



Experimental characterisation and evaluation of perlite as a sorbent for heavy metal ions in single and quaternary solutions



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ABSTRACT

Due to its unique properties such as low bulk density, high water retention capacity and high air-filled porosity, perlite has been recently employed as an important substrate additive to support vegetation in green roofs, vertical gardens and biofilters. Considering that the runoff quality of the above systems often comes under debate, it is important to explore the sorption capacity of substrate additives. Thus, the present study explores the potential of perlite to sorb important metal ions such as Cd^{2+} , Cu^{2+} , Ni^{2+} and Pb^{2+} in single and multi-component solutions. Characterisation of perlite indicated that the material possesses low bulk density (148 kg/m^3), high water holding capacity (27.5%) and high air-filled porosity (31.1%). Experimental results according to the Langmuir model revealed that perlite sorbed 0.130, 0.089, 0.057 and 0.025 mmol/g of Pb^{2+} , Cu^{2+} , Ni^{2+} and Cd^{2+} respectively, at an optimum pH of 5. The kinetics data were well described by pseudo-first order model, followed by the pseudo-second order and Elovich models. Quaternary sorption experiments showed that the presence of multiple ions had an adverse effect on the sorption capacity of perlite towards individual ions. Application of Sheindorf–Rebhun–Sheintuch equation to experimental quaternary isotherm data confirmed that sorption of Cd^{2+} ions was severely affected whereas Pb^{2+} ions were favoured.

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1. Introduction

Perlite is a naturally occurring glassy volcanic siliceous rock, mined and used throughout the world. The commercial product (commonly designated as expanded perlite) is produced by heating the material to 760–1100 °C, thereby converting its indigenous water (2–5% of the total weight) to vapour causing the material to expand up to 20 times its original volume, and forming lightweight glassy high-porosity aggregates [1]. Expanded perlite has unique properties such as high porosity, low density, chemical inertness and non-toxicity [2]. Due to above beneficial properties, perlite has found applications in the construction [3,4], chemical [5] and horticultural industries [1,6]. Perlite has been successfully employed as soilless growth medium in potting mixes [7] and provides benefits such as low bulk density, good water retention, high air space as well as superior nutrient retention for maximum plant growth. In recent years, perlite is preferred as substrate additive in green roofs, biofilters and vertical gardens. Considering that the above best management practices (BMPs) offer water quality improvement,

it is important to study the sorption potential of perlite towards different pollutants.

As an adsorbent, several investigators employed perlite for the removal of variety of heavy metals such as Cd [8], Cu [9], Pb [10], and Zn [11] from aqueous solutions. However, most of these studies explored the sorption potential of perlite under single component systems. In real field situations, the runoff (contaminated water) usually comprises of several pollutants and hence the knowledge of how one solute may influence the uptake of another in a multi-solute system is vital [12,13]. In multi-solute systems, the sorption of the solute of interest not only depends on the biomass surface properties and physical–chemical parameters of a solution, such as pH and temperature, but also on the number of solutes and their concentrations [12]. In such cases, adsorption becomes competitive, where one metal competes with another to occupy the binding sites of the sorbent.

Thus, the objective of the present work is to investigate the sorption potential of perlite towards Cd^{2+} , Cu^{2+} , Ni^{2+} and Pb^{2+} in single and multi-component solutions for its possible application in various BMPs. The effects of pH, contact time, initial solute concentration and co-ions on the sorption capacity of perlite were studied. The mechanism associated with the removal of heavy metals by perlite was also evaluated.

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2. Materials and methods

Perlite (0.25–1 mm) was purchased from Keltech Energies Ltd. (Bangalore, India). The chemical composition of perlite was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES, Perkin Elmer Optima 5300 DV) after solubilisation by acid digestion as reported by Rettig et al. [14]. The bulk density, water holding capacity, and air filled porosity were determined according to the Australian Standard Methods for potting mixes [15]. To evaluate the surface morphology of perlite, the sample was dried, coated with a thin layer of gold and subsequently analysed using scanning electron microscopy (Hitachi S4800, Japan).

Metal stock solutions were prepared by dissolving nitrate salts of heavy metals ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) in deionized (DI) water. All metallic salts were supplied by Sigma–Aldrich (India). Several experiments were performed in order to investigate the influence of pH, contact time, initial metal concentration and co-ion concentration. A batch-mode procedure was followed to study the above effects. A portion of 0.2 g perlite and 100 mL of known concentration of metal solution were mixed in a 250 mL Erlenmeyer flask and later, the flask was agitated in a rotary shaker at 160 rpm and $32 \pm 1^\circ\text{C}$. The pH of the suspension was initially adjusted and controlled using 0.1 M HCl or 0.1 M NaOH. After 8 h of agitation, the contents of the flask were filtered through a 0.45- μm -pore-size membrane syringe filter. The filtrate was analysed for metal concentrations using ICP-OES.

Quaternary experiments were conducted by contacting equal concentrations (mmol/L) of Cd^{2+} , Cu^{2+} , Ni^{2+} and Pb^{2+} with 0.2 g of perlite in Erlenmeyer flask. The remaining procedures were the same as described in single-solute sorption experiments.

The single-component sorption isotherms were modelled using:

$$\text{Langmuir model: } Q = \frac{Q_{\max} b_L C_e}{1 + b_L C_e} \quad (1)$$

$$\text{Freundlich model: } Q = K_F C_e^{1/n_F} \quad (2)$$

$$\text{Redlich–Peterson model: } Q = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{\beta_{RP}}} \quad (3)$$

where Q is the amount of metal ions sorbed per unit mass of sorbent (mmol/g), C_e is the equilibrium metal concentration (mmol/L), Q_{\max} is the maximum uptake (mmol/g), b_L is the Langmuir equilibrium constant (L/mmol), K_F is the Freundlich constant ($(\text{L/g})^{1/n_F}$), n_F is the Freundlich exponent, K_{RP} is the Redlich–Peterson isotherm coefficient (L/g), a_{RP} is the Redlich–Peterson isotherm coefficient ($(\text{L/mmol})^{\beta_{RP}}$), and β_{RP} is the Redlich–Peterson model exponent.

The single-component sorption kinetics data were described using:

$$\text{Elovich model: } Q_t = \frac{1}{b} \ln(1 + abt) \quad (4)$$

$$\text{Pseudo-first order model: } Q_t = Q_e(1 - \exp(-k_1 t)) \quad (5)$$

$$\text{Pseudo-second order model: } Q_t = \frac{Q_e^2 k_2 t}{1 + Q_e k_2 t} \quad (6)$$

where Q_e and Q_t represent the amount of metal ion sorbed at equilibrium and at any time, respectively (mmol/g), a is the initial adsorption rate (mmol/(g min)), b is the desorption constant (g/mmol), k_1 is the first order equilibrium rate constant (1/min) and k_2 is the second order equilibrium rate constant (g/mmol min). Both kinetic and isotherm data modelling were performed by non-linear regression using the Sigma Plot (version 4.0, SPSS, USA) software.

Table 1

Chemical composition of perlite.

Constituent	Weight percentage (%)
SiO_2	71–77
Al_2O_3	12–18
K_2O	4.0–5.0
Na_2O	2.9–4.0
CaO	0.5–2.0
Fe_2O_3	0.5–1.5
MgO	0.1–0.5

The average percentage error between the experimental and predicted values was calculated using:

$$\text{Error (\%)} = \frac{\sum_{i=1}^N (Q_{\text{exp},i} - Q_{\text{cal},i} / Q_{\text{exp},i})}{N} \times 100 \quad (7)$$

where Q_{exp} and Q_{cal} represent the experimental and calculated uptake values, respectively, and N is the number of measurements.

3. Results and discussion

3.1. Chemical composition and characterisation of perlite

The results of the chemical analysis of the perlite are shown in Table 1. The perlite was mainly composed of SiO_2 , Al_2O_3 , K_2O and Na_2O along with minor quantities of CaO , Fe_2O_3 and MgO . In horticulture, perlite is used as substrate additive as they found it to decrease the weight of plant medium, provide good aeration and have good water retention capacity. Through analysis, it was identified that perlite possesses low bulk density (148 kg/m^3), high air-filled porosity (31.1%), and high water retention capacity (27.5%). The low bulk density exhibited by perlite will be useful if there are load restrictions in the installation of BMPs as in the case of green roofs and vertical gardens. On the other hand, high air-filled porosity and water retention capacity will be helpful for better growth of plants.

The surface morphology of perlite sample was analysed using scanning electron microscopy as demonstrated in Fig. 1a. Perlite particles exhibited irregular morphology with broken or ragged edges. Through EDX analysis (Fig. 1b), peaks of Na, K, Al and Si were observed. This observation coincides with elemental composition of perlite as shown in Table 1.

3.2. Influence of pH on sorption of metal ions onto perlite

The results obtained by studying the effect of equilibrium pH during the sorption of Cd^{2+} , Cu^{2+} , Ni^{2+} and Pb^{2+} onto perlite are represented in Fig. 2. Experiments were conducted at fixed initial metal concentration of $0.25 \pm 0.01 \text{ mmol/L}$ in the pH range of 2.5–5, as some metal ions were expected to form metal hydroxide at pH values greater than 5. In the examined range, the sorption of metal ions increased with increase in equilibrium pH. For instance, the removal efficiency of 3.7% exhibited by perlite towards Pb^{2+} at pH 2.5 increased to 78.2% at pH 5. For other metal ions, overall increases of 14.7, 9.9 and 11.1 times were observed for Cu^{2+} , Ni^{2+} and Cd^{2+} respectively when pH increased from 2.5 to 5. The reason for less sorption at low pH values was due to increase in proton (H^+) concentration in the solution, which protonates the surface sites of perlite and thus, electrostatic repulsion occurred between the positively charged metal ions of interest and the edge groups with positive charge (Si-OH^{2+}) on the surface [9,10]. As the pH increases, the surface of perlite becomes negatively charged due to depletion of H^+ ions in the solution, thus resulting in an increased metal sorption.

From Fig. 2, it can be inferred that perlite sorbed more Pb^{2+} compared to other metal ions. The sorption uptake of

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