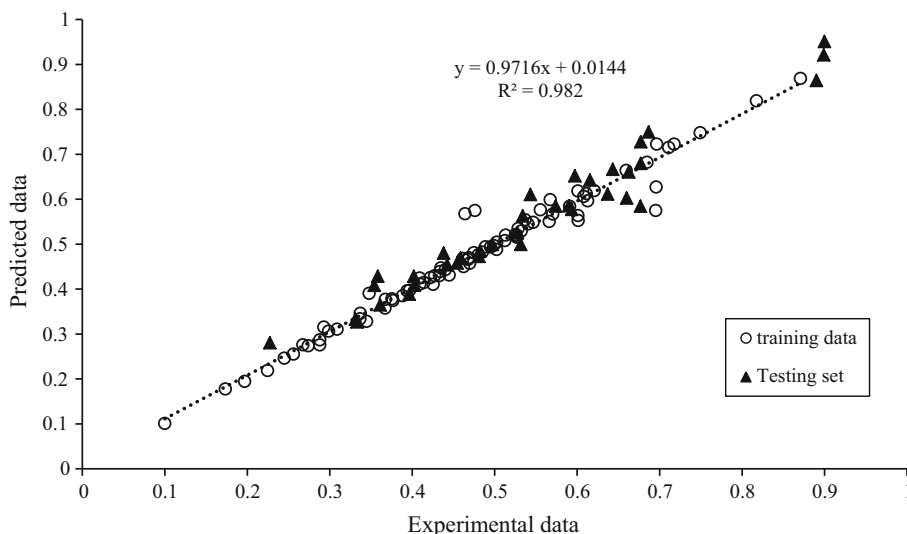
of the process. After a while, all functional bonds are saturated with 4-CP molecules resulting in equilibrium mode.

#### Neural network analysis

Since the number of hidden layer neurons is an important factor in the network training, the number of neurons in the hidden layer should be optimized (Khataee and Kasiri 2010). Unfortunately, there is no specific method for determining the optimal number of hidden layer neurons, and in most of the cases, trial and error approach has been used to select the number of neurons (Witek-Krowiak et al. 2014). In this study, different numbers of neurons in the range of 1–20 were used in the hidden layer. According to Fig. 4, the optimum number of neurons in the hidden layer



**Fig. 6** Linear regression analysis between experimental data and ANN model predicted values for training and test data



is equal to 10, with the minimum value of MSE being  $8.41 \times 10^{-4}$ . Therefore, a three-layer feed-forward back-propagation neural network (4:10:1) was used to model the adsorption process. The neural network performance is shown in Fig. 5. Regression analysis was used to find the relation between experimental values with outputs (predicted values) (Fig. 6). The plot in Fig. 6 consists of two lines, the dashed line represents the perfect fit ( $y = x$ ; i.e., predicted data = experimental data), and the solid line represents the best fit of the experimental and predicted data ( $y = 0.9716 x + 0.0144$ ) with acceptable determination coefficient  $R^2$  (0.98).

**Isotherm study**

Analysis of the isotherm data is important to develop an equation that accurately represents the results. Two

classical adsorption models such as Langmuir and Freundlich isotherms have been most frequently employed (Wu and Yu 2006). In this study, these two models were used to describe the relationship between the amount of 4-CP adsorbed and its equilibrium concentration in solution at different dosages. The equation of these models and their linear forms are shown in Table 2. All the constant of these two models were estimated by linear regression, and the results are summarized in Table 3.

**Langmuir**

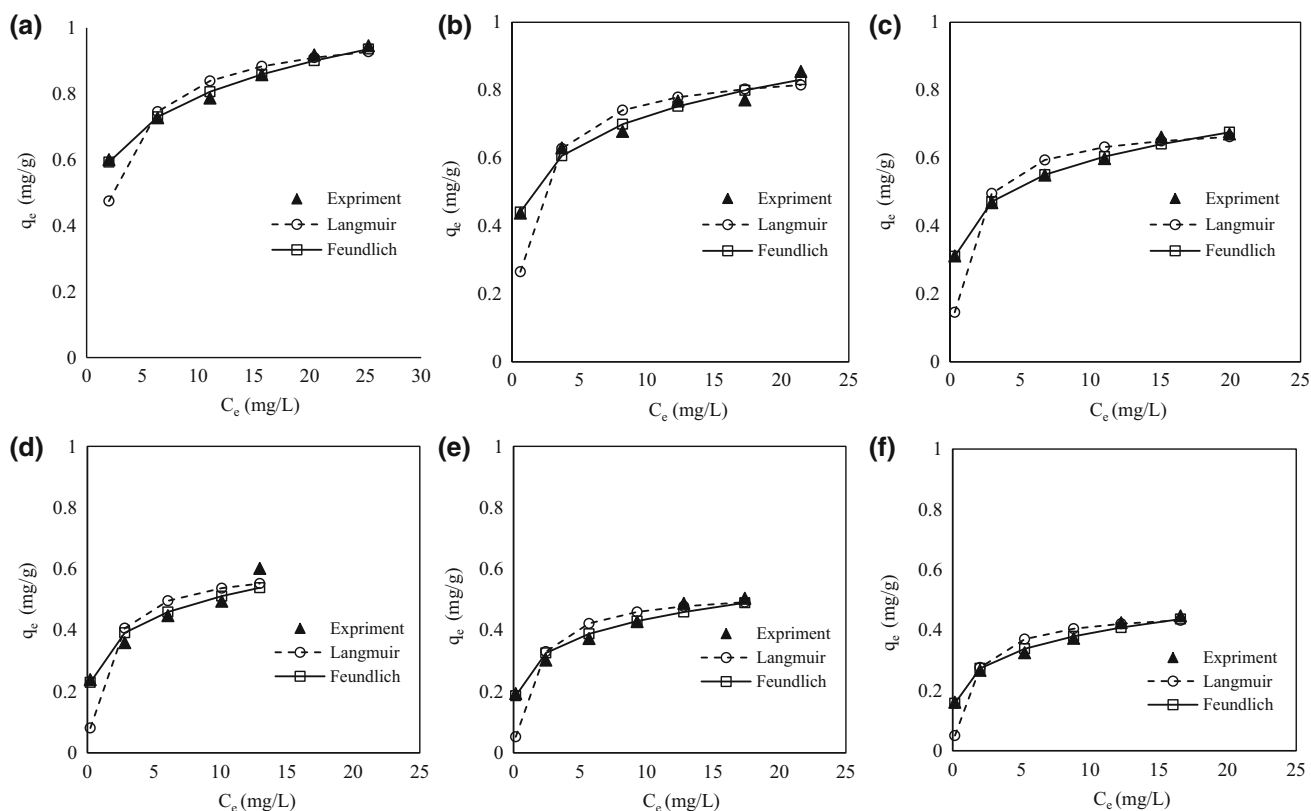
The Langmuir theory assumes a homogenous adsorption (Nadavala et al. 2009). That is, when a 4-CP molecule occupies a binding site, no further adsorption can occur at that site. In this equation, [Table 2]  $C_e$  is the 4-CP equilibrium concentration in the solution (mg/L).  $q_e$  is the equilibrium 4-CP uptake on the biosorbent (mg/g),  $Q_m$  is the maximum biosorption capacity (mg/g), and  $K_L$  is Langmuir constant (L/mg). The Langmuir model has a high  $R^2$  value, indicating that 4-CP covers the biosorbent surface. The suitability of the adsorbent for the adsorbate can be expressed using the Hall separation factor ( $R_L$ , dimensionless), which can be calculated as follows Eq. (5):

**Table 2** Nonlinear and linear forms of isotherm models

Isotherms	Equation	Liner form
Freundlich	$q_e = K_f C_e^{1/n}$	$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e$
Langmuir	$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \left(\frac{1}{K_L Q_m}\right) + \left(\frac{1}{Q_m}\right) C_e$

**Table 3** Isotherm constant parameters and determination coefficients calculated for adsorption of 4-CP

Isotherm	Parameters	Unit	Dose (g/L)					
			5	10	15	20	25	30
Freundlich	1/n	–	0.1804	0.1791	0.1898	0.208	0.207	0.222
	$K_f$	$\text{mg}^{1-(1/n)} \text{L}^{(1/n)} \text{g}^{-1}$	0.523	0.480	0.3840	0.316	0.271	0.234
	$R^2$	–	0.9916	0.982	0.997	0.953	0.98	0.993
Langmuir	$Q_m$	mg/g	1.01	0.869	0.704	0.613	0.534	0.469
	$K_L$	L/mg	0.443	0.705	0.802	0.701	0.665	0.712
	$R^2$	–	0.99	0.99	0.99	0.96	0.984	0.984



**Fig. 7** Comparison between experimental data, Langmuir, and Freundlich output, **a** 5 g/L, **b** 10 g/L, **c** 15 g/L, **d** 20 g/L, **e** 25 g/L, **f** 30 g/L

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

where  $K_L$  and  $C_0$  are the Langmuir constant (L/mg) and initial 4-CP concentration (mg/L) and  $R_L$  indicates the nature of the adsorption. The  $R_L$  parameter is considered as a more reliable indicator of the adsorption. The value of  $R_L$  indicates the type of the isotherm to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ) (Demirak et al. 2011; Kumar et al. 2012). All the  $R_L$  values of 4-CP adsorption are laid between the range of 0.423–0.702, indicating that the biosorption process was favorable.

### Freundlich

The Freundlich isotherm assumes a heterogeneous surface with nonuniform heat of adsorption. In this equation [Table 2],  $K_f$  and  $n$  are indicators of the adsorption capacity and adsorption intensity of the sorbent, respectively (Wu and Yu 2006). The plot of  $\log(q_e)$  versus  $\log(C_e)$  gave a straight line with slope  $1/n$  and intercept  $\log(K_f)$ . The slope

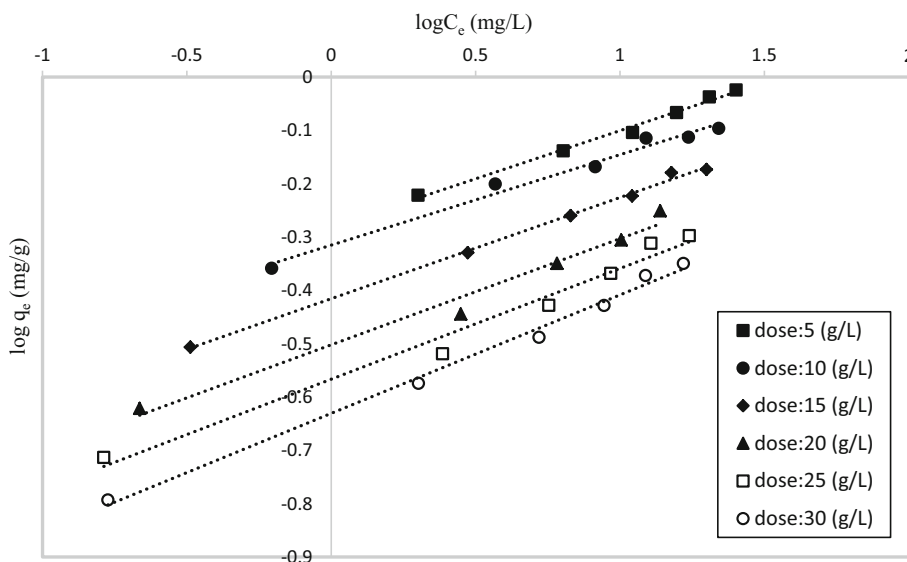
$1/n$  ranging between 0 and 1 is a measure of the adsorption intensity or surface heterogeneity, becoming more heterogeneous as its values get closer to zero; furthermore, the coefficient of  $1/n$  is less than 1 which means chemisorption mechanism is dominant in adsorption (Nadavala et al. 2009). Figure 7 shows that the Freundlich model exhibited a slightly better fit to the biosorption data than the Langmuir model in the dosage range studied. Moreover, earlier studies have indicated that the adsorption equilibrium of organic pollutants such as phenols and chlorophenols followed the Freundlich isotherm better than the Langmuir one (Kennedy et al. 1992; Benoit et al. 1998; Antizar-Ladislao and Galil 2004). Figure 8 shows the linear form of the Freundlich model for the biosorption of 4-CP.

### Biosorption kinetic study

Adsorption kinetics was investigated to understand the sorption dynamics of the 4-CP molecules on the DADS. Pseudofirst-order and pseudosecond-order models and *Elovich* equation were used to study the kinetics of the adsorption process. In addition, intraparticle diffusion



**Fig. 8** Freundlich sorption isotherm on biosorbent



**Table 4** Nonlinear and linear forms of kinetic models

Kinetic	Equation	Liner form
Pseudofirst order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$
Pseudosecond order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t$
Elovich	$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t)$	$q_e = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln t$
Intraparticle diffusion	–	$q_t = K_{dir}t^{0.5} + C$

model was tested to determine the diffusion mechanism of the adsorption system. Table 4 shows the nonlinear and linear forms of these kinetic equations. All the constants of these models were estimated using linear regression, and the results are listed in Table 5. The determination coefficient of the kinetic models based on reduction, either pseudofirst order or pseudosecond order, is close to each other. Hence, it is difficult to evaluate which model better describes the kinetic of biosorption. To have a more clear comparison, the three kinetic models mentioned above were further evaluated according to their  $r^2$  value, which is defined as follows Eq. (6):

$$r^2 = \frac{\sum (q_{t(Pre)} - \overline{q_{t(Exp)}})^2}{\sum (q_{t(Pre)} - \overline{q_{t(Exp)}})^2 + \sum (q_{t(Pre)} - q_{t(Exp)})^2} \quad (6)$$

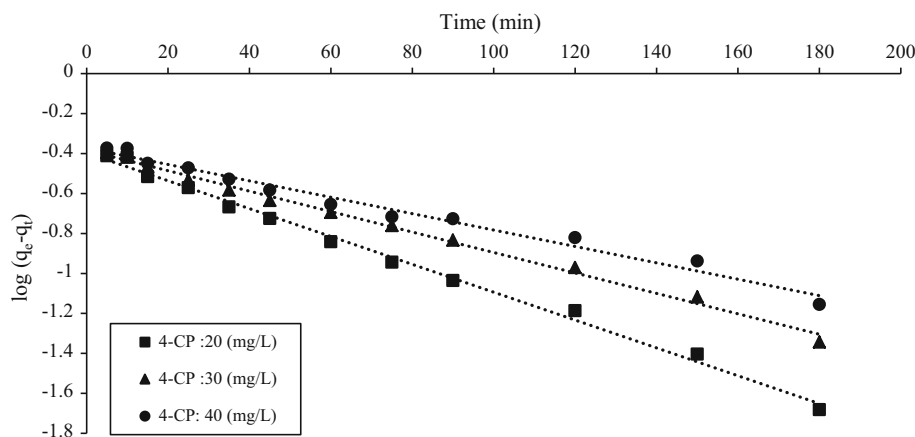
where  $q_{t(Pre)}$  and  $q_{t(Exp)}$  are the calculated adsorption capacity at time  $t$  of the kinetic model and experiments, respectively. The higher the value of  $r^2$ , the better the fit of

**Table 5** Kinetic constant parameters and determination coefficients for 4-CP adsorption

Kinetic	Parameter	4-CP concentration (mg/L)		
		20	30	40
Pseudofirst order	$k_1$	0.016	0.011	0.008
	$q_e$ (cal)	0.728	0.947	1.098
	$q_e$ (exp)	0.718	0.905	1.032
	$R^2$	0.99	0.99	0.98
	$r^2$	0.98	0.99	0.99
	Pseudosecond order	$k_2$	0.101	0.108
$q_e$ (cal)		0.755	0.926	1.041
$q_e$ (exp)		0.718	0.905	1.032
$R^2$		0.99	0.99	0.99
$r^2$		0.91	0.89	0.92
Elovich		$\alpha$	0.52	1.25
	$\beta$	2.56	1.31	0.88
	$R^2$	0.98	0.95	0.97
	$r^2$	0.518	0.536	0.532
Intraparticle diffusion	$K_{dir}$	0.034	0.032	0.031
	$C$	0.297	0.485	0.612
	$R^2$	0.95	0.98	0.98

the data. All the determination coefficient values are listed in Table 5. The results suggested that the first-order adsorption mechanism was predominant, indicating that, in the presence of a large excess of 4-CP, the rate of sorption largely depends on the capacity of the biosorbent, which in turn depends on the number of available sites for binding or ion

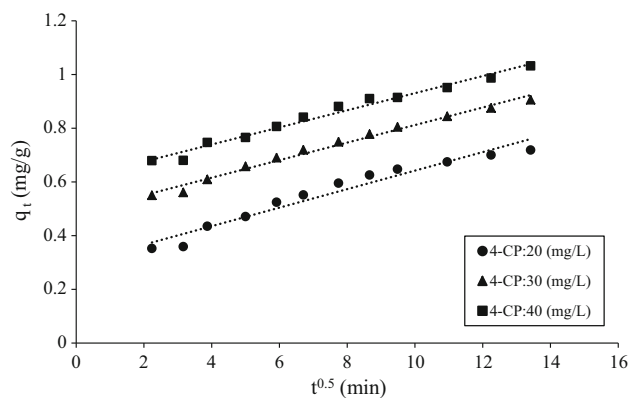
**Fig. 9** Pseudofirst-order model for biosorption of 4-CP



exchange. Therefore, the rate-limiting step for the sorption is the biosorbent capacity (Paul et al. 2012; Namasivayam and Kavitha 2003). Figure 9 shows the linear form of the pseudofirst-order model for the biosorption of 4-CP.

#### Intraparticle diffusion (Webber–Morris model)

The intraparticle diffusion model was tested to identify the diffusion mechanisms and rate-limiting steps in the adsorption process. The theory of this model was proposed by Weber and Morris (Table 4). Based on this model, it is an empirical functional relationship common to most adsorption processes, in which the uptake varies almost proportionally with  $t^{0.5}$  rather than with the contact time ( $t$ ) (Namasivayam and Kavitha 2003). In this model,  $q_t$  (mg/g) is the amount adsorbed at time  $t$  (min),  $K_{dif}$  ( $\text{mg g}^{-1} \text{min}^{1/2}$ ) is the intraparticle diffusion rate constant which is affected by particle diameter and temperature, and  $C$  is the value of the intercept, which gives an estimation of the boundary layer thickness, i.e., the larger is the intercept, the greater is the boundary effect. The values of  $K_{dif}$  and  $C$  were obtained by plotting  $q_t$  versus the square root of time and are listed in Table 5. If the adsorption process follows the intraparticle diffusion model, then  $q_t$  versus  $t^{0.5}$  is linear, while if the plot passes through the origin, the intraparticle diffusion is the sole rate-limiting step. Otherwise, other mechanisms along with intraparticle diffusion are also involved (Nadavala et al. 2009; Wu and Yu 2006). As shown in Fig. 10, the plots present a linear relationship, but did not pass through the origin, suggesting that the intraparticle diffusion was not the only rate-controlling step and other rate-limiting steps may be involved and affect the adsorption of 4-CP.



**Fig. 10** Intraparticle diffusion plot for adsorption of 4-CP on biosorbent

#### Conclusion

It might be indeed true to state that sludge produced during wastewater treatment process is a towering issue in solid waste management. The present study indicates that dried anaerobic digested sludge was efficient as a biosorbent for the removal of 4-chlorophenol from aqueous solutions. The adsorption capacity was affected by operating parameters like contact time, 4-CP concentration, pH, and amount of DADS. An increasing trend was observed in removal efficiency by increasing contact time and biosorbent dosage and also, by increasing 4-CP concentration, the removal efficiency was reduced. The biosorbent had better efficiency in acidic condition, and the optimum pH was detected to be 3. Maximum biosorption capacity calculated from Langmuir isotherm was 1.01 mg/g. The adsorption equilibrium followed the Freundlich isotherm, and the kinetics of adsorption fitted well with the pseudofirst-order



model. The Weber-Morris model suggested that some other mechanisms in addition to intraparticle diffusion may affect biosorption process. The 4-CP/biosorbent interactions and participation of oxygen-containing functional bands were confirmed by FTIR, and heterogeneous, smooth, and porous structures were observed by SEM technique. A three-layer feed-forward network with 10 neurons in hidden layer was developed to predict the removal efficiency. The present work suggests that ANN predicted results are very close to the experimental values. The average mean square error is  $8.41 \times 10^{-4}$ , which is sufficient to have an error within  $\pm 1.0\%$ . A high degree of correlation ( $R^2 = 0.98$ ) between actual and predicted removal efficiency was observed for data set. Since the ANN can contribute this field of research in two distinct extents. First, in real situations, researchers may encounter different amount of parameters affecting biosorption process. In this case, the ANN can estimate outputs with a reasonable accuracy without any limitation for the range of parameters. Second, there is no need for further experiments to estimate outputs which leads to save time and costs.

**Acknowledgments** The authors would like to thank the environmental research center at Isfahan University of Medical Sciences. This work was supported by Ferdowsi University of Mashhad Grant No. 28749/3.

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