Adsorption of cefixime from aqueous solutions using modified hardened paste of Portland cement by perlite; optimization by Taguchi method
Mohammad Hossein Rasoulifard, Soghra Khanmohammadi and Azam Heidari

ABSTRACT
In the present study, we have used a simple and cost-effective removal technique by a commercially available Fe-Al-SiO₂ containing complex material (hardened paste of Portland cement (HPPC)). The adsorbing performance of HPPC and modified HPPC with perlite for removal of cefixime from aqueous solutions was investigated comparatively by using batch adsorption studies. HPPC has been selected because of the main advantages such as high efficiency, simple separation of sludge, low-cost and abundant availability. A Taguchi orthogonal array experimental design with an OA₁₆ (4⁵) matrix was employed to optimize the affecting factors of adsorbate concentration, adsorbent dosage, type of adsorbent, contact time and pH. On the basis of equilibrium adsorption data, Langmuir, Freundlich and Temkin adsorption isotherm models were also confirmed. The results showed that HPPC and modified HPPC were both efficient adsorbents for cefixime removal.

Key words | adsorption, cefixime, equilibrium isotherm, Portland cement, Taguchi method

INTRODUCTION
Portland cement is a low-cost fine-powdered building material usually consisting of four main components such as tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetracalcium aluminoferrite (Kundu et al. 2004; Kagne et al. 2008). The widespread availability of limestone, shales, and other naturally occurring materials used in Portland cement makes it one of the lowest cost construction materials widely used over the last century throughout the world. Moreover it has been used as an adsorbent in wastewater treatment because of its high number of heterogeneous pores (Kundu et al. 2004; Kagne et al. 2008; Rasoulifard et al. 2010; Saadatjou et al. 2011). In wastewater treatment, various methods are utilized to remove pollutants, including chemical precipitation, ion exchange, electrochemical precipitation, reduction, adsorption, solvent extraction, membrane separation, reverse osmosis and biosorption. Among these methods, adsorption has been found to be an efficient and economic process to remove any pollutants, and to control the bio-chemical oxygen demand (Dogan & Alkan 2005). Different adsorbents such as fly ash and lignite (Mall et al. 2007; Gürses et al. 2014), clay (Seki et al. 2015), sawdust (Keränen et al. 2015), barley husk (Robinson et al. 2002), activated carbon (Ayranci & Hoda 2005), soya cake (Daneshvar et al. 2002) and perlite (Dogan & Alkan 2003; Ghassabzadeh et al. 2010; Akkaya 2013) have been found in the literature. Also using hardened cement for removal of different pollutants such as arsenic (Kundu et al. 2004), fluoride (Kagne et al. 2008), Basic Yellow 2 (Rasoulifard et al. 2010) and Basic Red 46 (Saadatjou et al. 2011) has also been reported recently.

In our previous work (Rasoulifard et al. 2010; Saadatjou et al. 2011), we used hardened paste of Portland cement (HPPC) for removal of some organic dyes such as Basic Yellow 2 and Basic Red 46 from aqueous solutions. However, in this study we have used perlite for modification of HPPC. Perlite is a naturally occurring, dense, glassy volcanic rhyolitic rock and can be expanded to 20 times its original volume when heated rapidly at 800–1,200 °C. It is generally chemically inert and has a pH of approximately 7. It is very cheap and easily available in local markets. So it could be a viable candidate as an economical adsorbent for removal of pollutants (Ghassabzadeh et al. 2010). The main advantages of this adsorbent are simple separation of sludge, low cost
and abundant availability (Kundu et al. 2004; Kagne et al. 2005). Also, the generated sludge could be used in soil-cement bricks for civil construction (Rodrigues & Holanda 2015).

Cefixime is a broad-spectrum cephalosporin antibiotic that was approved by the US Food and Drug Administration (FDA) in 1997. It is commonly used to treat bacterial infections of the ear, urinary tract, and upper respiratory tract. There are only a few studies investigating the occurrence of antibiotics and antibiotic-resistant bacteria in the environment from different sources (hospital effluents, aquaculture and so on) (Duong et al. 2008; Hoa et al. 2011). Recently concentrations of up to several milligrams per litre have been found in effluents in some Asian countries for single compounds (Larsson et al. 2011). Hue et al. (2014) reported the concentrations of cefixime residue measured in samples collected in an effluent system of a pharmaceutical plant in Hanoi, Vietnam (Hue et al. 2014).

The purpose of this work is to study the removal of cefixime (Table 1) onto modified HPPC, and a Taguchi experimental method was used to determine optimal adsorption conditions.

**MATERIALS AND METHODS**

**Materials**

Portland cement and perlite used for this study were obtained from local commercial sources. Powdered and granular activated carbon were also purchased from local commercial sources. Cefixime was purchased from Farabi pharmaceutical Company (Iran) and a solution was prepared by dissolving in distilled water. Sodium hydroxide and hydrochloric acid for pH adjusting were purchased from Merck (Germany).

**Preparation of adsorbent**

In the first step, 500 g of commercially available Portland cement was taken into a vessel and the required amount of distilled water added to make a slurry. The slurry was then kept for 7 days under ambient condition for hardening/drying. After complete air drying, the hardened solid paste of cement was broken into small granules of 3 mm size. The granules were kept immersed under water for 3 days and dried in an oven at 100–110 °C for 5 h. The modified HPPC samples with 10%, 15% and 20% w/w perlite were also prepared following this method. The point of zero charge (Mustafa et al. 2002) was determined to be 2.0 for HPPC and 2.5 for modified HPPC with perlite.

Scanning electron microscopy (SEM) images of HPPC were taken by a VEGA//TESCAN (Czech Republic), and Fourier transform infrared (FTIR) spectra were measured with a Jasco6300 FTIR spectrometer.

**Batch adsorption studies**

The working solutions were prepared day by day by diluting of the stock standard solution of cefixime. All the

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Physicochemical properties of cefixime</th>
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<tbody>
<tr>
<td>Color</td>
<td>Light yellow powder</td>
</tr>
<tr>
<td>CAS number</td>
<td>125110-14-7</td>
</tr>
<tr>
<td>Chemical name</td>
<td>7-[2-(2-Amino-4-thiazolyl)glyoxylamido]-8-oxo-3-vinyl-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic acid, 7-beta-[O-(carboxymethyl)oxime] trihydrate</td>
</tr>
<tr>
<td>Chemical structure</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$</td>
<td>300 nm</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C$<em>{16}$H$</em>{13}$N$<em>{2}$O$</em>{7}$S$<em>{2}$3H$</em>{2}$O</td>
</tr>
<tr>
<td>Molecular weight (g mol$^{-1}$)</td>
<td>507.50</td>
</tr>
<tr>
<td>pH range</td>
<td>2.6–4.1</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>~100–200 mg L$^{-1}$</td>
</tr>
</tbody>
</table>
Experiments were performed using a batch equilibrium method by placing definite amounts of adsorbent granules in a glass bottle containing different concentrations of cefixime solutions, which were shaken using a Heidolph MR 3001 K magnetic stirrer at 200 rpm. The pH of the solution was adjusted to the desired level with 0.1 M NaOH or HCl solutions using a Metrohm 780/Swiss pH meter. The residual concentration of cefixime was determined at λ_{max} = 300 nm using a Shimadzu UV 160 spectrophotometer. The efficiency of removal (R) was expressed as the percentage ratio of removed cefixime concentration to that of the initial concentration (Equation (1)), where C_{0} is the initial concentration of cefixime (mg L^{-1}) and C_{t} the concentration of cefixime at time t.

\[ R = \frac{C_{0} - C_{t}}{C_{0}} \times 100 \] (1)

The isotherms of adsorption were determined on the basis of batch analysis as follows. Definite amounts of optimized adsorbent granules were allowed to equilibrate with 50 mL of 25, 50, 75 and 100 mg L^{-1} cefixime solutions. In order to reach complete equilibrium, all solutions stayed for about 3 days under experimental conditions. The amount of cefixime adsorbed per mass unit of optimized adsorbent in equilibrium conditions, q_{e}, was calculated using Equation (2),

\[ q_{e} = \frac{V}{m} \frac{C_{0} - C_{e}}{C_{0}} \] (2)

where V is the volume of solution in litres, C_{0} and C_{e} are the initial and equilibrium concentrations of cefixime solutions, respectively, and m is the mass of optimized adsorbent in grams. Also kinetic parameters for the adsorption process were studied under optimized conditions. The residual concentration values of cefixime were measured in 30 min intervals.

Orthogonal array and experimental factors for experimental design

Herein, a Taguchi experimental design method was used to optimize the adsorption conditions. For this purpose, the main parameters and their levels that influenced the removal efficiency of cefixime were selected and are shown in Table 2. The orthogonal array of L_{16} type was used and is represented later in this paper in Table 3; ‘L’ and ‘16’ mean Latin square and the number of experiments, respectively (Kim et al. 2004).

Repeated batch operations

In order to study repeated batch operations, 2 g of HPPC with 15% perlite was added to a cefixime solution of 25 mg L^{-1} with shaking at 200 rpm. Then the residual concentration of cefixime was measured spectrophotometrically at 1 h intervals. This procedure was repeated five times in
45 h and each batch lasted for 9 h and adsorbent granules were washed after the end of each batch.

RESULTS AND DISCUSSION

Adsorbent characterization

The FTIR and SEM patterns of HPPC before treatment with cefixime are shown in Figures 1 and 2, respectively. The FTIR studies (Figure 1) showed the appearance of bands at 3,644, 3,421, 1,416, 1,083, 875, 857, 713 and 540 cm\(^{-1}\). The absorption band at 3,644 cm\(^{-1}\) was due to the stretching vibrations of \(\nu_1\) (OH) of Ca(OH)\(_2\) which was formed as silicate phases in the dissolved cement (Zhou et al. 2015). The wide band in the region 3,100–3,500 cm\(^{-1}\) may be due to –OH or H\(_2\)O stretching vibrations. The bands at 1,416, 875 and 713 cm\(^{-1}\) are attributed to \(\nu_3\), \(\nu_2\) and \(\nu_4\) CO\(_3^2-\), respectively. The presence of CaCO\(_3\) is attributed to atmospheric CO\(_2\) absorbed during the air drying of sample (Trezza 2007). The wide band that is observed in the region 900–1,100 cm\(^{-1}\) is due to overlapping of stretching vibrations of \(\nu_3\) Si-O and \(\nu_3\) SO\(_4^{2-}\). The peaks at 540 and 857 cm\(^{-1}\) may be due to the Si-O and Al-O stretching vibrations of the silicate and aluminate groups (Trezza 2007; Zhou et al. 2012).

In order to evaluate the surface of HPPC before adsorption, scanning electron microscopy for untreated HPPC was utilized. From Figure 2, it is clear that the SEM images of HPPC before treatment of cefixime show irregular shapes with agglomerations of small particles adhered on bigger particles. The adsorption of cefixime on HPPC may be improved due to the many pores with heterogeneous composition of CaO, SiO\(_2\), Al\(_2\)O\(_3\) and Fe\(_2\)O\(_3\).

Determination of optimal conditions using Taguchi method

A Taguchi method was used to identify the optimal conditions and to select the parameters having the most influence on cefixime removal. The structure of Taguchi’s L16 design and the results of measurement are shown in Table 3. In the Taguchi method, the terms ‘signal’ and ‘noise’ represent the desirable and undesirable values for the output characteristic, respectively. Taguchi method uses the signal/noise (S/N) ratio to measure the quality characteristic deviating from the desired value. The S/N ratios are different according to the type of characteristic. In the case that bigger characteristics are better, the S/N ratio is defined as factor (Kim et al. 2004)

\[
S/N = -10 \log \left( \frac{1}{y_1^2} + \frac{1}{y_2^2} + \frac{1}{y_3^2} + \ldots + \frac{1}{y_n^2} \right) \tag{3}
\]

where \(y_i\) is the characteristic property and \(n\) is the replication number of the experiment. The unit of S/N ratio is decibel (dB) which is frequently used in communication. Table 3 shows the S/N ratio for removal of the solution containing cefixime calculated using Equation (3). The mean S/N ratio for each level of the parameters was summarized as S/N response, which is shown in Table 4.
Figure 3 shows the S/N response graph for removal of cefixime from solution. Therefore, the optimum condition is A1, B3, C3, D4 and E1. In other words, based on the S/N ratio, the optimal parameters (conditions) for cefixime removal are A (concentration) at level 1 (25 mg L\(^{-1}\)), B (adsorbent dosage) at level 3 (2 g), C (type of adsorbent) at level 3 (HPPC with 15% perlite), D (time) at level 4 (9 h) and E (pH) at level 1 (2.5). In order to conduct an analysis of the relative importance of each factor more systematically, an analysis of variance (ANOVA) was applied to the data. The main objective of ANOVA is to extract

<table>
<thead>
<tr>
<th>Parameters</th>
<th>S/N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Level 1</td>
</tr>
<tr>
<td>A Cefixime conc.</td>
<td>35.58</td>
</tr>
<tr>
<td>(mg L(^{-1}))</td>
<td></td>
</tr>
<tr>
<td>B Adsorbent dose</td>
<td>32.92</td>
</tr>
<tr>
<td>C Kind of adsorbent</td>
<td>34.85</td>
</tr>
<tr>
<td>D Time (h)</td>
<td>34.36</td>
</tr>
<tr>
<td>E pH</td>
<td>35.03</td>
</tr>
</tbody>
</table>
from the results how much variation each factor causes relative to the total variation observed in the result. From the results of ANOVA in Table 5, the initial concentration of cefixime had the largest variance. The adsorbent dosage showed the second largest variance. Consequently, it can be concluded that the most influential factor was in the order of the concentration of cefixime. On the other hand, the degree of freedom (DOF) for each factor was 3 and total DOF was 15, so the DOF for error term was 0, and finally the variance for the error term ($V_e$), obtained by calculating error sum of squares and dividing by error
degrees of freedom, could not be calculated. Henceforth, it was impossible to calculate the F-ratio, defined as the variance of each factor dividing by $V_e$. In order to eliminate the zero DOF from the error term, a pooled ANOVA was applied. The process of ignoring a factor once it is deemed insignificant is called pooling.

**Effect of repeated uses**

Our results showed that HPPC with 15% perlite had the best effect in comparison with the other modified HPPCs. So the effect of repeated uses of HPPC with 15% perlite was investigated. The experiment was performed for 45 h in batches and each batch lasted for 9 h to investigate the successive reuse of modified HPPC for the adsorption of cefixime. During five repeated runs, HPPC with 15% perlite showed the same removal rate. Figure 4 shows the results of repeated batch removal of cefixime. The results indicate that optimized adsorbents retain excellent reusability and persistence in repetitive removal operations.

**Adsorption isotherms of cefixime**

Equilibrium adsorption isotherms play an important role in the predictive modelling used for the analysis and design of adsorption systems. These models are simple, give a good description of experimental behaviour in a large range of operating conditions and are characterized by a limited number of adjustable parameters. The isotherm models Langmuir, Freundlich and Temkin were attempted in the present study. In the Langmuir theory, the basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent. This equation can be written as follows (Benefield et al. 1982; Alley 2000):

$$q_e = \frac{q_{max} b C_e}{1 + b C_e}$$

(4)

where $q_e$ is the amount of cefixime adsorbed on adsorbent at equilibrium, $C_e$ is the equilibrium concentration of cefixime solution, $b$ is an equilibrium constant and $q_{max}$ is the maximum adsorption capacity. The linear form of Equation (4) is:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{b q_{max}}$$

(5)

The essential characteristic of the Langmuir isotherm can be expressed by the dimensionless constant called the equilibrium parameter, $R_L$, defined by Equation (6):

$$R_L = \frac{1}{1 + b C_0}$$

(6)

where $b$ is the Langmuir constant and $C_0$ is the initial cefixime concentration (mg L$^{-1}$); $R_L$ values indicate the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The $R_L$, $b$ and $q_{max}$ values for the adsorption of cefixime on optimized adsorbent are shown in Table 6.

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. The Freundlich isotherm is expressed by Benefield et al. (1982) as:

$$q_e = K_f C_e^{1/n}$$

(7)

where $q_e$ is the amount of cefixime adsorbed onto the adsorbent at equilibrium conditions (mg g$^{-1}$), $C_e$ is the equilibrium concentration of cefixime solution (mg L$^{-1}$), $K_f$ is adsorption capacity at unit concentration and $1/n$ is adsorption intensity. The values of $K$ and $1/n$, which can be calculated from the plot of ln $q_e$ versus ln $C_e$, are shown in Table 6. Values of
1/n indicate the type of isotherm to be irreversible (1/n = 0), favorable (0 < 1/n < 1) or unfavorable (1/n > 1) (Alley 2000).

Equation (7) can be rearranged to a linear form:

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e
\]  
(8)

The Temkin isotherm assumes that: (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate–adsorbate interactions; and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The Temkin isotherm is represented by the following equation:

\[
q_e = \frac{RT}{b} \ln(K_T C_e)
\]  
(9)

Equation (9) can be expressed in its linear form as:

\[
q_e = B_1 \ln K_T + B_1 \ln C_e
\]  
(10)

where

\[
B_1 = \frac{RT}{b}
\]  
(11)

The adsorption data can be analyzed according to Equation (10). A plot of \(q_e\) versus \(\ln C_e\) enables the determination of the isotherm constant \(K_T\) and \(B_1\). \(K_T\) is the equilibrium binding constant (L mg\(^{-1}\)) corresponding to the maximum binding energy and constant \(B_1\) is related to the heat of adsorption (J mol\(^{-1}\)) (Mall et al. 2007). \(R\) and \(T\) are the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and temperature (K) respectively. The predicted isotherm constants for the cefixime and their corresponding \(r^2\) values by the linear regression method are shown in Table 6.

**Comparison of optimized adsorbent and activated carbon**

In order to make a comparative study for adsorption of cefixime with optimized adsorbent and activated carbon (powdered and granular) in a fixed amount of adsorbent (\(m = 2\) g), the initial concentrations of cefixime (\(C_0 = 25\) mg L\(^{-1}\)), initial pH (pHi) (6.7) and temperature (\(T = 25\) C) were kept the same in all adsorption experiments. This is shown in Figure 5. Also, it may be concluded that optimized adsorbent was the same as granular activated carbon because of the high silica content and high heterogeneous pores where adsorption could occur.

**Kinetic study**

Adsorption of cefixime in optimized conditions on HPPC and modified HPPC was performed by the procedures described above. Absorbance data of cefixime were obtained in 30-minute intervals and were converted into concentration data using the corresponding calibration plots. Then, the concentrations were plotted as a function of time. Initial concentration in all experiments was adjusted to be the same (25 mg L\(^{-1}\)) in order to compare their adsorption behaviors easily. Some probable kinetic models were applied to fit them to experimental data. These models include:

- intraparticle diffusion, which can be formulated as:
  
  \[
  q_t = k_i t^{1/2}
  \]  
  (12)

- first order model which can be formulated as:
  
  \[
  \ln C_t - \ln C_0 = -k_1 t
  \]  
  (13)

- and second order model which can be formulated as:
  
  \[
  \frac{1}{C_t} - \frac{1}{C_0} = k_2 t
  \]  
  (14)

where \(q_t\) is the amount of cefixime adsorbed at any time, \(C_0\) the initial concentration of cefixime, \(C_t\) the concentration of cefixime at any time, \(t\) is the time and \(k_i, k_1\) and \(k_2\) are the rate constants for diffusion, first order and second order models, respectively.

The value of \(q_t\) is obtained from \(C_0\) and \(C_t\) values by the following equation:

\[
q_t = \frac{(C_0 - C_t) V}{m}
\]  
(15)
Table 7 | The first order, second order and intraparticle diffusion kinetic constants for the adsorption of cefxime on modified HPPC with perlite

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>First order</th>
<th>Second order</th>
<th>Intraparticle diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$</td>
<td>$r^2$</td>
<td>$k_2$</td>
</tr>
<tr>
<td>HPPC</td>
<td>0.003</td>
<td>0.992</td>
<td>0.00</td>
</tr>
<tr>
<td>10% perlite</td>
<td>0.002</td>
<td>0.971</td>
<td>0.00</td>
</tr>
<tr>
<td>15% perlite</td>
<td>0.002</td>
<td>0.974</td>
<td>0.00</td>
</tr>
<tr>
<td>20% perlite</td>
<td>0.002</td>
<td>0.983</td>
<td>0.00</td>
</tr>
</tbody>
</table>

$[k_2] = \text{min}^{-1}; [k_3] = \text{min}^{-1} \cdot \text{M}^{-1}; [k_i] = \text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2}.$

where $V$ (L) is the volume of cefxime solution and $m$ (g) is the mass of the adsorbent. The applicability of the three models was studied by drawing a linear plot of $q_t$ versus $t^{1/2}$ for intraparticle diffusion, In $C$ versus $t$ for first order and $1/C$ versus $t$ for second order models. The rate constants $k_i$, $k_1$ and $k_2$ obtained from the slopes of the corresponding linear plots are given in Table 7. When the regression coefficients of the three models are compared for each adsorbent, it can be seen that all of them in first order and intraparticle diffusion models are greater than 0.97. So, it is very difficult to predict a certain kinetic model to fit the adsorption data of all kinds of HPPC adsorbents (Ayranci & Hoda 2005).

**CONCLUSION**

HPPC, a low-cost building material, has considerable potential for the removal of pollutants from aqueous solution. One of the major advantages of using HPPC for cefxime removal over other chemical treatment methods is that it does not produce any chemical sludge. The Taguchi method results in this work show that the removal was dependent on adsorbent dosage and initial cefxime concentration. The experimental data generated from batch adsorption experiments fitted well into the linearly transformed Freundlich and Temkin isotherms. Also in the kinetic study, regression coefficients of all adsorbents are greater than 0.97 in first order and intraparticle diffusion models. The repeated use of HPPC with 15% perlite for cefxime removal was performed and the results indicated that optimized adsorbents hold excellent reusability and persistence in repetitive removal operation. The results suggest that this adsorbent can be compared with granular activated carbon and may be an economical adsorbent for wastewater treatment.

**ACKNOWLEDGEMENTS**

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