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Adsorption behaviour of Cr(VI) onto macro and micro-vesicular volcanic rocks from water

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ABSTRACT

Adsorption by volcanic rocks is investigated as a possible alternative to the conventional method of Cr(VI) removal from polluted waters. In this work, adsorption of Cr(VI) onto pumice (VPum) and scoria (VSco) has been studied by using a batch method at room temperature. The following factors affecting sorption of Cr(VI) were investigated: solution pH, contact time, type and size of adsorbents, adsorbent dose and initial metal ion concentration. The maximum adsorption yield, 77% for VSco and 80% for VPum, was obtained at low pH of about 2. The applicability of the Langmuir as well as Freundlich adsorption isotherms for the present system is tested. The batch sorption kinetics has been mathematically described using the Lagergren pseudo-first order, pseudo-second order equations and equations for intra-particle and liquid film diffusion. For both VPum and VSco, the entire kinetic data fitted well with pseudo-second-order reaction rate model. In the case of VSco, the rate constant was the highest ($338 \times 10^{-3}\,\mathrm{kg\,mg^{-1}\,h^{-1}}$) and the VPum gave the lowest ($7 \times 10^{-3}\,\mathrm{kg\,mg^{-1}\,h^{-1}}$). The experimental results inferred that electrostatic attraction and surface complexation are the major adsorption mechanisms for binding Cr(VI) ions to the macro and micro-vesicular volcanic rocks. The two volcanic rocks tested have potential for an inexpensive and suitable method for removal of Cr(VI) from polluted waters.

1. Introduction

In the aquatic environment, chromium primarily exists in two oxidation states: Cr(VI) and Cr(III). These two oxidation states have different chemical, biological and environmental properties. The abundant ratio of Cr(VI) and Cr(III) depends on many factors, such as the redox potential, pH, the presence of oxidizing and reducing compounds, the kinetics of the redox reactions, and the total chromium concentration [1]. Public concerns with chromium are mostly related to hexavalent compounds, because these compounds are toxic to humans, animals, plants and microorganisms [2]. Cr(VI) species, having mobile and strongly oxidant characters, are known as mutagen and potential carcinogenic [3]. In humans, Cr(VI) mostly affects skin, liver, kidney and respiratory organs, resulting in a variety of diseases such as dermatitis, hepatic and renal tubular necrosis, bronchitis, perforation of the nasal septum and bronchogenic carcinoma [4]. Two major sources of Cr(VI) contamination are sludge-treated soil [5] and uncontrolled disposal of wastes [6]. In most developing countries (e.g., Ethiopia), the latter is believed to be the major source for chromium pollution in water bodies, since land application of sludge has not been widely practiced [7–9]. The chromium electroplating treatment and tanning industries are the largest sources of Cr(VI) emissions to the environment [10].

In view of the pollution hazard caused by Cr(VI), several methods of removal have been reported, including chemical reduction-precipitation, reverse osmosis, ion exchange and electrolysis. Among these methods the chemical reduction–precipitation is the most applicable and considered to be the most economical. Such a method involves two steps; firstly Cr(VI) is chemically reduced to Cr(III) in acid (pH ≈ 2.0) using generally sodium metabisulphite as reducing agent, and subsequently Cr(III) is precipitated as chromium hydroxide (pH ≈ 9.0–10.0) using sodium hydroxide or lime as precipitating agents. The main concern of this technique is the generation of a great amount of sludge that requires further treatment. The other available treatments, although usually effective, are not free of drawbacks, i.e. high capital investment, high running costs and low capability to treat high water volumes and high metal concentrations are the most common [11]. Therefore, the need exists for a purification strategy that is simple, effective and low-cost. In this way, adsorption appears as a highly promising alternative to treat such polluted waters.

A variety of materials are used as adsorbents for Cr(VI), and various studies have been published documenting its adsorption on natural and commercial materials [12–14]. From the light of these studies adsorption emerges as a robust and versatile method that

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could solve the problems of sludge handling and render the purification system more economically viable, especially if low-cost adsorbents are involved. Among natural materials having better features to be used as low-cost adsorbents of heavy metals are volcanic rocks. The most abundant volcanic rocks include pumice (VPum), a textural term for microvesicular, and scoria (VSco) for macrovesicular. VPum and VSco deposits originate in areas with young volcanic fields. These rocks are abundant in many parts of the world [15]. The potential of volcanic rocks to remove both cationic and anionic ions has been reported [16–19]. However, little or no information is available about the adsorptive interactions between Cr(VI) and the volcanic rocks in the aqueous system [20]. Thus, an attempt is made to study their feasibility as an adsorbent for removal of hexavalent chromium from aqueous solution. The effects of major design parameters (pH of solution, initial concentration of Cr(VI), contact time, particle size, and adsorbent/solution ratio) on Cr(VI) adsorption onto VPum and VSco are described.

2. Experimental

2.1. Adsorbent characteristics and adsorbate solutions

The rock samples were taken from volcanic cones (VPum: 8°10′N 39°50′E; VSco: 8°33′N 39°16′E) of the Main Rift Valley of Ethiopia; approximately 100 km East of Addis Ababa. The rocks are indigenous volcanic rocks of different chemical and mineralogical composition, which covers around 1/3 of the area of the country [15,21,22]. VPum is composed of highly *microvesicular pyroclastic* with very thin, translucent bubble walls of extrusive igneous rock [23,24]. It is characterized by a high water absorption capacity (20–30%) due to its high degree of porosity and a very low density. VPum has a skeleton structure that allows ions and molecules to reside and move within the over all framework. It is amorphous with mainly quartz and feldspar as crystalline phases, such mineral composition is typical for *rhyolite* rocks [25,26]. VSco is commonly, but not exclusively, *basaltic* or *andestic* in composition [16,27]. It differs from VPum in being denser, with larger vesicles and thicker vesicle walls; it sinks rapidly. The difference is the result of the lower viscosity of the magma that formed VSco. With regard to its mineral composition, VSco consists of most of the *mafic* minerals: pyroxene, olivine, plagioclase, amphibole (hornblende) and hematite. Such mineral composition is typical for basaltic rocks [16].

In agreement with the American Society for Testing and Materials (ASTM D 422), soil textural classification system [28], the rock samples were crushed and separated into four mesh size fractions: 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 diameter. Preparation and characterization of the rock samples was done as reported earlier [18,19]. The chemical compositions and the physical properties of the adsorbents are listed in Table 1.

All chemicals used in our experiments, such as $K_2Cr_2O_7$, $CaCl_2$ $2H_2O$, NaOH and HCl, were analytical reagent grade chemicals from Merck (Darmstadt, Germany). The varying concentrations of metal solution for adsorption experiments were prepared by diluting the stock solution (1000 mg L^{-1}). In addition, the initial ionic strength of the prepared solutions was adjusted to 0.01 M by adding $CaCl_2$ $2H_2O$ into the solution. The calcium chloride solution was used as the solvent phase to maintain a constant ionic strength and minimize cation exchange.

2.2. Adsorption procedures

Two types of batch adsorption experiments (kinetic and equilibrium) were carried out in batch containers (acid-washed

Table 1
Physical and chemical characteristics of adsorbents used in the experiments.

Chemical composition	Percent	
	VSco	VPum
SiO_2	47.4	68.6
Al_2O_3	21.6	8.9
Fe_2O_3	8.9	4.9
CaO	12.4	1.8
K_2O	0.5	5.5
Na_2O	3.0	4.1
MgO	3.3	0.2
TiO_2	1.7	0.3
Others	1.2	5.7
Physical properties[a]		
Porosity (%)	36	73
Particle density (g cm^{-3})	2.96	2.33
Specific surface area (BET) (m^2 g^{-1})	2.49	3.50
Cation exchange capacity (CEC), mequiv. 100 g^{-1}	0.09	0.84

[a] Particle size = 0.075–0.425 mm.

polypropylene bottles) and were shaken at 200 rpm to homogenize the sample and to facilitate the reaction. The adsorbents were equilibrated by shaking with 0.01 M $CaCl_2$ $2H_2O$ overnight (12 h) before the date of the actual experiments. To check the repeatability of the experimental data, each experiment was conducted twice and data represent the mean value. The errors in the data of blanks and controls were typically less than 5%. Preliminary experiments had shown that Cr(VI) adsorption losses to the container walls and to the filter membrane were negligible (data not shown).

2.2.1. Kinetic experiments and data presentations

The experiments were conducted as a function of time with constant initial Cr(VI) concentration of 2.5 mg L^{-1}, an adsorbent/solution ratio of 1:10, and the particle size ranged from silt to fine grain size (Section 2.1). Before mixing with the adsorbent, the initial pH value was adjusted to 2. The selection of this low pH was also based on the actual pH value of industrial effluents such as tannery effluent (at pH 2) [29], electroplating effluent (at pH 2.2) [30], chromium plating effluent (at pH 1) [31] and the experimental studies reported in the literature [32–34]. After the pH adjustment, the solutions were permitted to attain to equilibrium without further pH control. After shaking the samples, the suspension was allowed to settle for 1 min, and 10 mL of the supernatant were sampled by a syringe. The remaining solids were separated by filtration (0.2 μm, Nylon Membrane Filters, Whatman) and the final pH was measured (Microprocessor pH 196, WTW, Germany). The amount of residual chromium was determined using ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometer, JY 238, Jobin Yvon, Longjumeau, France). To determine kinetic adsorption parameters, the obtained kinetic adsorption data were evaluated by using the simple Lagergren pseudo-first order equation (Eq. (1)) and the pseudo-second order equation (Eq. (2)) [35]. The equations are expressed as:

$$\log(q_e - q_t) = \log \quad q_e - \frac{k_1 t}{2.303} \tag{1}$$

where k_1 is the pseudo-first order rate constant of adsorption (h^{-1}), q_t and q_e (both in mg kg^{-1} adsorbent) is the amount of Cr(VI) adsorbed at time t and at equilibrium, respectively. Straight line plots of $\log(q_e - q_t)$ versus at different times for solute t were obtained to calculate the rate constants and the determination coefficients (R^2).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{2}$$

where k_2, the pseudo-second order sorption rate constant (kg mg^{-1} h^{-1}), gives the steepness of the curve. Plots of t/q_t ver-

sus t for solute were obtained to calculate the rate constants and the determination coefficients (R^2).

Due to rapid stirring in the batch reactor, metal ions are transported from aqueous phase to the surface of adsorbent and subsequently they may diffuse into the interior of the particles if they are porous. The intra-particle diffusion can be expressed by the equation [36]:

$$q_t = k_i t^{0.5} \qquad (3)$$

The plot of q_t versus $t^{0.5}$ yield straight lines passing through the origin and the slope gives the diffusion rate constant, k_i ($mg\,kg^{-1}\,h^{-0.5}$).

When the transport of the adsorbate from the liquid phase up to the solid phase boundary plays the most significant role in adsorption, the liquid film diffusion model [37] may be applied to experimental data:

$$\ln(1 - F) = -k_{fd}t \qquad (4)$$

where F is the fractional attainment of equilibrium ($F = q_t/q_e$) and k_{fd} is the adsorption rate constant. A linear plot of $-\ln(1 - F)$ versus t with zero intercept would suggest that kinetics of the adsorption process is controlled by diffusion through the liquid film surrounding the solid adsorbent.

2.2.2. Equilibrium experiments and data presentations

Separate sets of equilibrium batch experiments were performed to investigate the effect of pH and initial Cr(VI) concentration on adsorption. Solution pH was adjusted to different values ranging from pH 2 to 10 using HCl and NaOH, respectively. Adsorbent dose from 10 to $100\,g\,L^{-1}$, particle size from silt to coarse and initial Cr(VI) concentrations from 0.5 to $10\,mg\,L^{-1}$ were tested. The sample bottles were agitated for 30 h (VSco) and 66 h (VPum); the equilibrium time was determined by kinetic sorption experiments. Temperature (22.4 °C) and shaking speed (200 rpm) were constant for all experiments. Following equilibration, all other experimental conditions were conducted based on the procedures stated in Section 2.2.1. Adsorption isotherms for Cr(VI) were obtained from equilibrium sorption experiments under the following conditions: adsorbent size = 0.075–0.425 mm and initial pH (pH$_{int}$) value ≈2.

To determine isotherm parameters, non-linear isotherm models due to the inherent bias resulting from linearization [38] were fitted to the equilibrium adsorption data. This provides a mathematically rigorous method for determining isotherm parameters using the original form of the isotherm equation. The two widely used isotherms, Langmuir and Freundlich adsorption isotherms were applied to the data, in order to estimate adsorption constants that indicate the adsorption capacity and affinity of the adsorbents. The isotherm equations have been optimized using the sum of the squares of the errors (ERRSQ).

The Langmuir equation is expressed as a non-linear function as follow:

$$q_e = \frac{a_L K_L C_e}{1 + K_L C_e} \qquad (5)$$

where q_e ($mg\,kg^{-1}$) is the specific amount of Cr(VI) adsorbed, and C_e ($mg\,L^{-1}$) is the Cr(VI) concentration in the liquid phase at equilibrium. The Langmuir parameters are a_L ($mg\,kg^{-1}$), which is related to adsorption density, and K_L ($L\,mg^{-1}$), which is indicative of the adsorption energy.

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

$$R_L = \frac{1}{1 + K_L C_o} \qquad (6)$$

where is C_o ($mg\,L^{-1}$) is initial concentration of Cr(VI) in contact with adsorbents. The shapes of the isotherms are indicated by R_L values,

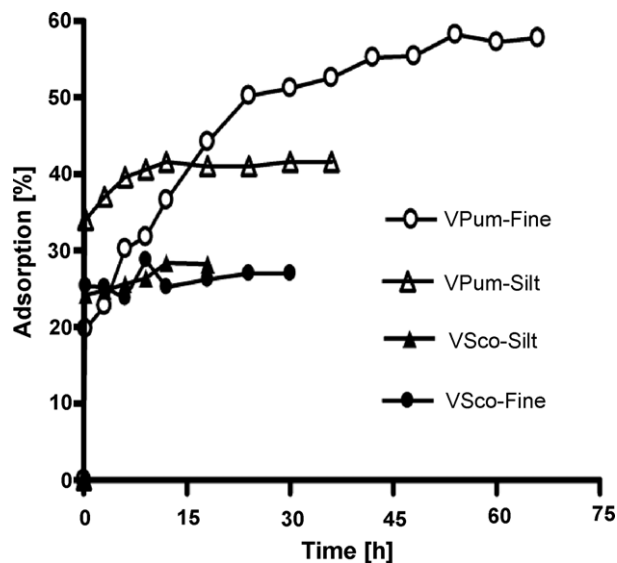

Fig. 1. Effect of contact time on the adsorption of Cr(VI) onto VSco and VPum.

as $0 < R_L < 1$ indicates favorable adsorption, and $R_L > 1$, $R_L = 1$ and 0 represent unfavorable, linear and irreversible isotherm, respectively as demonstrated [38].

The Freundlich equation is written as a non-linear equation:

$$q_e = K_F C_e^{n_F} \qquad (7)$$

where q_e ($mg\,kg^{-1}$) is the specific amount of Cr(VI) adsorbed, and C_e ($mg\,L^{-1}$) is the Cr(VI) concentration in the liquid phase at equilibrium. The parameter K_F ($L\,kg^{-1}$) and n_F (dimensionless) are the Freundlich constants, which are related to the total adsorption capacity and intensity of adsorption, respectively. The Freundlich constant K_F is used to evaluate the relative capacity or power of adsorption for a sorbent.

3. Results

3.1. Effect of contact time

Kinetic adsorption experiments were carried out to find the optimum contact time. It was found that the Cr(VI) adsorption percentage increased with increasing contact time (Fig. 1). In the case of VPum, it is evident that adsorption of Cr(VI) is much stronger than that of VSco, which is clear from the steep increment in removal percentage. This is in agreement with our experimental observation showing higher cation exchange capacity (CEC) and larger porosity of VPum (Table 1). As shown, adsorption process has continued up to 36 h (VPum-silt size) and 66 h (VPum-fine size) before reaching equilibrium. However, in the case of VSco, most of sorption takes place within 18 h (VSco-silt size) and 30 h (VSco-fine size) of contact time, indicating that the adsorption sites are well exposed (adsorption on superficial sites dominated). There does not seem to be much benefit from a contact time longer than 30 h and 66 h for VSco and VPum, respectively. Alemayehu and Lennartz [18,19], using the same adsorbents for removal of divalent cations from water by adsorption, found that the equilibrium time needed for Cu(II), Cd(II), and Ni(II) was shorter (≈2 h for Cu(II); ≈24 h for Cd(II) and Ni(II)) than is shown in this study. This clearly indicated that metal species, initial concentrations of the metal ions as well as the kind of the adsorbents will influence the adsorption processes significantly.
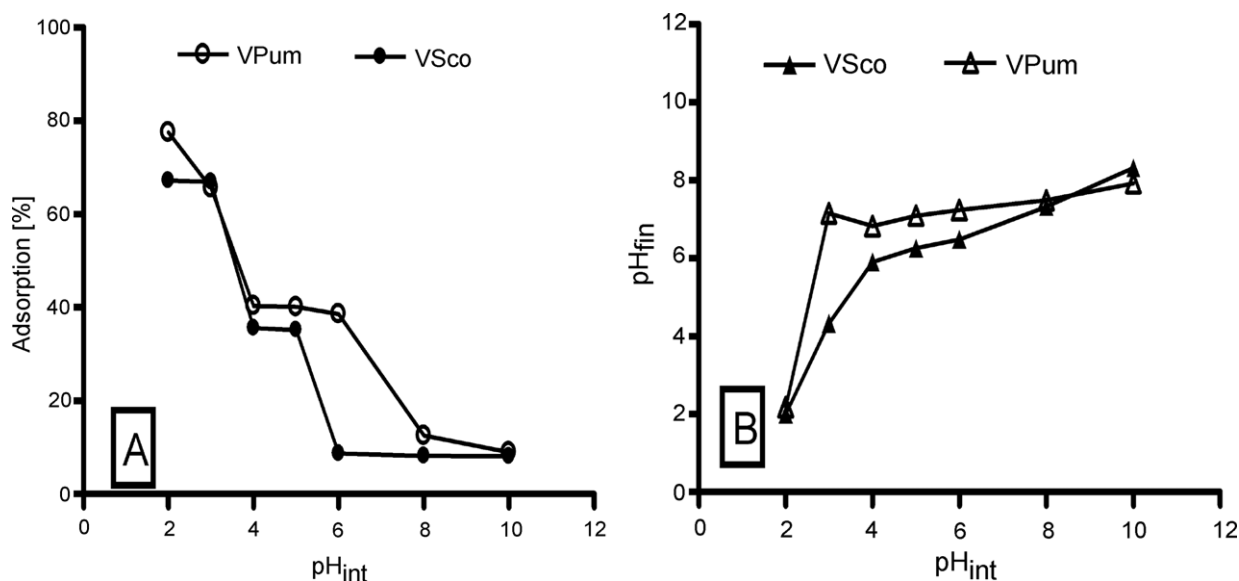
Fig. 2. Effect of the initial solution pH on the adsorption of Cr(VI) onto VSco and VPum (A) and solution pH at the experiment (B).

3.2. Effect of pH

The influence of pH on the adsorption of Cr(VI) onto VPum and VSco was investigated in the pH range of 2–10. Generally, the adsorption of Cr(VI) on the adsorbents increased markedly with declining pH (Fig. 2A). For VPum, the amount adsorbed increased from 8.97 to 77.5% while for VSco, the amount adsorbed increased from 8.11 to 67.2% as the pH decreased from 10 to 2. This indicates that the adsorption capacity of the adsorbent is clearly pH dependent. As pH changes, surface charge also changes, and the sorption of charged species is affected. Hence, the behaviour for better adsorption at low pH by the adsorbents may be attributed to the large number of H^+ ions present at low pH values which in turn neutralize the negatively charged adsorbent surface [39,40], thereby reducing hindrance to the diffusion of chromate ions. This fact can also be explained on the basis of the pH value at the point of zero charge (pH_{pzc}) of the adsorbent ($pH_{pzc} = 7.5$(VSco) and 9.3(VPum)). Below these pH_{pzc}, the surface charge of the adsorbents is positive and surface positive charge density should further increase with decreasing pH. This is confirmed by our experiments showing insignificant adsorption at alkaline pH while adsorption was very strong at pH 2 (Fig. 2A). Thus, Cr(VI)-sorption is due to electrostatic phenomenon as well as surface complexation that work individually or in combinations for the adsorption of Cr(VI) ions on the adsorbents. These mechanisms are in agreement with the findings of previous studies on the low cost adsorbents, such as those used by Rao et al. [41], Goswami and Ghosh [42] and Potgieter et al. [43].

The pH effect was also attributed to the different complexes that Cr(VI) can form in aqueous solution. From the stability diagram for Cr(VI)–H_2O system [44], it is evident that out of various species of Cr(VI), the $HCrO_4^-$ species is more stable in aqueous solution up to pH 7 beyond which it decreases. The H_2CrO_4 species is also stable within the low pH range; however, its concentration decreases sharply in aqueous solution with increasing pH. The CrO_4^{2-} species is stable in the higher pH range. In this study the maximum adsorption at low pH (pH < 5) indicates that it is the $HCrO_4^-$ species of Cr(VI), which is adsorbed preferentially on the adsorbents [45].

As seen from Fig. 2B, at low initial pH ($pH_{int} \leq 6$), the final pH values (pH_{fin}) are higher than pH_{int} values, which is due to an acid neutralization effect and proton adsorption of hydroxylated rock surface. Similar observations were also reported in previous studies [46].

Thus, it is concluded that the effect of pH on the adsorption capacity of the adsorbents may be attributed to the a combined influence of pH on the nature of the adsorbent surfaces, the presence of acid and base used to adjust the pH of solution as well as the adsorbed solute species.

3.3. Effect of adsorbent amount and particle size

By changing the dose from 10 to $100 \, g \, L^{-1}$, regardless of the particle size fraction of the sorbent, the removal of Cr(VI) ions increased from the range of 60–70 to 68–78% for VPum and 58–61 to 62–67% for VSco (data not shown). The maximum removal was exhibited at $100 \, g \, L^{-1}$ (1:10 ratio) of the adsorbents. This observation was attributed to the increase of the number of free adsorption sites. Similar results have been found with the adsorption of Cr(VI) ions on other adsorbents [11,43]. However, the amount of Cr(VI) ions adsorbed per unit mass of the adsorbents significantly decreased with increasing adsorbent dose (from the range of 61–72 to 7–8 mg kg^{-1} for VPum and from the range of 58–61 to 6–7 mg kg^{-1} for VSco). As seen from Fig. 3a and b, both adsorbents showed the highest distribution coefficient (K_D) value ($248 \, L \, kg^{-1}$ for VPum and $156 \, L \, kg^{-1}$ for VSco) at the smallest adsorbent dose ($10 \, g \, L^{-1}$). This may be attributed to the higher adsorbent amount creating particle aggregation, resulting in a decrease in the total surface area and an increase in diffusional path length both of which contribute to decrease in amount adsorbed per unit mass. It also confirms observations by other investigators [43,47–49].

Furthermore, the effect of the adsorbent particle size as a function of adsorbent dose with constant initial Cr(VI) concentration of $2 \, mg \, L^{-1}$ on the removal of Cr(VI) was studied. The removal and the K_D value of Cr(VI) increased significantly with decreasing particle size. On changing the particle size from 4.75 to 0.075 mm, the amount adsorbed increased from 5.7 to 61 mg kg^{-1} and from 7.0 to 68 mg kg^{-1} in case of VSco (Fig. 4a) and VPum (Fig. 4b), respectively.

However, the smallest particle size (<0.075 mm, powder) did not exhibited an enhanced removal, which was attributed to a loss of porosity, and thus of diffusion controlled sorption of Cr(VI) (Fig. 4a and b). This further confirms that both surface complexation and electrostatic attraction as well as diffusion into micropores of the adsorbent are responsible for the immobilization of Cr(VI) in the presence of volcanic material. In brief, the presence of a larger number of smaller particles for a given weight as well as large per-
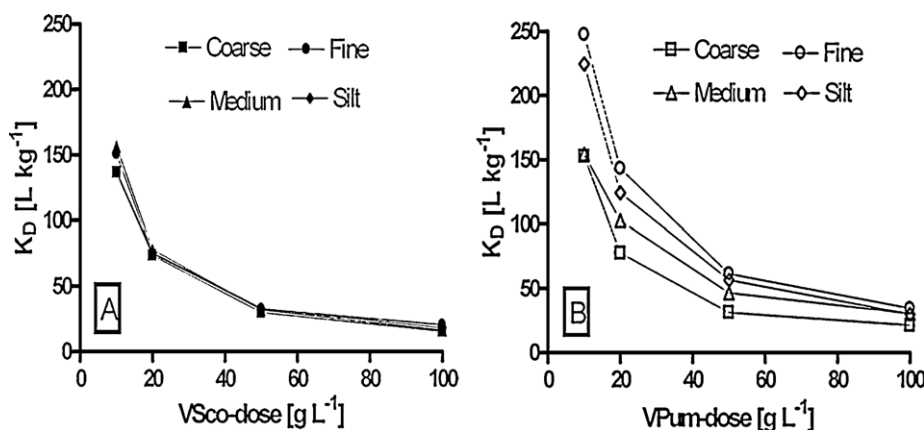
Fig. 3. Effect of the adsorbent amount on the adsorption of Cr(VI) onto VSco (A) and VPum (B).

centage of porosity provides the sorption system with a greater surface area available for Cr(VI) removal and it is also reduces the external mass transfer resistance [41]. Consequently, a particle size of 0.075–0.425 mm has been used for the rest of the experiments.

3.4. Effect of initial concentration

The effect of the initial Cr(VI) concentration that was varied in the range of 0.5–10.0 mg L^{-1} on the adsorption was investigated under the specific conditions (initial pH of 2; adsorbent/solution ratio of 1:10 (10 g adsorbent and 100 mL aqueous solution); particle size 0.075–0.0425 mm; at room temperature). The Cr(VI) adsorption efficiencies and calculated adsorption densities depending on the initial concentration are shown in Fig. 5. In the processes, the concentrations of the metal ion play an important role. On changing the initial concentration of Cr(VI) solution from 0.5 to 10.0 mg L^{-1}, the adsorption densities increases from 3.86 to 27.21 mg of Cr(VI) per kilogram of VSco and from 4.02 to 35.78 mg of Cr(VI) per kilogram of VPum, respectively. This finding is in agreement with the recent work by other authors [43] who found the same behaviour

by studying the adsorption capacity of palygorskite clay for the removal of Cr(VI) from aqueous solutions.

On the other hand, with lower initial concentration of Cr(VI) the adsorption efficiency (percentage removal) is higher than the efficiency attained when higher initial concentrations are used (Fig. 5). While the Cr(VI) adsorption yield was found as 80% (VPum) and 77% (VSco) for 0.5 mg L^{-1} of initial concentration, these values were 36% (VPum) and 27% (VSco) for that of 10 mg L^{-1}. These results indicate that the competition for adsorption sites becomes rigorous, energetically less favorable sites become involved with increasing Cr(VI) concentrations in the aqueous solution. This is a common finding and has been largely reported in the literature [41,46–50].

3.5. Cr(VI) adsorption kinetics

To determine kinetic adsorption parameters, different models were fitted to the data obtained for Cr(VI) sorption onto VPum and VSco. First, Lagergren pseudo-first-order model (Eq. (1)), and Ho's pseudo-second-order reaction rate model (Eq. (2)) were tested to describe the kinetic processes. The rate constants obtained from the kinetic models are given in Table 2. For both VPum and VSco, the entire kinetic data fitted well with pseudo-second-order reaction rate model, which is evident from the higher determination coefficient values (R^2). From Table 2, it is evident that the rate of adsorption of Cr(VI) onto VSco is faster than that of VPum.

Though the adsorption process is mainly considered as surface phenomenon, it is postulated that the rate-limiting step in the
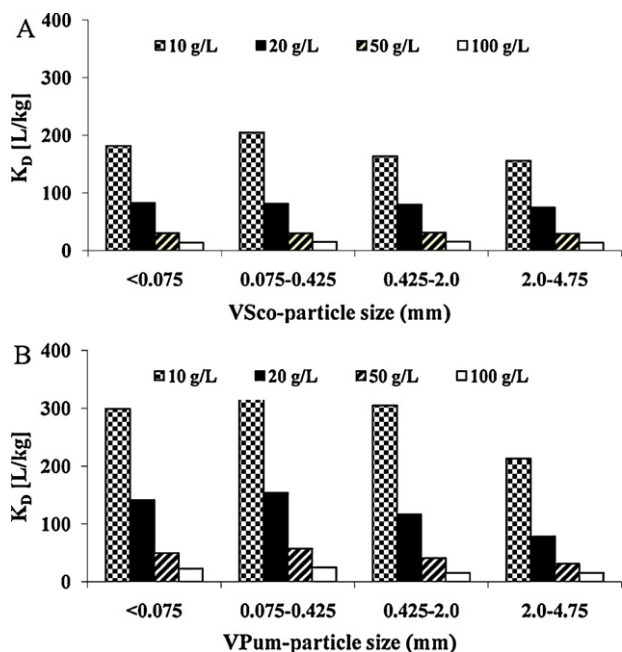

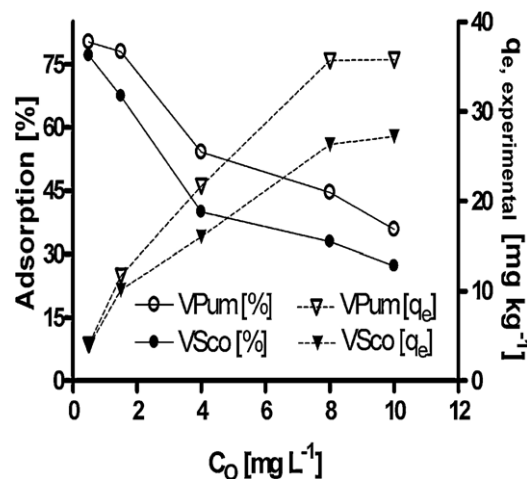**Fig. 4.** Effect of the particle size on the adsorption of Cr(VI) onto VSco (A) and VPum (B).

Fig. 5. Effect of the initial concentration on the uptake (dotted lines) and removal (solid lines) of Cr(VI) onto VPum and VSco.

Table 2
Values of Lagergren pseudo first order (Eq. (1)), pseudo second-order (Eq. (2)), intra-particle (Eq. (3)) and liquid film diffusion (Eq. (4)) rate constants for adsorption of Cr(VI) ions on VPum and VSco of different particle sizes.

Adsorbent	Particle size	First order		Second order		Intra-particle		Liquid film	
		k_1 (h^{-1})	R^2	k_2 (kg mg^{-1} h^{-1})	R^2	k_i (mg kg^{-1} h$^{-0.5}$)	R^2	k_{fd} (h^{-1})	R^2
VPum	Silt	0.11	0.69	0.205	0.99	0.268	0.80	0.14	0.86
	Fine	0.08	0.94	0.007	0.99	2.782	0.95	0.08	0.95
VSco	Silt	0.26	0.75	0.262	0.99	0.614	0.87	0.32	0.83
	Fine	0.11	0.67	0.338	0.99	0.204	0.20	0.14	0.67

Table 3
Freundlich and Langmuir isotherm constants of VPum and VSco.

Adsorbent	Freundlich constants			Langmuir constants			
	K_F (L kg^{-1})	n_F	R^2	a_L (mg kg^{-1})	K_L (L mg^{-1})	R^2	R_L
VPum	16.15	0.46	0.97	46.05	0.59	0.96	0.15–0.77
VSco	9.74	0.53	0.88	44.82	0.22	0.87	0.31–0.90

adsorption process might include liquid film and/or intra-particle diffusion and the respective equations were fitted to the data. As expected the plots of $-\ln(1-F)$ versus t according to the liquid film diffusion model, were linear and the related parameters are listed in Table 2. The k_{fd} values of the liquid film diffusion model tend to increased with decreasing particle size. Similarly, application of the intra-particle diffusion model by plotting q_t versus $t^{0.5}$ gave a linear relation. On the contrary, the k_i values of the intra-particle diffusion model were independent of the particle size of the adsorbents (Table 2). The deviation of the calculated parameters from the origin indicates that intra-particle transport and liquid film diffusion are not the only rate limiting steps [51].

In conclusion, the sorption of Cr(VI) to volcanic rock grains and its kinetics depended on different processes. The transport of Cr(VI) ions from solution through the particle-solution interface into the pores of the particles as well as the adsorption on the available surface of adsorbents were both responsible for the adsorption of Cr(VI) ions.

3.6. Adsorption isotherms

Analysis of the relationship between the adsorption capacity of the materials (VPum and VSco) and different Cr(VI) initial concentrations at equilibrium was performed using the equations of Freundlich (Eq. (7)) and Langmuir (Eq. (5)). The adsorption data were determined at constant pH (pH$_{int}$ = 2). The data satisfied both models when VPum was used as an adsorbent while the curve fit was less good for the data obtained with VSco. The related parameters for the fitting of both equations at constant temperature are summarized in Table 3. As expected the Freundlich adsorption capacity, K_F, of VPum is large as compared to that of VSco (Table 3). The n_F values for both adsorbents were less than unity, which indicates that an increased adsorption can modify the adsorbent and that a chemical rather than a physical adsorption was dominant [52]. This confirms our finding of surface complexation as a dominant sorption mechanism. The Langmuir monolayer capacity, a_L, was similar for both adsorbents (Table 3). In all cases, the R_L values for the experimental data fell between 0 and 1, which is indicative of the favorable adsorption of Cr(VI) on the adsorbents. Besides, the R_L values showed that the adsorption of Cr(VI) was more favorable for the higher concentration than the lower one, C_o = 0.5–4 mg L^{-1}: R_L = 0.78 (VSco); 0.59 (VPum) and C_o > 4 mg L^{-1}: R_L = 0.40 (VSco); 0.21 (VPum), which is due to the effect of the pore diffusion sorption phenomenon [42].

4. Conclusions

The following major conclusions can be drawn based on our investigations of Cr(VI) removal by VPum and VSco.

First, when volcanic rocks are used for water/wastewater purification, parameters such as solution pH, particle size, adsorbent/solution ratio, initial concentration of the adsorbate, and contact time must be optimally selected to obtain the highest possible removal of Cr(VI) from aqueous solutions. Apparently, the adsorption of Cr(VI) on VPum and VSco increased markedly at low-pH conditions (pH ≈ 2), which is the actual pH value of most industrial effluents such as tannery, electroplating, and chromium plating effluent.

Secondly, the adsorption kinetics for Cr(VI) at pH$_{int}$ 2.0 have been well described by the pseudo-second order equation in the concentration range studied, showing that the rate constant decreases with the particle size particularly in the case of VSco. The processes of Cr(VI) removal on the adsorbents were, however, found to be complex. The intra-particle and liquid film diffusions as well as surface adsorption contributed to the rate-determining step.

Thirdly, the equilibrium data followed the Langmuir and Freundlich isotherm models at constant temperature and fixed pH$_{int}$ examined in this study, and the calculated values of the dimensionless separation factor from the Langmuir constant confirmed favorable sorption of Cr(VI) onto VPum and VSco.

Therefore, this behaviour suggests that macro and microvesicular volcanic rocks (VSco and VPum) could represent an interesting low-cost adsorbent material to be used in Cr(VI)-bearing water/wastewater purification systems, and promotes an evaluation of a scale up procedure.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.seppur.2011.01.020

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