Use of porous volcanic rocks for the adsorptive removal of copper

Esayas Alemayehu[1], Fekadu Melak[2], Saroj K. Sharma[3], Bart Van der Bruggen[4] & Bernd Lennartz[5]

[1]School of Civil & Environmental Engineering, Institute of Technology, Jimma University, Jimma, Ethiopia; [2]Department of Environmental Health Sciences and Technology, Jimma Institute of Health, Jimma University, Jimma, Ethiopia; [3]UNESCO – IHE Institute for Water Education, Delft, The Netherlands; [4]Department of Chemical Engineering, KU Leuven, Belgium; and [5]Institute for Land Use, Rostock University, Rostock, Germany

Abstract

Low-cost adsorbents, pumice (VPum) and scoria (VSco) were investigated for the removal of Cu(II) as function of various parameters. Batch experiments were conducted to evaluate the influence of Cd(II) and Ni(II) on the adsorptive removal of Cu(II) from aqueous solutions. Kinetic data showed a trend of fast removal at initial stages, thereby achieving maximum adsorption after 1 h agitation. The adsorption process well explained by pseudo-second-order kinetics for both adsorbents. Adsorption capacity were found 1.432 and 1.015 mg/g using VPum and VSco, respectively. This work showed the promising nature of pumice and scoria to effectively remove copper from water.

Introduction

Contamination of water networks via copper (Cu) has been known from natural as well as anthropogenic sources. Natural sources of copper mainly from weathering of copper-bearing rocks whereas anthropogenic sources including discharge from municipal and industrial wastes, as well as from corrosion of pipes and agricultural applications are among the major sources of copper in water bodies (Jarup 2003; Shrivastava 2009). Cu is an essential element to living organisms, however, its excessive occurrence in drinking water supplies causes undesirable health effects. Moreover, the toxicity of Cu on aquatic organisms occurs even at very low concentrations in natural waters (WHO 2006; Shrivastava 2009). To reduce such effects, stringent regulations were set by different organisations and countries (WHO 2011).

Various methods have been used for copper removal from water including ion exchange, precipitation, membrane separation and adsorption processes (Dabrowski et al. 2004; Bhattacharyya & Gupta 2007; Shrivastava 2009). Most of them posses multiple drawbacks such as removal inefficiency, high sludge production and high cost requirement. However, adsorption using low-adsorbents has received wide attention to mitigate trace elements, including Cu (Zhou et al. 2012).

Several adsorbents have been examined for Cu(II) adsorptive removal and some of them warrant for further research.

For instance, sawdust (Yu et al. 2000), bentonite clay (Helena et al. 2011), gisenyi volcanic rocks (Sekomo et al. 2012), scoria (Seyfi et al. 2015) and iron oxide nanoparticle-coated volcanic rocks (Zhu et al. 2015) have been investigated for Cu(II) removal.

Alternatively, the application of virgin volcanic rocks for Cu(II) removal, VPum and VSco, which are aboundantly found in many parts of the world, including Ethiopia has become a focus of the study. VPum is part of rhyolite volcanic rocks which has a microvesicular texture formed from the solidified forthy lava when rocks are violently heated and pressurised to rise from a volcano. VPum is characterised with its high porosity and skeletal structure which allow ions to reside in its overall framework. VPum is amorphous in nature, and it also posseses contents mainly quartz and feldspar, which are crystaline phases. Similarly, VSco is among texturally macrovesicular volcanic rocks which is relatively more denser than VPum. Its formation is from the lower viscous magma and mostly composed of mafic minerals such as pyroxene, olivine, plagioclase, hornblende and hematite (Moufti et al. 2000; Hossain 2004).

Therefore, the main objectives of this work were: (1) to investigate Cu(II) removal capacity of VPum and VSco under batch system, (2) to establish the competitive effects of divalent metal ions, Cd(II) and Ni(II) upon Cu(II) adsorption and (3) to compare the cost of VPum and VSco with other types of adsorbents.

Materials and methods

Adsorbent characterisation

VPum and VSco from main Rift Valley, Ethiopia were used as adsorbents. VPum and VSco were washed repeatedly with double-distilled water. The adsorbents were separated into four parts as silt (<0.075 mm), fine (0.075–0.425 mm), medium (0.425–2.0 mm) and coarse (2.0–4.75 mm) size in accordance with (ASTM D 422) (Liu & Evett 1992, 2003). All the experiments, excluding the study on the effects of particle size and adsorbent dose, were performed using the fine particles. The chemical composition of the adsorbents were determined using X-ray fluorescence (XRF) spectrometry. Surface area of each of VPum and VSco was determined using BET method by a Thermo Sorptomatic 1990 Analyzer. Surface area analyser works by N_2 adsorption method after degassing. The procedure for specific surface area determination was made according to a standard procedure following Dogan and his colleagues (2006). Cation exchange capacity of the adsorbents was performed following (Meier & Kahr 1999) procedures.

Reagents

1000 mg/L stock solution of Cu(II) was prepared from $CuCl_2.2H_2O$ (Merck, Germany). Working solutions were prepared in 0.01 M $CaCl_2.2H_2O$ ionic strength solution, keeping the ionic strength nearly constant. Fresh dilutions were utilised during each experiment. Cu(II) stock solution was stored at 4°C in a capped plastic bottles. The pH of the system was adjusted using 0.1 M HCl and 0.1 M NaOH. The experiments were conducted under CO_2 free conditions to ensure no influence in pH from the system.

Experimental Procedure

Batch adsorption experiments were carried out in triplicate with blank (adsorbents without test substance) and control (test substance without adsorbents), and the average results were reported. To evaluate the adsorption of Cu(II), solutions of known initial concentration were agitated with a horizontal shaker of (SM 25, Edmund Bühler GmbH, Hechingen, Germany) at pretested speed of 200 rpm. In the experiment, each adsorbent was added to 0.5 L of known concentrations of Cu(II) solutions. After equilibration, supernatant solutions were sampled using a syringe and filtered through 0.2 μm membrane filters. Then, the concentration of Cu(II) in the filtrate was determined by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometer), JY 238. The pH was measured using a pH 196 Microprocessor (WTW-GmbH, Germany).

Table 1 Chemical composition of VPum and VSco from main rift valley of Ethiopia based on XRF analysis

Composition (% wt)	VPum	VSco
SiO_2	68.6	47.4
Al_2O_3	8.9	21.6
Fe_2O_3	4.9	8.9
CaO	1.8	12.4
K_2O	5.5	0.5
Na_2O	4.1	3.0
MgO	0.2	3.3
TiO_2	0.3	1.7
Others	5.7	1.2

Competition of divalent ions

To investigate the effect of divalent ions on Cu(II) removal, both metal ions, Cd(II) and Ni(II) in separate and in binary level were added into the 2 mg/L Cu(II) containing solutions. The adsorption processes have been tested using 2 mg/L of each metal ions, keeping all other experimental conditions at optimal (temperature 25°C, dose 50 g/L, speed 200 rpm).

Results and discussion

Adsorbent characterisation

The chemical composition of VPum and VSco showed relatively high percentage of SiO_2, Al_2O_3 and Fe_2O_3 oxides (Table 1). Previous studies (Fan *et al*. 2000; Ehrampoush *et al*. 2013) indicated that the expected reason for the enhancement of adsorption of Cu(II) could be due to the presence of amphoteric oxides.

The percent composition of SiO_2 analysed for VSco was found comparable to the commercial scoria, which is mostly reported in the range of 50–60% (Harben & Kužvart 1996; Le Maitre 2007). The composition of main oxides of VSco: SiO_2, Al_2O_3, Fe_2O_3 and CaO found in good agreement with Iranian scoria (Seyfi *et al*. 2015). Important physichochemical properties of adsorbents are detailed in Table 2.

Effect of agitation time

Cu(II) removal kinetics was illustrated in Fig. 1. Thus, adsorption followed a trend of fast removal during the first 0.5 h and progressively decreased thereafter attaining equilibrium after 1h agitation for both adsorbents. However, to avoid

Table 2 Physicochemical properties of VPum and Vsco adsorbents

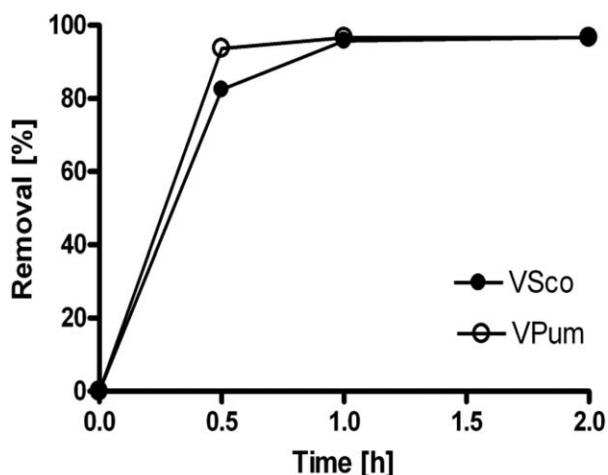| Components	VPum	VSco
Specific surface area (m^2/g)	3.5	2.49
Cation exchange capacity, meq/100 g	0.84	0.09
Fraction size (mm)	0.075–0.425	0.075–0.425
pH in water	7.7	7.6
Density (g/cm^3)	2.46	2.98

Fig. 1. Effect of agitation time on the adsorption of Cu(II) using VPum and VSco (mean ± standard deviation, $n = 3$; conditions: initial concentration 2 mg/L, dose 50 g/L, pH 5 ± 0.1, working volume 0.5 L and temperature 25°C).

uncertainty in equilibrium time, 2 h agitation was considered in this study. Alternatively, studies conducted using same adsorbents for Cd(II) and Ni(II) removal showed longer equilibrium time, 24 h (Alemayehu & Lennartz 2009, 2010).

Effect of particle size

The results on adsorbent particle size showed that the grain-size reduction significantly influenced Cu(II) removal in the VSco-system. On changing the particle size of VSco from coarse to silt, Cu(II) removal increased from 74 to 98% (Fig. 2b), indicating that the adsorption efficiency is dependent on the particle size of the grains. This can be explained by the presence of larger number of smaller particles, which provide the adsorption system with a high surface area (Alemayehu *et al*. 2012) and also reduce the external mass transfer, film diffusion resistance (Alemayehu & Lennartz

2009). On the other hand, the effect of particle size in case of VPum found unimportant (Fig. 2a). The porous nature of Vpum would be tailored on further size changes. As a result, the increase in surface area of Vpum due to the particle size decrement would not outperform in enhancing adsorption efficiency. The extent of adsorption could increase with decreasing particle size due to surface area increment, for most cases, however, there were cases reported differently due to the nature of adsorbents (Tsai *et al*. 2003; Müller 2010).

Effect of adsorbent dose

The effect of amount of adsorbent (4–50 g/L) on the adsorption of Cu(II) was investigated maintaining other conditions constant. The effect of adsorbent dose for both adsorbents were shown in Fig. 3a,b. VPum was more efficient than VSco at all levels of adsorbent dose assayed (e.g. VPum: 85% and VSco: 39% at 4 g/L of adsorbent dose). Upon further increment of adsorbent dose right from 4 g/L, relatively a smaller change on the removal efficiency of VPum system was observed (Fig. 3a). However, on changing VSco dose from 4 to 50 g/L, the removal of Cu(II) increased from 39 to 97%. Maximum removal was observed at 50 g/L in solid (adsorbent) – solution ratio of 1 : 20 for VSco adsorbent (Fig. 3b).

Effect of pH

The influence of solution pH upon Cu(II) adsorption onto VPum and VSco, was studied in the pH range of 2–12, as shown in Fig. 4. It was observed that adsorptive removal of Cu(II) increased as the pH of the solution increased for both adsorbents. In the range of initial pH 2–6, percent efficiency increased from 30 to 98% for VPum and from 10 to 95% for VSco. It was reported that metal oxide surfaces of adsorbents in water develop a favourable charge through hydrolysis of amphoteric oxides, which favour the removal of
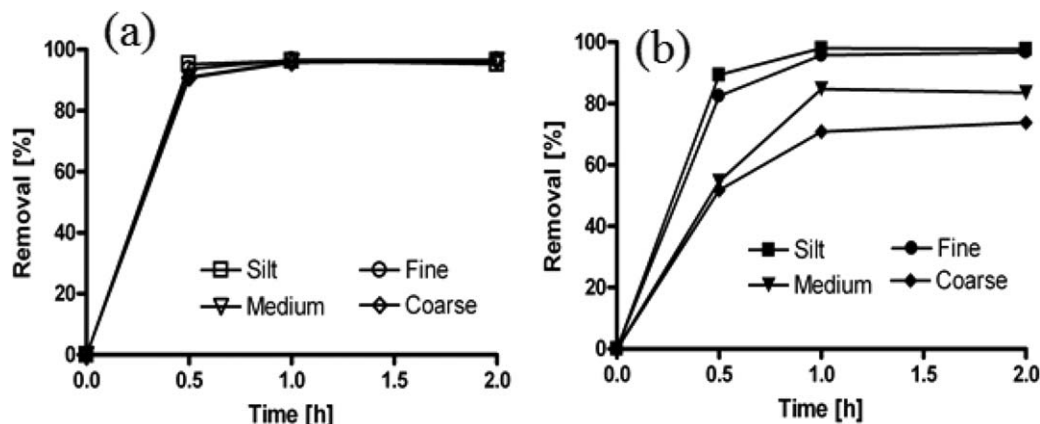

Fig. 2. Effect of particle size on the adsorption of Cu(II) using VPum (**a**) and VSco (**b**) (mean ± standard deviation, $n = 3$; conditions: contact time 2 h, initial concentration 2 mg/L, dose 50 g/L, pH 5 ± 0.1, working volume 0.5 L and temperature 25°C).
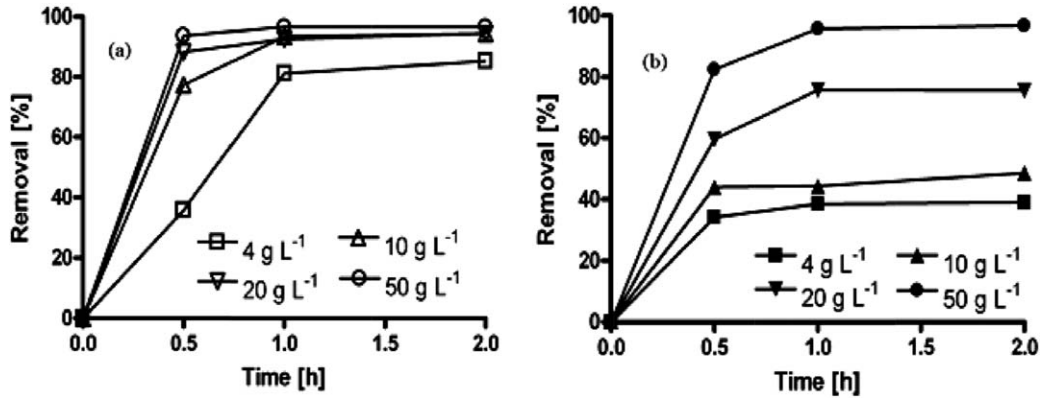
Fig. 3. Effect of VPum (**a**) and VSco (**b**) dosage on the adsorption of Cu(II) (mean ± standard deviation, $n = 3$; conditions: initial concentration 2 mg/L, pH 5 ± 0.1, working volume 0.5 L and temperature 25°C).

cations at higher pH (Bhattacharyya & Gupta 2007; Yavuz *et al*. 2008). When pH increased beyond pH 7, precipitation of Cu(II) occurs simultaneously with the adsorption of Cu(II) ions as is affirmed in literature (Weng *et al*. 2007). However, little Cu(II) removal at low pH values indicated that oxide groups Al_2O_3, SiO_2, Fe_2O_3 etc., could be protonated, and excess of the hydronium ions compete with Cu(II) ions for active binding sites. The optimal pH for adsorption was found to be between 4 and 6. Thus, an initial pH value of 5 was chosen for Cu(II) adsorption experiments.

Effect of initial Cu(II) concentration

The equilibrium adsorption capacity of Cu(II) ions on both VPum and VSco increased when the initial concentration increased (Fig. 5a). Changing the concentration in the range from 0.5 to 50 mg/L increased the amount of Cu(II) ions per unit mass from 10 to 932 mg/kg on VPum and from 10 to 752 mg/kg in case of VSco.
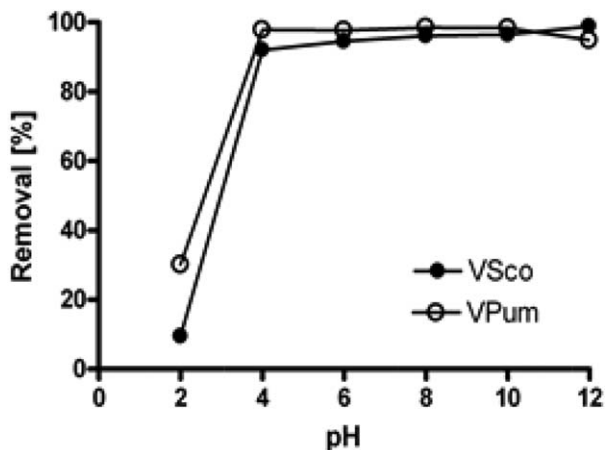

Fig. 4. Effect of pH on the adsorption of Cu(II) (conditions: Initial concentration 2 mg/L, dose 50 g/L, working volume 0.5 L and temperature 25°C).

Competitive adsorption

The effect of Cd(II) and Ni(II) on the uptake of Cu(II) was studied. The initial concentrations used for each metal was 2 mg/L, keeping all other experimental conditions at optimal. It was found that the adsorption efficiency of VSco for Cu(II) in the presence of Cd(II) and Ni(II) was relatively lower (85%) than that under non-competitive conditions (97%). However, the presence of these metals did not suppress the removal of Cu(II) ions in the VPum system (<1% difference). This could be due to the valuable properties of VPum such as surface-exposed ionic charge, porosity, wearability and surface area (Skoog *et al*. 2004; Yavuz *et al*. 2008; Alemayehu & Lennartz 2009). The result was in support of the observations that bentonite clay, montmorillonite, sericite, kaolinite, halloysite and allophane clays revealed the strong adsorption ability of Cu(II) over Cd(II) (Itami & Yanai 2006; Helena *et al*. 2011).

Kinetic models

To express the removal kinetics of Cu(II), the experimental data were fitted with Lagergren pseudo-first-order and pseudo-second-order models (Ho & McKay 1999). The pseudo-first-order equation of Lagergren is generally expressed as:

$$dq_t/dt = k_1(q_e - q_t) \qquad (1)$$

Where q_e and q_t are adsorbed amounts of Cu(II) (mg/kg) at equilibrium and at time (t), respectively, and k_1 is the pseudo-first-order adsorption rate constant in (h^{-1}). Integrating equation (1) provides:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (2)$$

The pseudo-first-order rate parameters were presented in Table 3, where k_1 being defined from the slope of the graph of $\log(q_e-q_t)$ versus time t (h).
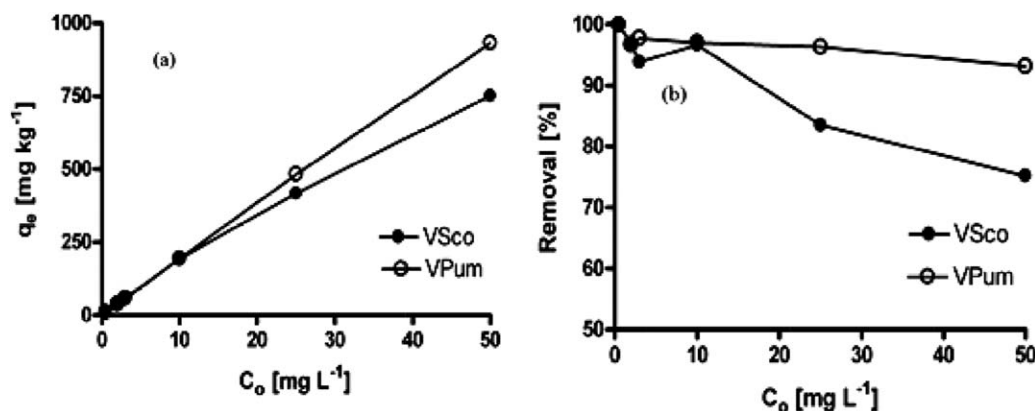
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Fig. 5. Effect of initial Cu(II) concentration on the adsorption capacity (**a**) and percentage removal (**b**) (mean ± standard deviation, $n = 3$; conditions: contact time 2 h, dose 50 g/L, pH 5 ± 0.1, working volume 0.5 L, concentration of 0.5–50 mg/L and temperature 25°C)

Table 3 Pseudo-first-order rate constants of Cu(II) ions on fine particle sizes

Adsorbents	$q_{e, \, exp}$ (mg/kg)	q_e (mg/kg)	k_1 (1/h)	R^2
VPum	35.47	36.45	4.52	0.95
VSco	33.43	35.12	2.14	0.89

Table 4 Values of pseudo-second-order rate constants of Cu(II) ions on various particle sizes and adsorbent doses

Adsorbents	Variables	$q_{e, \, exp}$ (mg/kg)	q_e (mg/kg)	k_2 (kg/mg h)	R^2
VSco	Silt[a]	39.13	39.53	1.28	0.99
	Fine[a]	38.71	39.23	0.65	0.99
	Medium[a]	33.43	35.10	0.26	0.99
	Coarse[a]	29.50	30.60	0.34	0.99
VPum	Silt[a]	38.13	38.17	13.73	1.00
	Fine[a]	38.69	38.76	3.33	0.99
	Medium[a]	38.57	38.76	2.22	0.99
	Coarse[a]	38.53	38.76	2.22	0.99
VSco	50[b]	38.71	39.22	0.001	0.99
	20[b]	30.23	30.96	0.58	0.99
	10[b]	19.41	19.49	1.25	0.99
	4[b]	15.59	15.77	2.12	0.99
VPum	50[b]	38.69	38.76	3.33	0.99
	20[b]	37.78	38.02	1.38	0.99
	10[b]	37.77	38.76	0.56	0.99
	4[b]	34.11	38.61	0.08	0.85

[a]Particle size.
[b]Dose (g/L).

As shown in Table 3, the adsorption kinetics were not well explained using pseudo-first-order kinetics (from observation of R^2).

The experimental data was also evaluated using pseudo-second-order reaction as:

$$(t/q_t) = (1/k_2 q_e^2) + (1/q_e)t \qquad (3)$$

where k_2 is the rate constant (kg/mg h). The values of k_2 and q_e were calculated from the intercept ($1/k_2 q_e^2$) and slope ($1/$

q_e) of plot t/q_t versus t of Eq. (3). Parameters q_e, $q_{e,\mathrm{exp}}$ (mg/kg), coefficient of determination (R^2) and pseudo-second-order rate constant k_2 (kg/mg h) were reported in Table 4. A high degree of correlation in the experimental data to pseudo-second-order equation indicated that adsorption process was governed by chemisorption processes as described in literatures (Ho & McKay 1998, 1999).

Isotherm models

Freundlich and Langmuir non-linear model equations were used to define the adsorption behaviour of the experimental data as expressed in Eqs. (4) and (5).

$$\text{Langmuir equation: } q_e = (a_L K_L C_e)/(1 + K_L C_e) \qquad (4)$$

$$\text{Freundlich equation: } q_e = K_F C_e^{nF} \qquad (5)$$

where q_e (mg/kg) is the Cu(II) quantity adsorbed per unit mass of the adsorbent and C_e (mg/L) is the concentration of Cu(II) in the solution at equilibrium. The Langmuir constants a_L (mg/kg) and K_L (L/mg) refer adsorption density and adsorption energy, respectively. Langmuir parameters can be obtained from the linear correlation of C_e/q_e and C_e. Model parameters of the above equations were summarised in Table 5. The adsorption of Cu(II) on VPum and VSco were well fitted with both Freundlich and Langmuir

Table 5 Freundlich and Langmuir isotherm constants of VPum and VSco

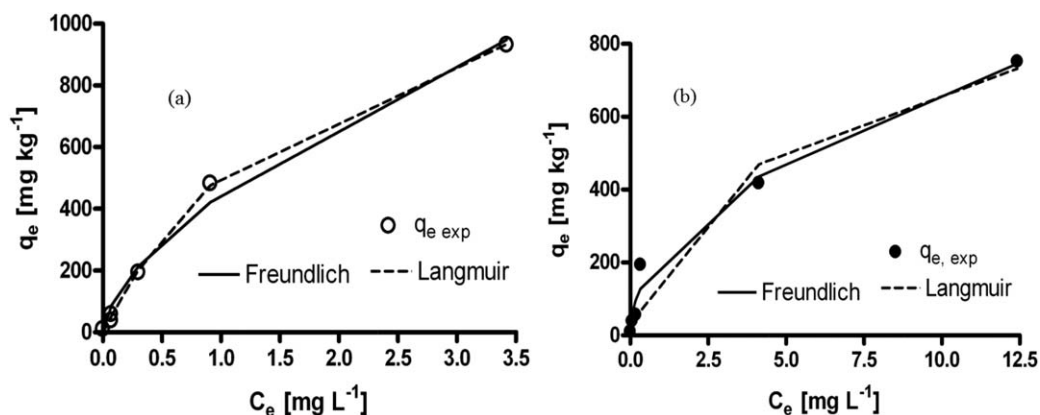| Adsorbent	Freundlich constants			Langmuir constants			
	K_F (L/kg)	n_F	R^2	a_L (mg/kg)	K_L (L/mg)	R^2	R_L
VPum	446	0.61	0.99	1432	0.55	0.99	0.04-0.79
VSco	219	0.49	0.98	1015	0.21	0.97	0.09-0.91

Fig. 6. Freundlich and Langmuir isotherms of Cu(II) using VPum (**a**) and VSco (**b**) (mean $\pm$ standard deviation, $n = 3$; conditions: concentration of 0.5 to 50 mg/L, contact time 2 h, dose 50 g/L, pH 5 $\pm$ 0.1, working volume 0.5 L and temperature 25°C).

Table 6 Previously reported adsorption capacities of various adsorbents for Cu(II)

Adsorbent	Adsorption capacity (mg/g)	Reference
Lignite	1.5	Karabulut *et al.* (2000)
Natural kaolinite clay	1.12	Jiang *et al.* (2010)
Sawdust	1.79	Yu *et al.* (2000)
Ball clay	1.6	Chantawong *et al.* (2003)
Gisenyi Volcanic Rock	10.87	Sekomo *et al.* (2012)
Dolomite	3.24	Pehlivan *et al.* (2009)
Organosolv lignin	1.7	Harmita *et al.* (2009)
VSco	1.02	In this study
VPum	1.43	In this study

Comparison of VPum and VSco adsorption capacities (Table 6) showed that these adsorbents are relatively comparable and good adsorbents in considering Cu(II) removal from water.

adsorption isotherms (Fig. 6a,b). The results confirmed that Freundlich adsorption capacity, K_F, of VPum was larger as compared to VSco. The combined effects of n_F values being less than unity for both adsorbents and the kinetic model

fitting to pseudo-second-order, notify the chemical nature of adsorbate-adsorbent binding in the adsorption process.

In Table 6, an insight of the adsorption capacities of various low-cost sorbents for Cu(II) removal were presented. Although the adsorbents studied, VPum and VSco seem efficient, further work on the regeneration of the adsorbents and copper recovery as well as modifying the adsorbents for better efficiency is essential.

Cost estimation

In Ethiopia, VPum has an average cost of about US \$40 ton^{-1} and VSco of US \$45 ton^{-1} including the transportation cost. This price was basically obtained from an average Ethiopian local market under negotiation base on the year 2012. In Table 7, estimation of the costs of adsorbents were presented along with volcanic rocks (VPum and VSco).

Table 7 Cost of volcanic rocks and other adsorbents as reported in literature

Adsorbent	Price (US \$ton^{-1})	Reference
Diatomite (without processing)	7	Crangle (2012)
Diatomite from high-grade deposits	> 400	Crangle (2012)
Commercial granular activated carbon	3 300	Toles *et al.* (2000)
Perlite	<1500	Mathialagan &Viraraghavan (2002)
Commercial activated carbon	20 000	Atun *et al.* (2003)
Spheroidal cellulose	1070	Babel & Kurniawan (2003)
Chitosan	7000-28 000	Kyzas *et al.* (2013)
Chitosan	16 000	Babel & Kurniawan (2003)
Coconut shell charcoal	340	Babel & Kurniawan (2004)
VSco[a]	<45	In this study
VPum[a]	<40	In this study

[a]Initial cost, in 2012 Ethiopian market price.

Conclusions

Batch adsorption of Cu(II) using VPum and VSco was found to be rapid in the first 0.5 h which ~75% Cu(II) was removed. The rate of adsorption process (pseudo-second order) indicated that the plausible mechanism of adsorption could be chemosorption for both adsorbents studied. The estimated maximum adsorption capacity of 1.432 and 1.015 mg/g was observed for Cu(II) removal upon VPum and VSco, respectively, for the studied concentration ranges. The adsorption efficiency of VSco in the presence of Cd(II) and Ni(II) was relatively lower (85%) than that under non-competitive conditions (97%), indicating Cd(II) and Ni(II) ions compete for Cu(II) removal. It is concluded that the two abundantly available sorbents were found to be promising for the removal of Cu(II) from aqueous solutions.

Acknowledgement

Declaration

Authors confirmed that there is no any actual or potential conflicts of interest including any financial, personal or other relationships with other people or organisations that could inappropriately influence the work.

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