



Virgin volcanic rocks: Kinetics and equilibrium studies for the adsorption of cadmium from water

Esayas Alemayehu*, Bernd Lennartz

Institute for Land Use, Rostock University, Justus-Von-Liebig-Weg 6, 18059 Rostock, Germany

ARTICLE INFO

Article history:

Received 22 October 2008

Received in revised form 6 March 2009

Accepted 24 March 2009

Available online 31 March 2009

Keywords:

Pumice

Scoria

Cadmium

Adsorption

ABSTRACT

This study was initiated to investigate the adsorption of cadmium from aqueous solution by two different rock types—Pumice (VPum) and Scoria (VSco), which are readily available in Ethiopia and other countries. The influence of operational conditions, such as particle size, adsorbent/solution ratio, contact time, cadmium initial concentration, and pH was analyzed. The competition between metals was also evaluated. The Cd(II) removal capacity was predominantly affected by the pH conditions, being increased under alkaline conditions. For both adsorbents, when particle size was 0.075–0.425 mm, the maximum Cd(II) adsorption was observed at pH 6.0 (contact time = 24 h, shaking speed = 200 rpm, adsorbent dose = 50 g L⁻¹). Adsorption process revealed that the initial uptake was very fast during the first 1 h. The kinetics of the interactions follows pseudo second-order. Equilibrium assays confirm that VPum has a larger capacity and affinity for Cd(II) adsorption than VSco. Both Langmuir and Freundlich models described equally well the experimental data. VPum and VSco were found to be promising material for the removal of cadmium from metal bearing water.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Water quality is one of the main issues in many countries. The increasing population and the scarcity, as well as the anthropogenic and natural contamination of water resources pose a serious problem for water supply. Cadmium (a metal with extremely hazardous effects) has become a threat to public health worldwide since it is increasingly recognized in fresh water resources [1,2]. Water treatment plants which draw water from such contaminated resources are thus facing growing problems in delivering desired water quality. The presence of cadmium over the permissible levels is a severe human health problem. Excessive cadmium intakes cause damage to liver, spleen and kidney, lung inefficiency, mental deterioration, hypertension, bone degeneration, muscular and cardiovascular disorders and cancer [3,4].

A number of technologies have been developed over the years for the removal of excess cadmium and other heavy metals from contaminated water and soil *viz.* precipitation, ion exchange, membrane separations and adsorption onto activated carbon. In conventional treatment systems, the processes (coagulation, sedimentation and filtration) employed can not remove cadmium efficiently [5,6]. Therefore, it has become necessary to develop an innovative remediation technique to improve water quality.

The adsorption methods have received extensive attention for the removal of pollutants from aqueous solutions. It has long been recognized that, if the adsorbent is chosen carefully and the conditions are adjusted appropriately, adsorption-based processes are capable of removing contaminants over a wide pH range and too much lower levels than conventional precipitation methods [7]. The applicability of adsorption methods is highly dependent on the nature of the adsorptive materials. It has been reported that various types of natural adsorbents have the capacity to adsorb heavy metals from aqueous solutions [6,8–10]. However, available methods have several disadvantages, which make them not effective and/or not sustainable for non-developed areas around the globe. Therefore, numerous efforts have been oriented to obtain low-cost but efficient adsorbents that may be used in poorly developed areas such as Ethiopia for water purification purposes.

Volcanic rocks are formed from volcanic magma. The most abundant volcanic rocks include Pumice, a finely porous rock frothy with air bubbles; and Scoria, a rough rock that looks like furnace slag [11,12]. Pumice and Scoria deposits originate in areas with young volcanic fields. These rocks are abundant in Europe (Italy, Turkey, Greece and Spain), Central America, Southeast Asia and East Africa (Eritrea, Djibouti, Kenya and Ethiopia) [13,14]. The Ethiopian Rift Valley, which covers around 30% of the area of the country, has several of these cinder cones and lava fields [15,16]. Volcanic rocks have received considerable interest for heavy metals removal mainly due to their valuable properties: high surface area, low cost and local availability in large quantities. In recent year, the potential of vol-

* Corresponding author. Tel.: +49 381 498 3184; fax: +49 381 498 3122.
E-mail address: esayas16@yahoo.com (E. Alemayehu).

Table 1
Chemical composition of VPum and VSco, determined by XRF analysis.

Components	VSco	VPum
SiO ₂ (wt%)	47.4	68.6
Al ₂ O ₃ (wt%)	21.6	8.9
Fe ₂ O ₃ (wt%)	8.9	4.9
CaO (wt%)	12.4	1.8
K ₂ O (wt%)	0.5	5.5
Na ₂ O (wt%)	3.0	4.1
MgO (wt%)	3.3	0.2
TiO ₂ (wt%)	1.7	0.3
Others (wt%)	1.2	5.7

canic rocks to remove metals from water and wastewater has been reported [17–19].

The primary objectives of the present work were to determine cadmium(II) adsorption isotherms of the rock grains; compare the adsorption properties of both adsorbents with each other; identify the effect of pH, particle size, initial concentrations of Cd(II), and adsorbent/solution ratio on the removal kinetics. The influence of other divalent metals on the removal of cadmium was also addressed.

2. Material and methods

2.1. Adsorbents

Pumice is a light, porous igneous volcanic rock produced by the release of gases during the solidification of lava. It is characterized by a porous structure, its large surface area, and a high water absorption capacity (20–30%). Due to its high degree of macro-porosity it can easily be processed [12]. The rough surface and porous structure provide a large number of possible attachment sites for pollutants. Pumice has a skeleton structure that allows ions and molecules to reside and move within the over all framework. The large proportion of free silica sites at the grain surface results in a negative charged surface. The density value is low, but depends on the thickness of solid material between bubbles [18,19].

Scoria is formed of vesicular fine to coarse fragments, reddish or black colour, and light in weight. It consists of glass and phenocrysts basaltic minerals such as plagioclase, olivine, hornblende and pyroxene [13,20]. It has been reported that scoria has a higher adsorption capacity and affinity for metals than commercial activated powder [17].

Pumice (VPum) and Scoria (VSco) from the Main Rift Valley (Ethiopia), was used in this study. The rocks were washed repeatedly with demineralised water to remove any water-soluble deposits and dried at room temperature (23–25 °C). In agreement with the American Society for Testing and Materials (ASTM D 422) and soil textual classification system [21], the samples were crushed and separated into four mesh size fractions: silt (<0.075 mm), fine-sand (0.075–0.425 mm), medium-sand (0.425–2.0 mm), and coarse-sand fraction (2.0–4.75 mm) respectively. Other physical properties of the material used were: VPum (pH 7.5, particle density for <0.075 mm size = 2.46 g cm⁻³), VSco (pH 7.6, particle density for <0.075 mm size = 2.98 g cm⁻³). The chemical composition of the adsorbents was determined by X-ray Fluorescence (XRF) spectrometry (Table 1). As expected, the SiO₂ content was greater in VPum than VSco. The characterized adsorbents were kept in airtight plastic container at room temperature until commencement of the batch adsorption experiments.

2.2. Adsorbate solutions

All solutions were prepared from analytical reagent grade chemicals and 0.01 M aqueous solution of CaCl₂·2H₂O. The calcium

chloride solution was used as the solvent phase to maintain a constant ionic strength and minimise cation exchange. The stock solution containing 1000 mg of Cd(II) per litre was prepared by dissolving CdCl₂·H₂O (Merck, Germany). In order to investigate the influence of dissolved Cu(II) and Ni(II) on the uptake of cadmium by VPum and VSco, the solutions of the metals were prepared by dissolving their chloride and nitrates. The solutions (pH < 2) were stored in tightly closed bottles at 4 °C.

Cadmium solutions of desired concentrations were prepared by appropriate dilutions of the stock solution immediately prior to their use. Before mixing these solutions with the adsorbent, the solutions were adjusted to pH value of 5 ± 0.1 (minimizing precipitation of cadmium) by adding 0.1 M HCl or 0.1 M NaOH. To avoid pH change during experiments due to CO₂ escape, bottles were capped and kept closed during the whole experiments. All experiments other than tests on pH effects were conducted at a pH of 5 ± 0.1.

2.3. Experimental set-up and procedures

Cadmium adsorption was investigated by using a batch equilibrium technique. For the determination of adsorption isotherms, 100 ml of Cd(II) solution of known initial concentration was shaken with a certain amount of the adsorbents on a shaker (SM 25) at 200 rpm for 24 h. The adsorbents (VPum and VSco) were equilibrated by shaking with 0.01 M CaCl₂·2H₂O overnight (12 h) before the day of the actual experiments. All experiments were in triplicate at room temperature (24–25 °C). Control (only the test substance without adsorbent) and Blank (only the adsorbent without the test substance) experiments had been carried out for each set of experiments. At the end of the experiment the batch container (acid washed PE-bottle) was allowed to settle for about 1 min and 10 mL supernatant was sampled with a syringe. The remaining solids were separated from the solution by filtration (0.2 μm, Nylon Membrane Filters, Whatman). Then the pH was measured (Microprocessor pH 196), and acidified samples were analysed for the residual Cd(II) concentrations using ICP–AES (Inductively Coupled Plasma–Atomic Emission Spectrometer, JY 238).

The amount of Cd(II) adsorbed at time *t*, *q_t* and *A*(%) was calculated from the mass balance equation:

$$q_t = (C_0 - C_t) \frac{V}{M} \quad (1)$$

$$A(\%) = \left\{ \frac{(C_0 - C_t)}{C_0} \right\} \times 100 \quad (2)$$

where *C*₀ = initial concentration of Cd(II) in contact with adsorbents (mg L⁻¹), *q_t* = the amount of Cd(II) adsorbed per unit mass of the adsorbent (mg kg⁻¹), *M* = dry mass of the adsorbent (kg), *C_t* = mass concentration of Cd(II) in aqueous phase, control correction included, at time *t* (mg L⁻¹), *V* = initial volume of the aqueous phase in contact with the adsorbents during the adsorption test (L), *A*(%) = adsorbed amount give as percentage at time *t_i* (%).

2.4. Theoretical foundation

2.4.1. Adsorption kinetics

Numerous models can be used to express the mechanism of adsorbate sorption onto adsorbent. The parameters of these models are important in water and wastewater treatment process design. When the removal of a solute follows a two step processes ((i) sharp increase of the solute removal during the initial contact time between the solution and solid phase, (ii) slow increase until a state of equilibrium is reached), it can be represented by a pseudo

second-order kinetic model [22]:

$$\frac{\partial q_t}{\partial t} = k_2(q_e - q_t)^2 \quad (3)$$

where k_2 is the pseudo-second order rate sorption constant ($\text{kg mg}^{-1} \text{h}^{-1}$), which represents the steepness of the curve. Integrating, and applying the boundary conditions $q_t = 0$ at $t = 0$, $q_e = q_t$ when $t = t_e$, the linear form of Eq. (3) can be written as follows:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) + \left(\frac{1}{q_e} \right) t \quad (4)$$

The parameters k_2 ($\text{kg mg}^{-1} \text{h}^{-1}$) and $q_{e,\text{calc}}$ (mg kg^{-1}) were described by linear regression analysis of the experimental kinetic data (4).

2.4.2. Adsorption isotherms

The Langmuir and Freundlich models are the most frequently employed for describing the adsorption isotherms from experimental data. These models can be used to design and optimize an operating procedure. Furthermore, they provide information to predict removal efficiency of solute and an estimation of adsorbent amounts needed to remove solute ions from aqueous solution. In this work, the following non-linear isotherm models were used to compare the cadmium adsorption mechanisms between VPum and VSco:

$$\text{Freundlich equation: } q_e = K C_e^{1/n} \quad (5)$$

$$\text{Langmuir equation: } q_e = \frac{ab C_e}{(1 + b C_e)} \quad (6)$$

where q_e (mg kg^{-1}) is the specific amount of cadmium adsorbed, and C_e (mg L^{-1}) is the cadmium concentration in the liquid phase at equilibrium. The parameter K (L kg^{-1}) and $1/n$ are the Freundlich constants that are related to the total adsorption capacity and intensity of adsorption, respectively. The Langmuir parameters are a (mg kg^{-1}), which is related to adsorption density, and b (L mg^{-1}), which is indicative of the adsorption energy. The isotherm equations have been optimized using the solver function in EXCEL.

The Langmuir equation is also used to obtain R_L , the separation factor, from the expression:

$$R_L = \frac{1}{1 + b C_0} \quad (7)$$

where C_0 is the initial concentration of cadmium, mg L^{-1} . The shapes of the isotherms are expressed by R_L ; values of $0 < R_L < 1$ indicate favourable adsorption, and $R_L > 1$, $R_L = 1$ and $R_L = 0$ represent unfavourable, linear and irreversible isotherm, respectively [23].

When the initial section of an isotherm is nearly linear, its slope is defined as the distribution coefficient (K_d). The distribution coefficient is the ratio between the content of the substance in the solid phase and the mass concentration of the substance in the aqueous solution, under the test conditions, when adsorption equilibrium is reached. It is often used to characterize the mobility of heavy metals: low K_d values imply that most of the metal remains in solution while high K_d values indicate that the metal has great affinity to the adsorbent [24]. The initial section of adsorption isotherms was described by the following linear equation:

$$q_e = K_d C_e \quad (8)$$

where q_e (mg kg^{-1}) and C_e (mg L^{-1}) are the solute quantity adsorbed and the solution concentration at equilibrium, respectively.

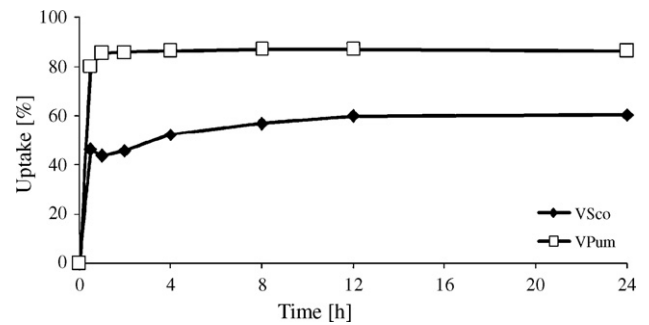


Fig. 1. Effect of contact time on the adsorption of Cd(II) by VPum and VSco (operative conditions— C_0 : 2 mg L^{-1} ; time: 0–24 h; particle size: fine; adsorbent/solution ratio: 1:20; pH 5).

3. Results and discussion

3.1. Effect of contact time

Batch kinetic experiments were conducted by taking 500 ml of the test solution containing 2 mg L^{-1} of Cd(II). The adsorbent/solution ratio was kept constant at 1:20. The time-course of Cd(II) adsorption is shown in Fig. 1. As can be seen, the adsorption increased with increasing contact time, and the equilibrium was attained after shaking for 24 h. The shaking time for the equilibrium tests was chosen accordingly. Moreover, adsorption followed a linear rise with fast uptake during the first 1 h and decreased progressively thereafter giving a very slow approach towards equilibrium (Fig. 1). It may be assumed that the first molecules to arrive at the bare surface are preferentially adsorbed on the most active sites, and the high initial uptake rate may be attributed to the availability of a large number of adsorption sites. The amount of Cd(II) adsorbed on VPum ($34.6 \mu\text{g g}^{-1}$; 86.5%) was much higher than the values obtained for VSco ($24.2 \mu\text{g g}^{-1}$; 60.5%) at the same interaction time (24 h).

3.2. Effect of initial cadmium concentrations

The amount of cadmium adsorbed per unit mass of adsorbent increased gradually with an increasing Cd(II) concentration of the solution (Fig. 2). By changing the initial concentration of the solution from 2.0 to 50 mg L^{-1} , the absolute amount of adsorbed Cd(II) increased from 0.66 to 284 mg Cd(II) per kilogram of VSco and from 13 to 566 mg Cd(II) per kilogram of VPum, respectively. This is in agreement with the findings from various investigations that suggest the more concentrated solution the better is the adsorption [25].

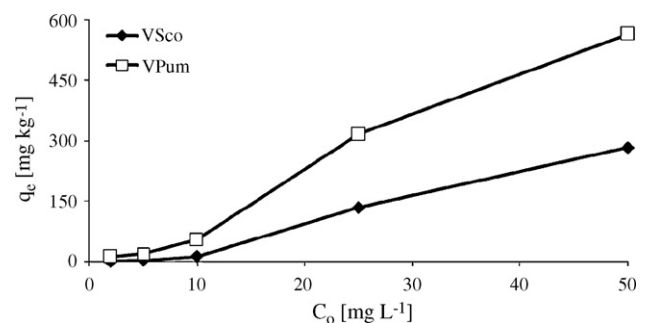


Fig. 2. Effect of Cd(II) initial concentration (operative conditions— C_0 : 2.0– 50 mg L^{-1} ; time: 24 h; particle size: fine; adsorbent/solution ratio: 1:20; pH 5).

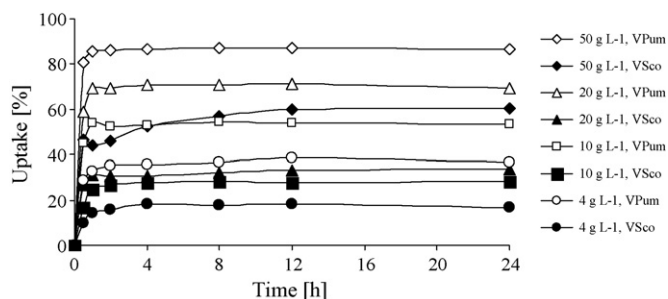


Fig. 3. Effect of adsorbent/solution ratio on the adsorption of Cd(II) by VScO and VPum (operative conditions— C_0 : 2 mg L^{-1} ; time: 0–24 h; particle size: fine; adsorbent/solution ratio: 1:250–1:20; pH 5).

3.3. Effect of adsorbent/solution ratio

Adsorbent dosage is an important design parameter because it quantifies the capacity of an adsorbent for a given initial concentration of adsorbate. The experiments were conducted as a function of time with constant cadmium concentrations (2 mg L^{-1}); the adsorbent/solution ratio varied from 1:250 to 1:20. As can be seen from Fig. 3, the effect of both adsorbents dose on cadmium uptake was similar. By changing the dose from $4 \text{ to } 50 \text{ g L}^{-1}$, the removal of Cd(II) ions significantly increases from 36.5 to 86.5% for VPum and 17 to 60.5% for VScO. The maximum removal is exhibited at 50 g L^{-1} (1:20 ratio) of the adsorbents. This observation can be attributed to the increase of the adsorption surface area and the availability of free adsorption sites.

3.4. Effect of adsorbents on pH

For both adsorbents significant pH changes occurred during the 24 h of contact time (Table 2). The pH variation during the experiments was between 1.0 and 3.0 units in average. At low pH (pH 2–4 for VScO and pH 2–6 for VPum), a marked increase of pH was detected (Table 2), which was interpreted in terms of proton adsorption. However, at high pH (pH 8–10), a significant decrease of pH was determined. At pH of 12 there were no considerable changes. The behaviours observed may be related to the reaction of hydroxide with the adsorbent surface or to proton release from surface groups. Similar observations were also reported for cadmium ions with other indigenous adsorbents [26,27].

3.5. Effect of pH on cadmium adsorption

It is well known that pH has a dramatic effect on the adsorption of metal onto the adsorbent, which may affect the degree of ionization, speciation of the metal ions and the surface charge of the adsorbent [28]. To characterize the effect of pH on Cd(II) adsorption using VPum and VScO, separate set of batch equilibrium adsorption experiments were conducted modifying the pH from 2 to 12. The results obtained for both adsorbents are presented in Fig. 4. As can be seen, in acidic medium (pH 2), the uptake was about 24.6 and 67.5% by VScO and VPum respectively, indicating that the H^+ ions react with the adsorbent, thus limiting the number of binding sites for cadmium ions. However, increasing the pH to 6, the adsorption increased to 67.47 and 89.7% by VScO and VPum respectively. This sharp increase in the adsorption efficiency may be accounted for

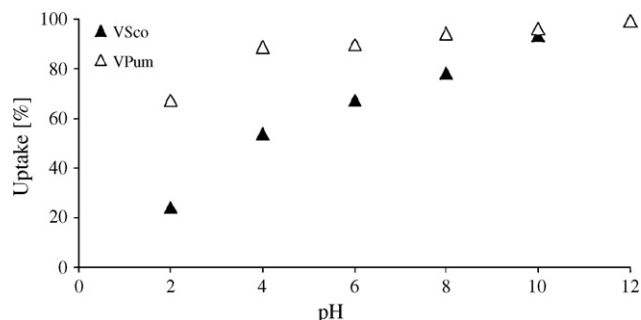


Fig. 4. Effect of pH on the adsorption of Cd(II) by VScO and VPum (operative conditions— C_0 : 2 mg L^{-1} ; time: 24 h; particle size: fine; adsorbent/solution ratio: 1:20; pH 2–12).

the lowered competition of H^+ ions with Cd^{2+} for the active sites [27]. At the alkaline solution increment in the adsorption is slow-down. It is most likely that in the alkaline medium, $\text{Cd}(\text{OH})_2$ was the dominant species and precipitation played a significant role in the removal mechanism. Thus, all the experiments other than on pH effects were conducted at $\text{pH } 5 \pm 0.1$. At this pH, three species are present in the solution, namely: $\text{Cd}(\text{OH})_2$ (in very small quantity); $\text{Cd}(\text{II})$ and CdOH^+ (in large quantity) [7]. We avoid working over initial pre-fixed pH (5 ± 0.1) to prevent the possible precipitation of cadmium hydroxide, which would introduce uncertainty into the interpretation of the results.

3.6. Effect of particle size

Effect of particle size on adsorption was investigated for different times (0.5–24 h). The particle size ranged from silt to coarse sand size (<0.075 , 0.075 – 0.425 , 0.425 – 2.0 , 2.0 – 4.75 mm). As seen from Fig. 5a and b, the kinetics of cadmium removal exhibited a biphasic curve for the two adsorbents. On reducing the particle size from

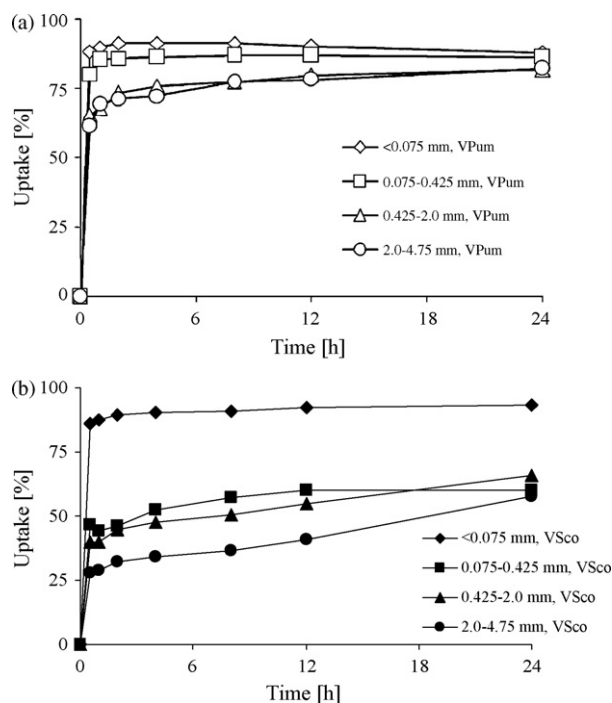


Fig. 5. (a) Effect of particle size on the adsorption of Cd(II) by VPum (operative conditions— C_0 : 2 mg L^{-1} ; time: 0–24 h; particle size: silt–coarse; adsorbent/solution ratio: 1:20; pH 5). (b) Effect of particle size on the adsorption of Cd(II) by VScO (operative conditions— C_0 : 2 mg L^{-1} ; time: 0–24 h; particle size: silt–coarse; adsorbent/solution ratio: 1:20; pH 5).

Table 2
Effect of adsorbents (VScO and VPum) on the pH of solution after 24 h exposure.

pH_{int}	2	4	6	8	10	12
$\text{pH}_{24, \text{VScO}}$	2.85	4.96	4.41	6.16	5.61	11.83
$\text{pH}_{24, \text{VPum}}$	6.30	6.99	6.94	7.16	7.12	11.75

Table 3

Values of pseudo second-order rate constants of Cd(II) ions on different particle sizes and adsorbent/solution ratios.

Adsorbent	Variables	q_e (mg kg ⁻¹)	$q_{e,calc}$ (mg kg ⁻¹)	k_2 (kg mg ⁻¹ h ⁻¹)	R^2
VScO	Silt ^a	37.4	37.5	0.24	0.99
	Fine ^a	24.0	24.4	0.09	0.99
	Medium ^a	26.4	26.7	0.03	0.98
	Coarse ^a	23.0	23.1	0.02	0.95
VPum	Silt ^a	35.2	35.2	0.24	0.99
	Fine ^a	34.6	34.6	8.35	1.00
	Medium ^a	32.8	33.0	0.11	0.99
	Coarse ^a	33.0	33.2	0.08	0.99
VScO	50 ^b	24.2	24.7	0.08	0.99
	20 ^b	33.5	33.7	0.12	0.99
	10 ^b	56.0	56.5	0.10	0.99
	4 ^b	85.0	87.0	0.66	0.99
VPum	50 ^b	34.6	34.5	8.40	1.00
	20 ^b	69.5	71.4	0.39	0.99
	10 ^b	107.0	111.1	0.81	0.99
	4 ^b	182.5	200.0	0.06	0.99

^a Size fractions.^b Dose (mg L⁻¹).

4.75 to 0.075 mm, the uptake of cadmium increased from 57.5 to 93.5% and from 82.5 to 88% for VScO and VPum respectively. The relatively higher adsorption with smaller adsorbent particles may be attributed to the fact that smaller particles provide large surface areas and/or that sorption sites are more readily available. There is a tendency of the smaller particles to require shorter time to the equilibrium stage (Fig. 5a and b).

Our results show that the grain-size reduction of a medium is significantly important in Cd(II) ions–VScO system (with the adsorbent particles size of <0.075 mm the uptake was the highest) indicating that its adsorption capacity highly depends on the particle size of the grains. On the contrary, the effect of particle size on VPum removal capacity is not as such important. This means that the pore spaces (and according sorption sites) are more readily

available in VPum than in VScO independent of grain size, indicating that the pore space of VPum is a continuum (skeletal structure) while the pore space of VScO is dominated by dead-end pores.

3.7. Adsorption kinetics modelling

In order to define the kinetics of the cadmium adsorption, the parameters for the adsorption process were studied for contact time ranging between 0.5 and 24 h by monitoring the percent removal of cadmium by adsorbents. The kinetics data for each adsorbent (VPum and VScO) was disaggregated for different particle sizes and adsorbent dosages. The equilibrium parameters q_e , and $q_{e,calc}$ (mg kg⁻¹) and the adsorption rate constant k_2 (kg mg⁻¹ h⁻¹) are reported in Table 3. The kinetic plots were prepared for both adsorbents (VPum and VScO) (examples, Fig. 6a and b). For all particle

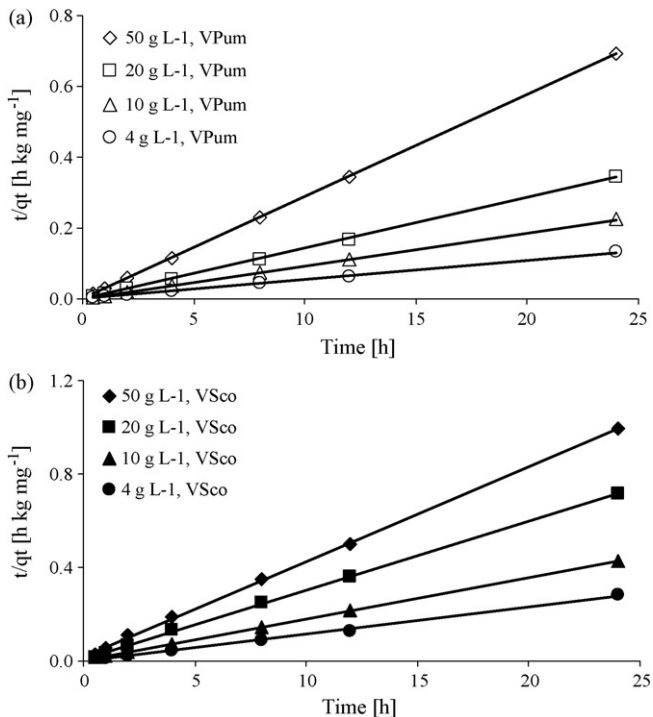


Fig. 6. (a) Pseudo second-order sorption kinetics of Cd(II) on VPum with different particle size. (b) Pseudo second-order sorption kinetics of Cd(II) on VScO with different particle size.

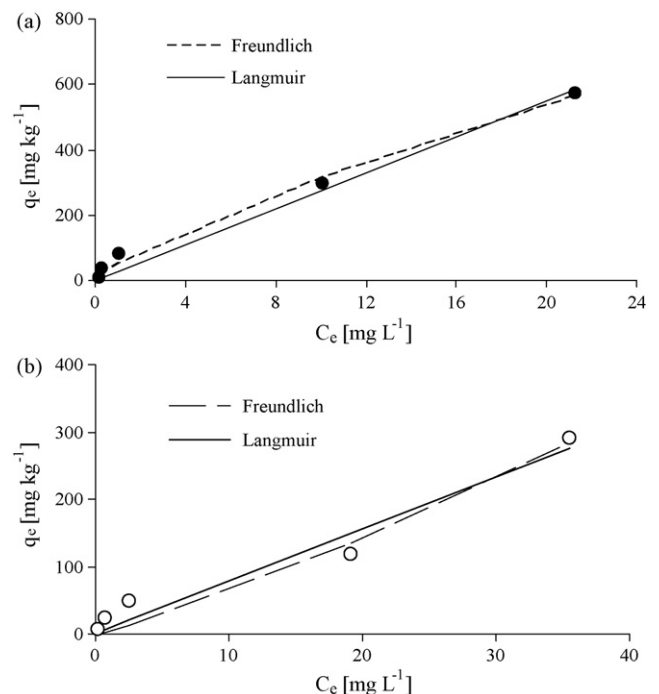


Fig. 7. (a) Freundlich and Langmuir isotherm of Cd(II) by VPum. (b) Freundlich and Langmuir isotherm of Cd(II) by VScO.

Table 4
Freundlich and Langmuir isotherm constants of VPum and VScO.

Adsorbent	Freundlich constants			Langmuir constants			
	K (L kg ⁻¹)	$1/n$	R^2	a (mg kg ⁻¹)	b (L mg ⁻¹)	R^2	R_L
VPum	53.6	0.6	0.99	3.84	5.7	0.99	0.67
VScO	3.89	1.2	0.98	2.24	2.4	0.96	0.14

sizes and adsorbent dosages, the calculated equilibrium capacity values ($q_{e,calc}$), were very close to the experimentally determined values (q_e). The k_2 values represent the steepness of the curve and describe the rate of Cd(II) uptake.

In general, excellent fits ($R^2 > 0.99$) for both VScO and VPum were observed for all particle sizes and adsorbent dosages indicating that the pseudo-second order kinetic model is applicable. The applicability of this model imply that the rate limiting step may be chemisorption involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate [22].

3.8. Adsorption isotherms

Plots and calculations of the adsorption isotherms in terms of Freundlich and Langmuir equations for cadmium (Fig. 7a and b) yielded characteristic parameters and the degree of correlation as shown in Table 4. Analysis of the relationship between the adsorption capacity of the materials (VPum and VScO) and different Cd(II) initial concentrations ($C_0 = 0.5, 2, 5, 25$ and 50 mg L^{-1}) was performed using the isotherm equations (Eqs. (5) and (6)), as given in subsection 2.4.1. The adsorption of Cd(II) on VPum as well as on VScO at pH of 5 follows both Freundlich and Langmuir type adsorption isotherms. Nevertheless, in the case of Cd(II)–VScO system, the Freundlich equation relatively better describes by the system than the Langmuir one as it is evident from the values of R^2 (Table 4).

The Freundlich adsorption capacity, K , for VPum is very large compared to that of VScO. For VPum the adsorption intensity ($1/n$) was less than unity. This indicates a favourable adsorption, as new sites could be available and the adsorption capacity would be increased. For VScO, $1/n$ value exceed 1 (Table 4), indicating the adsorption bonds are weak and that the capacity of adsorbents decreases as demonstrated by Aziz and co-workers [8]. In addition, the Distribution coefficient (K_d) of the linear adsorption isotherms at low cadmium concentrations ($0.5\text{--}5 \text{ mg L}^{-1}$) for VPum and VScO were calculated. The result revealed that, VPum has a higher K_d value (18.1 L kg^{-1} ; $R^2: 0.99$) than VScO (4.96 L kg^{-1} ; $R^2: 0.99$). This reflects the remarkable cadmium affinity of VPum and its adsorption capacity at low cadmium concentrations.

The Langmuir model has also been found to be applicable to fit the experimental data (Table 4). The monolayer capacity, a , is relatively large for both adsorbents. Different ‘ b ’ values (a constant related to the adsorption-desorption energy) for VPum and VScO indicate significant differences in the retention intensity. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor, R_L , which describes the type of isotherm (Section 2.4.2). The values of R_L calculated according to (Eq. (7)), indicate that a highly favourable adsorption for both adsorbents (Table 4).

3.9. Simultaneous removal

Equilibrium batch adsorption experiments were conducted to investigate the influence of dissolved Cu(II) and Ni(II) on the uptake of cadmium by VPum and VScO. Initial concentrations of 2 mg L^{-1} for each metal were used. The adsorption of the ternary Cd(II), Cu(II) and Ni(II) system on the adsorbents as well as under non-competitive conditions (isolated Cd(II)) was evaluated. The results revealed that the adsorption capacity of the adsorbents in the pres-

ence of the ternary metal mixture was lower (54.5 and 75.5% for VScO and VPum, respectively) than non-competitive conditions (60.5 and 86.5% for VScO and VPum, respectively). This confirms that the tested cations actually compete for similar (limited) adsorbing sites. The adsorption of metal ions is not only governed by the “free” metal concentration, but also by the nature and quantity of the adsorbents [29]. Therefore, given that enough volcanic rock grains are provided, Cd(II) ions could be removed even from a metal bearing ion matrix.

4. Conclusions

This study provides valuable information about the adsorption behaviour of VPum and VScO in aqueous solutions, and their efficiency to reduce cadmium mobility and availability. Both VPum and VScO are capable of removing cadmium ions from water. Although the study parameters such as the contact times, adsorbent/solution ratios, particle sizes, presence of other divalent metals and initial cadmium concentrations of the solution significantly affect the removal efficiency, Cd(II) uptake is primarily a function of pH. Adsorption increases with pH until the cadmium ions are precipitated out as cadmium hydroxide. It was found that the pseudo second-order kinetic model gave the best fit with the experimental data and therefore, the adsorption followed a mechanism based on second-order kinetics. The equilibrium data satisfied both the Langmuir and Freundlich isotherm models, and the related parameters indicated that while the interactions are predominantly chemical nature, the adsorption sites could be non-specific and not uniform in nature. Moreover, VPum was able to adsorb cadmium ions to a large extent compared to VScO, and the removal percentage was higher at the lowest cadmium concentration. The adsorption coefficients agree well with the conditions supporting favourable adsorption. Removal of cadmium from aqueous solutions by adsorption onto volcanic rocks (VScO and VPum), which are abundant and low cost adsorbents, could be technically feasible.

Acknowledgements

The first author is grateful to the Catholic Academic Exchange Service of Germany (KAAD) for its financial support during this study. Constructive and valuable comments provided by the reviewers were helpful to improve this manuscript.

References

- [1] T. Alemayehu, Heavy metal concentration in the Urban Environment of Addis Ababa, Ethiopia, Soil Sediment. Contaminat. 15 (2006) 1–12.
- [2] P.N.M. Schipper, L.T.C. Bonten, A.C.C. Plette, S.W. Moolenaar, Measures to diminish leaching of heavy metals to surface waters from agricultural soils, Desalination 226 (1–3) (2008) 89–96.
- [3] WHO, Guidelines for Drinking Water Quality. First Addendum to 3rd ed., vol. 1: Recommendations, World Health Organization, Geneva, Switzerland, 2006.
- [4] W. Teeykasem, M. Nishijo, R. Honda, S. Satarug, W. Swaddiwudhipong, W. Ruangyuttikarn, Monitoring of cadmium toxicity in Thai population with high-level environmental exposure, Toxicol. Lett. 169 (2007) 185–195.
- [5] M.M. Benjamin, R.S. Sletten, R.P. Bailey, T. Bennett, Sorption and Filtration of Metals Using Iron-Oxide-Coated Sand, Water Res. 30 (11) (1996) 2609–2620.
- [6] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, J. Hazard. Mater. B97 (2003) 219–243.
- [7] C.-H. Lai, C.-Y. Chen, B.-L. Wei, S.-H. Yeh, Cadmium adsorption on goethite-coated sand in the presence of humic acid, Water Res. 36 (20) (2002) 4943–4950.

- [8] H.A. Aziz, M.N. Adlan, K.S. Ariffin, Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr (III)) removal from water in Malaysia: post-treatment by high quality limestone, *Bioresour. Technol.* 99 (6) (2008) 1578–1583.
- [9] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, *Water Res.* 33 (11) (1999) 2469–2479.
- [10] S.S. Gupta, K.G. Bhattacharyya, Immobilization of Pb(II), Cd(II) and Ni(II) ions on kaolinite and montmorillonite surfaces from aqueous medium, *J. Environ. Manag.* 87 (1) (2008) 46–58.
- [11] S.E. Bryan, Pumice rafting and faunal dispersion during 2001–2002 in the Southwest Pacific: record of a dacitic submarine explosive eruption from Tonga, *Earth Planetary Sci. Lett.* 227 (2004) 135–154.
- [12] M. Khandaker, A. Hossain, Properties of volcanic pumice based cement and lightweight concrete, *Cement Concrete Res.* 34 (2004) 283–291.
- [13] M.R. Moufti, A.A. Sabtan, O.R. El-Mahdy, W.M. Shehata, Assessment of the industrial utilization of scoria materials in central Harrat, Saudi Arabia, *Eng. Geol.* 57 (2000) 155–162.
- [14] C.E. Suh, J.F. Luhr, M.S. Njome, Olivine-hosted glass inclusions from Scoriae erupted in 1954–2000 at Mount Cameroon volcano, West Africa, *J. Volcanol. Geotherm. Res.* 169 (1–2) (2008) 1–33.
- [15] G. Assefa, The mineral industry of Ethiopia: present conditions and future prospects, *J. African Earth Sci.* 3 (3) (1984) 331–345.
- [16] C. Reimann, K. Bjorvatn, B. Frengstad, Z. Melaku, R. Tekle-Haimanot, U. Siewers, Drinking water quality in the Ethiopian section of East African Rift Valley I—data and health aspects, *Sci. Total Environ.* 311 (2003) 65–80.
- [17] J.S. Kwon, S.T. Yun, S.O. Kim, B. Mayer, I. Hutcheon, Sorption of Zn (II) in aqueous solution by scoria, *Chemosphere* 60 (10) (2005) 1416–1426.
- [18] M.R. Panuccio, F. Crea, A. Sorgona, G. Cacco, Adsorption of nutrients and cadmium by different minerals: experimental studies and modelling, *J. Environ. Manag.* 88 (4) (2008) 890–898.
- [19] M. Yavuz, F. Gode, E. Pehlivan, S. Ozmert, Y.C. Sharma, An economic removal of Cu²⁺ and Cr³⁺ on the new adsorbents: pumice and polyacrylonitrile/pumice composite, *Chem. Eng. J.* 137 (3) (2007) 453–461.
- [20] J.M. Morgan-Sagastume, A. Noyola, Evaluation of an aerobic submerged filter packed with volcanic scoria, *Bioresour. Technol.* 99 (7) (2008) 2528–2536.
- [21] C. Liu, J.B. Evett, *Soil Properties—Testing, Measurement, and Evaluation*, Banta Book Company, USA, 2003, ISBN 0-13-093005-9.
- [22] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Process Biochem.* 34 (1999) 451–465.
- [23] Y.S. Ho, Removal of copper ions from aqueous solution by tree fern, *Water Res.* 34 (2003) 2323–2330.
- [24] M.T. Morera, J.C. Echeverria, C. Mazkarian, J.J. Garrido, Isotherms and sequential extraction procedures for evaluating sorption and distribution of heavy metals in soils, *Environ. Pollut.* 113 (2001) 135–144.
- [25] I. Kula, M. Ugurlu, H. Karaoglu, A. Celik, Adsorption of Cd(II) ions from aqueous solutions using activated carbon prepared from olive stone by ZnCl₂ activation, *Bioresour. Technol.* 99 (2008) 492–501.
- [26] B. Benguella, H. Benaïssa, Cadmium removal from aqueous solutions by chitin: kinetic and equilibrium studies, *Water Res.* 36 (2002) 2463–2474.
- [27] M.R. Panuccio, A. Sorgona, M. Rizzo, G. Cacco, Cadmium adsorption on vermiculite, zeolite and pumice: batch experimental studies, *J. Environ. Manag.* 90 (1) (2009) 364–374.
- [28] H.A. Elliott, C.P. Huang, Adsorption characteristics of some Cu (II) complexes on aluminosilicates, *Water Res.* 15 (1981) 849.
- [29] B.Y.M. Bueno, M.L. Torem, F. Molina, L.M.S. de Mesquita, Biosorption of lead (II), chromium (III) and copper (II) by *R. opacus*: equilibrium and kinetic studies, *Miner. Eng.* 21 (2008) 65–75.