



## Adsorption of cadmium from aqueous solutions by perlite

T. Mathialagan, T. Viraraghavan\*

*Faculty of Engineering, University of Regina, Regina, SK, Canada S4S 0A2*

Received 31 October 2001; received in revised form 29 March 2002; accepted 29 March 2002

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### Abstract

The present study examined the use of perlite for the removal of cadmium from aqueous solutions. The effects of pH and contact time on the adsorption process were examined. The optimum pH for adsorption was found to be 6.0. Residual cadmium concentration reached equilibrium in 6 h and the rate of cadmium adsorption by perlite was rapid in the first hour of the reaction time. Ho's pseudo-second-order model best described the kinetics of the reaction. Batch adsorption experiments conducted at room temperature ( $22 \pm 1$  °C) showed that the adsorption pattern followed the Freundlich isotherm model. The maximum removal of cadmium obtained from batch studies was 55%. Thomas model was used to describe the adsorption data from column studies. The results generally showed that perlite could be considered as a potential adsorbent for cadmium removal from aqueous solutions. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Perlite; Cadmium; Adsorption; Kinetics; Isotherms

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### 1. Introduction

Heavy metals are defined as those metals and metalloids generally considered to be of sufficient distribution and abundance as to be in some way environmentally or biologically significant as a toxic substance [1]. These include metals such as lead (Pb), chromium (Cr), copper (Cu), cadmium (Cd), nickel (Ni), and zinc (Zn). Cadmium, like other heavy metals, is released into natural waters by industrial and domestic wastewater discharges. In humans, cadmium is accumulated in the kidneys which will begin to malfunction at overdoses spilling proteins in the urine and disrupting protein metabolism [2]. It is well known that chronic cadmium toxicity has been the cause of Japanese Itai–Itai disease [3].

Activated carbon is a commonly used adsorbent for the removal of pollutants present in water and wastewaters. Studies by Sigworth and Smith [4] have shown that the removal of

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\* Corresponding author. Tel.: +1-306-585-4094; fax: +1-306-585-4855.

*E-mail address:* t.viraraghavan@uregina.ca (T. Viraraghavan).

various heavy metal ions from aqueous solutions can be achieved using activated carbon. In spite of its effectiveness in the removal of heavy metals from wastewaters, the high cost of activated carbon has restricted its more widespread use [5]. Hence, an economical and easily available adsorbent would certainly make an adsorption-based process a viable alternative for the treatment of wastewater containing heavy metals.

Perlite is inexpensive and easily available in North American markets; this could make it a viable candidate as an economical adsorbent for removing heavy metals such as cadmium from wastewaters. Perlite is defined as a naturally occurring glassy volcanic siliceous rock with a marked concentric onion-like structure of fracturing caused by contraction during cooling [6]. The naturally occurring perlite when heated to a suitable temperature expands to form a lightweight, glasslike material with a cellular structure. The expanded perlite finds use in the construction industry (65%); horticultural markets (11%); filter aids and filters (22%); and other industrial uses (2%). But only a limited number of published studies can be found on the use of perlite as an adsorbent. Antonacci et al. [7] studied the adsorption of some organic solutes like 1,2,3,4-tetrahydronaphthalene, *o*-dichlorobenzene, methyl nonyl ketone and borneol, on modified perlite. It was found that perlite was quite effective in the extraction of organic solutes from water. Conti et al. [8] used a modified perlite-activated charcoal mixture to study the adsorption of organic solutes. Recently, Dogan et al. [9] used unexpanded and expanded perlite activated by H<sub>2</sub>SO<sub>4</sub> and NaCl for the adsorption of methylene blue from aqueous solutions. In their studies, the experimental data were described reasonably well by the Langmuir isotherm and unexpanded perlite gave better results than the expanded one.

Perlite of different types (expanded and unexpanded) and of different origin would have different properties because of the differences in composition. Hence, the objectives of this study were: to investigate the effectiveness of a commercial expanded-horticultural perlite mined in United States for the removal of cadmium from aqueous solutions by batch and column studies, and to examine the applicability of known kinetic and adsorption isotherm models.

## 2. Materials and methods

### 2.1. Cadmium solutions

Cadmium stock solutions were prepared from atomic absorption spectroscopy reference solutions for cadmium. Atomic absorption spectroscopy reference solutions contained cadmium metal as solute dissolved in 2–5% nitric acid solvent. Stock solutions were diluted using deionized water to prepare all the cadmium solutions used in this study. Cadmium concentrations in solution were determined by a Varian AA10 atomic absorption spectrometer.

### 2.2. Perlite

Perlite used in this study was supplied by Green Harvest Ltd., Calgary, Alta., Canada, in the form of expanded-horticultural perlite. Perlite was screened through ASTM: 11 sieves

and perlite particles passing through #10 sieve (aperture: 2 mm) and retained in #12 sieve (aperture: 1.70 mm) were used throughout the experiments.

### 2.3. *Batch pH studies*

Batch pH studies were conducted by shaking 100 ml of metal solution containing approximately 1 mg/l of cadmium with 0.8 g of perlite for 12 h, over a range of initial pH values from 3 to 10 in increments of 1. The samples were shaken in 250 ml conical flasks sealed with Parafilm "M", on a New Brunswick Scientific Shaker manufactured by Fisher Scientific Ltd. The final pH of the reaction mixture was recorded and samples were vacuum filtered through 0.45  $\mu\text{m}$  polycarbonate filters (Micron Separations Inc.). Filtered samples were used for analyzing the cadmium ion concentrations. The experiments were conducted in duplicates and mean values were used in the analysis of the data. An optimum pH was selected for further studies.

### 2.4. *Batch kinetic studies*

Batch kinetic experiments were conducted at pH 3, 4, 5, 6, and 7 to study the effects of pH on the equilibrium time required for the adsorption of cadmium on perlite. The initial cadmium concentration of metal ion was adjusted to approximately 1 mg/l. pH of the solutions was adjusted using 1 M NaOH or HNO<sub>3</sub> solution. After adjusting the pH of the solution, 0.8 g of perlite was added to 100 ml of the metal solutions in 250 ml conical flasks and the reaction mixture pH was not controlled after initiation of the batch experiments. A blank, containing 100 ml of only the cadmium solution without any adsorbent was shaken simultaneously to determine any adsorption of cadmium ions onto the walls of the conical flasks. A control, with 100 ml of deionized water (no metal ion added) and 0.8 g of perlite was also shaken simultaneously to determine any leaching of cadmium ion from perlite. Ten samples were placed on a shaker and shaken at 170 rpm. Samples were collected at 0.5, 1, 2, 4, 6, 8, 12, 16, 20 and 24 h for each pH value. Upon collection, samples were vacuum filtered through 0.45  $\mu\text{m}$  polycarbonate filters and cadmium ion concentrations in the filtrate were determined. The experiment was duplicated.

Upon determining the equilibrium time for the optimum pH, the cadmium removal by perlite was studied at much closer intervals of time. For this, a separate set of experiments were run at pH 6 (optimum pH) and the samples were collected at 5 min, 0.25, 0.5, 0.75, 1, 2, 3, 4, 5, 6, and 7 h. Upon collection, samples were filtered and analyzed for cadmium.

### 2.5. *Batch isotherm studies*

After determining the optimum pH and equilibrium time, isotherm studies were conducted at room temperature ( $22 \pm 1$  °C) by varying the mass of perlite. Representative masses (0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, and 1.2 g) of perlite were mixed with 100 ml of the solution containing approximately 1 mg/l of cadmium ion for 6 h, which is the equilibrium time for the perlite and cadmium ion reaction mixture. The initial pH of the metal solutions was adjusted to an optimum value of 6.0 with 1 M NaOH or HNO<sub>3</sub>. The cadmium

concentration at the end of the study period was determined after filtering the samples. The experiment was repeated for duplicate values.

### 2.6. Column studies

Column studies were conducted using an acrylic column with an inner diameter of 3.18 cm (1.5 in.) and a length of 60.96 cm (24 in.). The column was packed with 55 g of perlite and a bed height of 38 cm was obtained; the bed volume was 0.3 l. The approximate influent concentration and flow rate of the cadmium solution were 1 mg/l and 8 ml/min, respectively. Samples were collected at regular intervals of time and acidified with trace metal grade nitric acid to a pH < 2 for storage in polyethylene bottles before analysis. Column studies were terminated when the column reached exhaustion.

## 3. Results and discussion

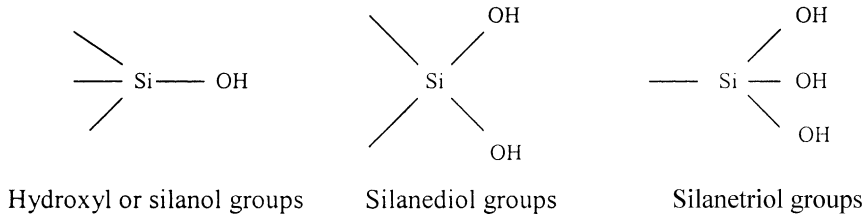
The chemical composition of perlite (Table 1) showed that it was mainly composed of silica as SiO<sub>2</sub> (72.44%), aluminum as Al<sub>2</sub>O<sub>3</sub> (14.5%), potassium as K<sub>2</sub>O (5.08%), and sodium as Na<sub>2</sub>O (4.65%). Varying amounts of other minor oxides and few elements made up the remaining composition. Expanded perlite is inert, non-combustible, and has low moisture absorption characteristics. It would also be useful to review the surface hydroxyl groups on the perlite because it is the one that contributes for its adsorption capacity.

Table 1  
Typical analysis of exfoliated-horticultural perlite (source: Idaho Minerals, USA)

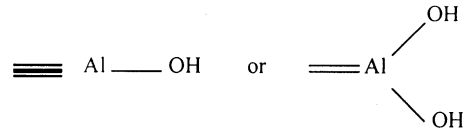
Parameter	Value
pH value (in water)	7–8
Specific gravity	2.4
Color	White (RI* = 1.5)
Elements/compounds (wt.%)	
SiO <sub>2</sub>	72.44
Al <sub>2</sub> O <sub>3</sub>	14.5
K <sub>2</sub> O	5.087
BaO	0.027
Na <sub>2</sub> O	4.652
CaO	0.831
MnO	0.093
MgO	<0.083
P <sub>2</sub> O <sub>5</sub>	<0.115
Fe <sub>2</sub> O <sub>3</sub>	<0.729
TiO <sub>2</sub>	<0.059
As (ppm)	<0.5
Ba (ppm)	237
B (ppm)	<10
Loss on ignition (LoI, %)	36.8
Moisture (%)	36.8

\* Refractive index.

In the surface hydroxyl groups, the silicon atoms at the surface tend to maintain their tetrahedral coordination with oxygen. They complete their coordination at room temperature by attachment to monovalent hydroxyl groups, forming silanol groups. The different types of silanol groups are shown as follows [9]:



The hydrous oxide surface groups in alumina are given as follows [9,10]:



It is these groups that give the adsorption property to perlite.

### 3.1. Batch pH studies

The removal of cadmium by adsorption on perlite was found to increase from 0 to 89% when the pH was increased from 3 to 10. The plot of pH versus percentage cadmium removed (Fig. 1) has two inflection points: one at pH 5, where significant adsorption of cadmium actually begins and the other at pH 9, where the adsorption increases drastically. The drastic increase in cadmium removal (59–90%) above pH 9 was probably due to the precipitation

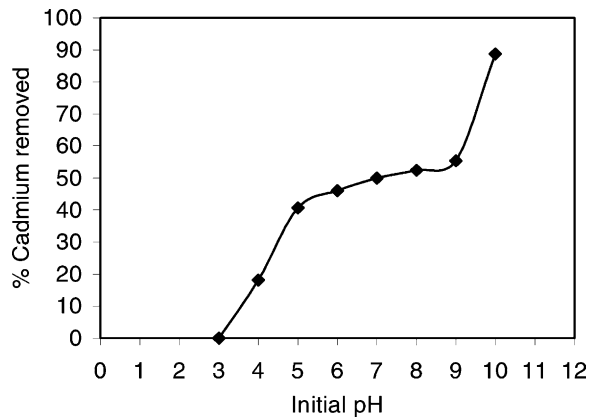
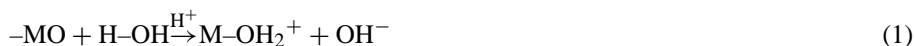


Fig. 1. Effect of pH on cadmium adsorption by perlite.

of cadmium ions as insoluble  $\text{Cd}(\text{OH})_{2(\text{s})}$  precipitate and not due to adsorption. This type of behavior had been observed for other hydrolyzable metals also [11,12].

The effect of pH on the adsorption of cadmium on perlite may be explained on the basis of aqua complex formation of the oxides present in the perlite. A positive charge develops on the surface of the oxides of perlite in an acidic medium as follows:



A lowering of cadmium adsorption at low pH is due to the fact that surface charge, thus, developed is not suitable for cadmium adsorption.

In an alkaline medium the surface of the perlite becomes negatively charged as shown in Eqs. (2) and (3), and thus, favors the adsorption of cadmium.



A similar theory was proposed by Yadava et al. [13] and Viraraghavan and Rao [5] for metal adsorption on fly ash which is also made up of various oxides.

Different researchers have observed different pH values at which cadmium precipitates as  $\text{Cd}(\text{OH})_{2(\text{s})}$ . Bhattacharya and Venkobachar [14] observed in their studies that cadmium precipitates at pH values greater than 10 and Gosset et al. [15] observed cadmium precipitation beyond pH = 6.5. Ozer et al. [16] reported that the optimum pH for cadmium adsorption was 6.3. This may be due to the difference in the aqueous medium employed in their experiments. In the present study, an optimum pH of 6.0 was selected for cadmium–perlite system.

### 3.2. Batch kinetic studies

Fig. 2 shows the adsorption kinetics for the removal of cadmium by perlite at various pH values. At pH 3, no significant adsorption was observed over the entire study period, while

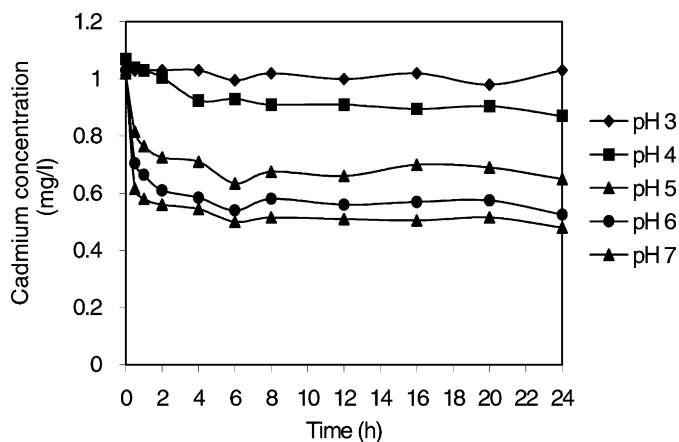


Fig. 2. Cadmium concentration vs. time at various pH values for perlite.

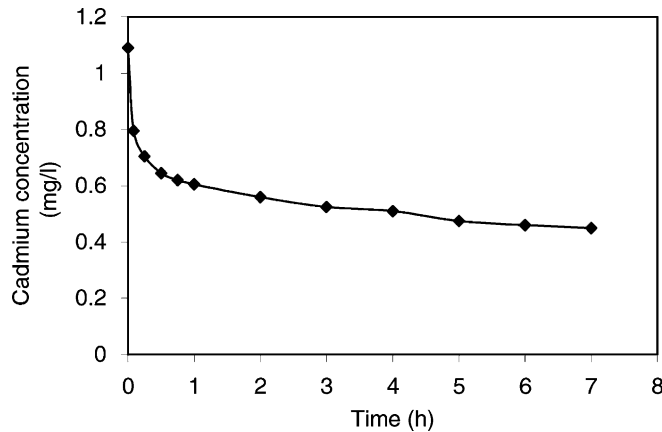


Fig. 3. Plot of cadmium concentration vs. time at pH 6.0 for perlite.

adsorption was insignificant at pH 4. For pH 5, 6, and 7, the adsorption of cadmium on perlite was significant and the adsorption system reached equilibrium in 6 h. Beyond 6 h, there was no significant adsorption of cadmium. As the precipitation of metal ions as hydroxides are likely at pH values above 7, kinetic studies above pH 7 were not attempted. The final pH of the reaction mixtures were generally higher than the initial pH values. The final pH for experiments of initial pH 3, 4, 5, 6, and 7 were 3.3, 6.4, 6.6, 6.7, and 6.9, respectively.

The kinetics of cadmium adsorption for perlite at its optimum pH of 6.0 was studied at much closer intervals of time for a period longer than 6 h. This helped in evaluating which reaction models were suitable for the cadmium adsorption on perlite. Fig. 3 shows the kinetics of cadmium adsorption on perlite at closer intervals of time at the optimum pH of 6.0. From the figure, it can be seen that the adsorption was rapid and significant during the first hour of the reaction time.

Lagergren first-order reaction rate model (Eq. (4)) and Ho et al.'s pseudo-second-order reaction model (Eq. (5)) were used to describe the kinetics of cadmium adsorption on perlite. The first-order Lagergren rate equation used by researchers [17,18] to study the kinetics of heavy metal adsorption is as follows:

$$\ln(q_e - q_t) = \ln(q_e) - K_L t$$

By rearranging it we can get:

$$q_t = q_e(1 - \exp(-K_L t)) \quad (4)$$

where  $K_L$  is the Lagergren rate constant for adsorption ( $\text{h}^{-1}$ ),  $q_e$  the amount of metal ion adsorbed at equilibrium (mg/g), and  $q_t$  is the amount of metal ion adsorbed at any given time  $t$  (mg/g).

Ho et al. [19] used a pseudo-second-order reaction rate equation to study the kinetics of adsorption of heavy metals on peat. The Ho et al. pseudo-second-order equation is given by

$$\frac{t}{q_t} = \frac{1}{2Kq_e^2} + \frac{t}{q_e}$$

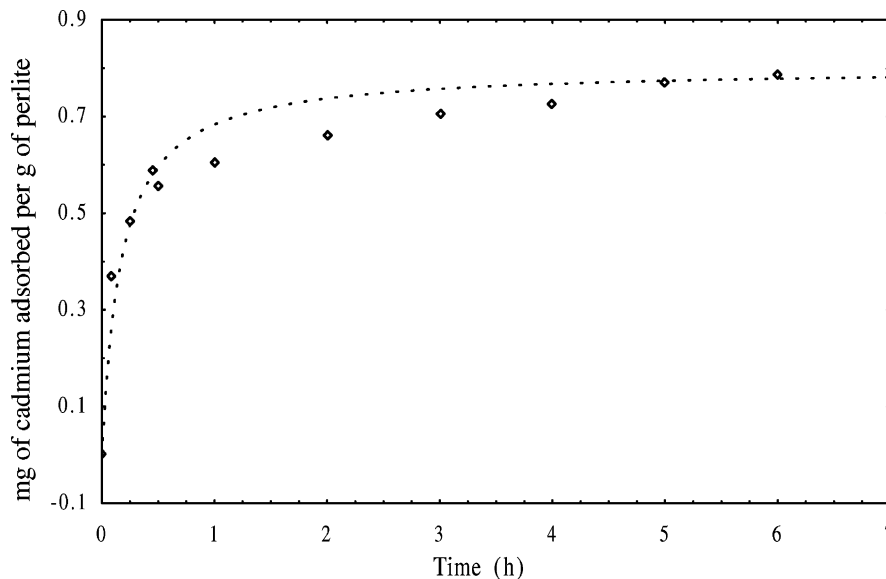


Fig. 4. The Ho's pseudo-second-order model plot for cadmium adsorption on perlite.

By rearranging it, we can get:

$$q_t = \frac{2Kq_e^2t}{1 + 2Kq_e t} \quad (5)$$

where  $K$  is the pseudo-second-order rate constant for adsorption (g/mg h),  $q_e$  the amount of metal ion adsorbed at equilibrium (mg/g), and  $q_t$  is the amount of metal ion adsorbed at any given time  $t$ .

The batch kinetic data for optimum pH 6 was fitted to both the models by non-linear regression analysis using software package STATISTICA (Release 5.0) for WINDOWS. Though both models adequately described the kinetic data at 95% confidence level, Ho's pseudo-second-order model best described the kinetic data with higher  $R$  values compared to the Lagergren first-order model. Fig. 4 shows the Ho's pseudo-second-order model plot for the kinetics of cadmium adsorption on perlite. Table 2 shows the Lagergren's first-order model equations and Ho's pseudo-second-order model equations for cadmium adsorption on perlite. The first-order and pseudo-second-order kinetic rate constants for cadmium

Table 2

First-order and pseudo-second-order reaction rate equations for cadmium adsorption on perlite

Model type	Model equation	$R$
First-order	$q_t = 0.8[1 - \exp(-3.29t)]$	0.90*
Pseudo-second-order	$t/q_t = 1/[2(3.7)(0.8)^2] + t/0.8$	0.97*

\* Indicates that model parameters are statistically significant ( $t$ -test) at 95% confidence level.



adsorption on perlite were  $K_L = 3.29 \text{ h}^{-1}$  and  $K = 3.67 \text{ g/mg h}$ . The first-order kinetic rate constants reported by few other researchers are  $0.0134 \text{ h}^{-1}$  for cadmium adsorption on peat [20],  $1.398 \text{ h}^{-1}$  for cadmium adsorption on fly ash [13], and  $0.44 \text{ h}^{-1}$  for cadmium adsorption on *Aspergillus niger* biomass [21]. A comparison of the first-order rate constant from this study with other studies showed that the rate of cadmium adsorption on perlite was quite rapid.

### 3.3. Batch isotherm studies

Isotherm experiments were carried out at an optimum initial pH of 6.0. The final pH were in the range 6.6–6.7. The adsorption data was fitted to the Freundlich (Eq. (6)), and the Langmuir (Eq. (7)) models using the non-linear regression analysis. The Freundlich equation is [22]:

$$q = K_f C_e^{1/n} \quad (6)$$

where  $q$  is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g),  $K_f$  the equilibrium constant indicative of adsorption capacity,  $n$  the adsorption equilibrium constant whose reciprocal is indicative of adsorption intensity, and  $C_e$  the concentration of adsorbate in solution at equilibrium (mg/l). The Langmuir equation can be expressed as

$$q = \frac{q^0 b C_e}{1 + b C_e} \quad (7)$$

where,  $q^0$  is the number of moles of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface,  $b$  the constant related to the energy or net enthalpy, and  $C_e$  is the concentration of adsorbate in solution at equilibrium (mg/l).

The non-linear regression analysis was conducted using the software package STATISTICA. It was found that the adsorption data obtained was best described by the Freundlich isotherm model. The constants estimated by the Freundlich model were statistically significant at 95% confidence level. Although adsorption data provided good fits with high  $R$  values for the Langmuir isotherm model, the Langmuir constants evaluated were not significant at 95% confidence level. Fig. 5 shows the Freundlich model plot for cadmium adsorption on perlite. Table 3 shows the isotherm model equations along with  $R$  values.

The Freundlich constants obtained can be used to calculate the theoretical adsorption capacity of perlite for cadmium. A value of 0.64 mg/g had been obtained as the adsorption capacity of perlite for cadmium from batch studies. This means that one gram of perlite could sorb 0.64 mg of cadmium ions from aqueous solutions, under present experimental conditions. The adsorption capacity of other adsorbents for Cd obtained by few other researchers are: 4 mg of cadmium/g of *Aspergillus niger* biomass [21]; and 0.91 and 0.83 mg of cadmium per gram of Giridh coal and crushed coconut shell [14]. A comparison of these values with the one obtained in this study (0.64 mg/g) showed that perlite used in this research exhibited a reasonable capacity for cadmium adsorption from aqueous solutions. It should be noted that these adsorption capacities of adsorbents for cadmium are calculated under their respective optimum experimental conditions.

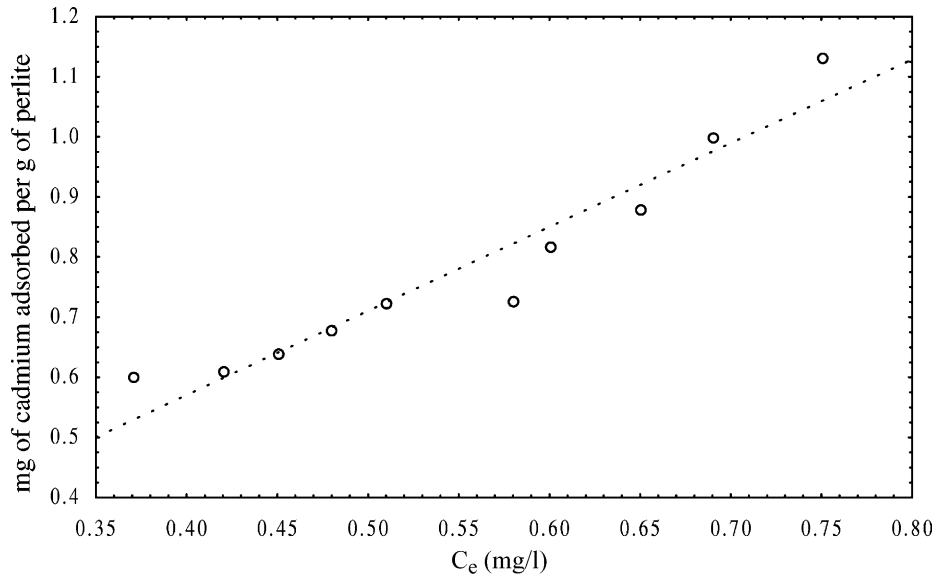


Fig. 5. The Freundlich model plot for cadmium adsorption on perlite.

### 3.4. Column studies

For column studies, the pH of the feed solution was 6.0, while the effluent pH was in the range 6.6–6.7. The adsorption data from column studies was analyzed using the Thomas model (Eq. (8)). The principal experimental information required is a breakthrough curve from a test column, either laboratory or pilot scale. The Thomas model has the following form [23]:

$$\frac{C_e}{C_0} = \frac{1}{1 + \exp[K_T(q_0m - C_0V)/Q]} \quad (8)$$

where  $C_e$  is the effluent adsorbate concentration (mg/l),  $C_0$  the influent adsorbate concentration (mg/l),  $K_T$  the Thomas rate constant (l/min mg),  $q_0$  the maximum solid phase concentration of the solute (mg/g),  $m$  the mass of the adsorbent (g),  $V$  the throughput volume (l), and  $Q$  is the volumetric flow rate (l/min).

The constants  $K_T$  and  $q_0$  are calculated using breakthrough data for use in the design of a full-scale adsorption bed.

Table 3

Freundlich and Langmuir model equations for cadmium adsorption on perlite

Model type	Model equation	R
Freundlich	$q = (1.4)C_e^{1/1.02}$	0.96*
Langmuir	$q = [(5.7)(0.3)C_e]/[1 + (0.3)C_e]$	0.95**

\* Indicates that model parameters are statistically significant (*t*-test) at 95% confidence level.

\*\* Indicates that model parameters are not statistically significant (*t*-test) at 95% confidence level.

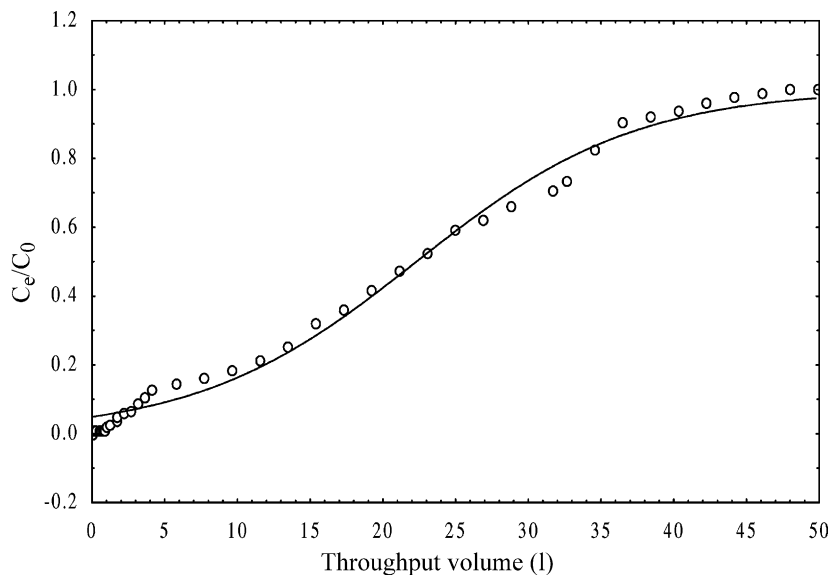


Fig. 6. Thomas equation plot for cadmium adsorption on perlite (1 bed volume = 0.31).

Fig. 6 shows the Thomas model plot. From the graph, it can be seen that the column achieved breakthrough ( $C_e/C_0 = 0.05$ ) almost immediately (2.16 l; 7.3 bed volumes) and took approximately 45 l (152 bed volumes) to exhaust. The Thomas equation coefficients for cadmium adsorption by perlite were  $K_T = 1.03$  ml/min mg and  $q_0 = 0.42$  mg/g. The value of  $q_0$  is a measure of the adsorptive capacity of the perlite for cadmium. In the present case,  $q_0 = 0.42$  mg/g; this means that every gram of perlite could sorb 0.42 mg of cadmium under the present column experimental conditions. Based on batch studies, a value of 0.64 mg/g was obtained as the adsorption capacity of perlite for cadmium. The reason for the lower adsorption capacity of perlite in column experiments than in batch experiments may be due to a high flow rate (8 ml/min) employed in the column studies, which could lead to short circuiting and flow through preferred path in the column which may avoid contact with some perlite particles.

### 3.5. General discussion

Based on the experimental results, it can be concluded that perlite exhibited quite a reasonable capacity for removing cadmium from aqueous solutions. The maximum cadmium removal at a pH of 6 was 55%. The rate of cadmium adsorption was rapid and the cadmium–perlite system attained equilibrium in 6 h. The reaction was best described by Ho's pseudo-second-order model and the adsorption followed the Freundlich isotherm. Regeneration and reuse of perlite was not considered in this study because the adsorbent was not expensive. However, such a study would be useful.

The cost of the adsorbent is also one important issue that must be considered when selecting an adsorbent. The cost of commercial activated carbon is US\$ 5–6 per kg

(approximately), whereas the cost of perlite is less than US\$ 1.50 per kg. The regeneration and reuse of perlite may play an important role in making this a practical process. Cadmium impregnated perlite could be disposed of in a hazardous waste landfill. The cost of regeneration/disposal of the spent adsorbent would also have to be considered in any detailed economic analysis required to determine the most economical adsorbent.

#### 4. Conclusions

The following conclusions were drawn from this study.

1. The batch pH studies indicated that the cadmium adsorption on perlite increased from 0 to 90%, when the pH was varied between 3 and 10. Beyond pH 9, cadmium removal was probably due to precipitation. The optimum pH was 6.0 and the maximum cadmium removal at this pH was 55%.
2. The kinetic studies at pH 6 indicated that equilibrium time for cadmium adsorption on perlite was 6 h.
3. The Ho et al.'s pseudo-second-order reaction rate model best described the kinetic data.
4. Isotherm analysis of the data showed that the adsorption pattern for cadmium on perlite followed the Freundlich isotherm.
5. The Thomas model was used to describe the column data and the adsorptive capacity of perlite for cadmium in column experiments using the Thomas model was 0.42 mg of Cd/g of perlite.

#### Acknowledgements

The authors would like to thank the Natural Sciences and Engineering Research Council (NSERC) of Canada for partial funding of this project.

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