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Adsorption and Regeneration of Indonesian Natural Pumice for Total Chromium Removal from Aqueous Solution

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Abstract

To investigate the potential of adsorption and regeneration of natural pumice from West Sumatera Indonesia for total chromium (Cr) removal from aqueous solution, batch experiments in multiple adsorption-desorption cycles were performed. The results indicated that the optimum condition of total Cr removal were 3 of pH solution, 0.3 g/L of adsorbent dose, 60 min of contact time of adsorption, < 63 μm of diameter of adsorbent, and 1 mg/L of total Cr initial concentration with 2.226 mg Cr/g pumice of total Cr uptake. The experimental data obtained were fitted with the Freundlich adsorption isotherm within the concentration range studied. Desorption efficiencies for total Cr ions by using 0.1 M HCl as desorbing agent were in the range of 31-32%. Although complete desorption were not attained, the natural pumice could be sufficiently reused up to 3 cycles of adsorption- desorption with increasing trend in total Cr uptake that may due to the surface modification of natural pumice caused by HCl. Overall results revealed that easy availability of natural pumice as local mineral in West Sumatra, Indonesia and its ability to adsorb and retain total Cr will create more interest to develop new natural adsorption method of pollutant removal from solution.

Keywords

Adsorption; desorption; natural pumice; regeneration; total chromium

1. INTRODUCTION

Chromium is an essential element that is required in small amounts for carbohydrate metabolism, but becomes toxic at higher concentrations. Chromium compounds are environmental pollutants occurring in soil, water and industrial effluents because they are widely used in many industrial activities. In the natural environment, chromium is present in two stable oxidation states, Cr(III) and Cr(VI), where the ratio of the two compounds varies depending on pH value, redox potentials, total chromium concentration and redox reaction kinetics. Cr(VI) is highly toxic, mutagenic, carcinogenic and teratogenic. Cr(III) is much less toxic and mutagenic than Cr(VI), but long-term exposure to high Cr(III) concentrations may cause allergic skin reactions, cancer and DNA damage (Malarvizhi et al., 2010; Wang et al., 2014). Because chromium consists of variable oxidation states in water the guideline value set by World Health Organization (WHO) regards total chromium concentration, this value is set to 0.05 ppm. Therefore, it is highly imperative to treat the water containing chromium before its discharge.

Various treatment techniques including oxidation, reduction, electro-chemical precipitation, ultrafiltration, ion exchange, reverse osmosis and adsorption have been employed to remove chromium in water and wastewater (Rengaraj et al., 2001; Yurlova et al., 2002). Adsorption on solid surfaces is the most common one since it is easy to be applied, has a simple design, and insensitive to toxic substances. Adsorption also offers selectivity in removing low levels of heavy metals from dilute solutions and environmental friendly if combined with appropriate adsorbent and regeneration steps (Bingöl et al., 2012; Indah et al., 2017). Many efforts are being made continuously to develop new, low cost and efficient adsorbents for removal of metals including chromium. Over the years, the role played by adsorbents in water and wastewater treatment had been critically and elaborately investigated. Several low cost adsorbents from agricultural wastes such as rice husk ash (Zhang et al., 2014) and maize husk (Indah et al., 2016) have been used as adsorbent. Moreover, the potential the use of natural materials or local minerals such as zeolite (Motsi et al., 2009) bentonite (Melichová and Hromada, 2012), and pumice (Sepehr et al., 2014; Indah et al., 2017) also have been widely considered because of better performance and low cost of these materials. Among these natural materials, pumice which is a volcanic stone and can be found in many regions of the world has a low weight and a porous structure (up to 85%). Because of its micro-porous structure, pumice has a high specific surface area,

so that, recently, pumice also has been used as adsorbent for pollutant removal from water and wastewater (Heibati et al., 2014).

On the other hands, despite the capability of adsorbents to remove pollutant in the water, the used adsorbent may generate a problem to environment because they have to be discarded after it becomes exhausted. In addition, the utilization of mineral like natural pumice as adsorbent may reduce the availability of natural resources. Therefore, the regeneration and reuse of the adsorbents is important to make the operation environmental friendly and minimize the requirement of adsorbent. In this sense, desorption and reutilization of the adsorbents in adsorption−desorption cycles could help in reducing the residues. However, so, far, there is only limited investigations on the adsorption and desorption as well as regeneration of natural pumice to remove pollutant in water or wastewater.

Due to several advantages of the pumice and its accessibility in Indonesia, the main objective of this study was to investigate its effectiveness for the removal of total chromium at various experimental conditions and its possibility to reuse after metal desorption. Laboratory batch experiments were performed to determine optimal pH, dose of adsorbent, contact time, diameter of adsorbent, initial concentration of chromium and the adsorption capacity of pumice. Furthermore, in order to study regeneration ability of the natural pumice, sequential adsorption-desorption cycles were conducted 3 times using the same adsorbent.

2. EXPERIMENTAL SECTION

2.1 Preparation of Adsorbent
Natural pumice sample were obtained from riverside of Sungai Pasak, West Sumatera, Indonesia as byproduct of the process of sand mining in that area. Pumice samples were washed with distilled water several times and dried out at room temperature, then crushed and sieved in order to obtain the desired particle size fractions. Energy dispersive x-ray (EDX) spectroscopy was employed to get information on the oxide content of the natural pumice. A scanning electron microscopy (SEM, model S-3400N, Hitachi, Japan) was performed to observe the surface morphology of pumice.

2.2 Batch Adsorption Experiment
Batch adsorption experiment were conducted at room temperature (25°C) by varying pH, dose of adsorbent, contact time, diameter of adsorbent and initial concentration of total chromium. In each experiment, in 500 ml erlenmeyer flasks with 100 ml of chromium solutions was contacted with pumice and gently agitated at 100 rpm. After a period of time, the mixture was filtered by using Whatman's filter paper no 42 and the total chromium concentration in the filtrate was measured by atomic absorption spectrometry (Rayleigh WFX 320, China). The amount of total chromium adsorbed by the pumice was generated as the difference between the initial and final concentration of the solutions. All experiments were performed in triplicate, and results provided are accordingly the

averaged values of replicate tests. The adsorption capacity of total chromium adsorbed (q_e, (mg/g)) can be calculated using the following equation.

$$q_e = \frac{C_o - C_e}{w} \cdot V \tag{1}$$

where C_o is the initial concentration of total chromium (mg/L), C_e is the equilibrium concentration of total chromium g(mg/L), V is the volume of the solution (L), and W is the mass of the pumice (g).

2.3 Batch Desoprtion Experiment
The desorption experiment was conducted using pumice with total chromium adsorbed on the surface at the end of the sorption experiment. Samples were mixed with 0.1 M HCl (a 1:200 solid to solution ratio), shaken at 100 rpm for 60 min and at room temperature (25°C). Afterwards, the mixture was filtered by using Whatman's filter paper no 42 and the total chromium concentration in the filtrate was measured by atomic absorption spectrometry (Rayleigh WFX 320, China). All experiments were repeated three times, and results presented are consequently the averaged values of replicate tests. The desorbed total chromium was calculated as percentage using equation (Eq. (2)).

$$Desorption = \frac{Concentration\,of\,desorbed\,metal}{Concentration\,of\,adsorbed\,metal} \cdot 100 \tag{2}$$

3. RESULTS AND DISCUSSION

3.1 Adsorbent Characterization
Si, Al and Fe are the major elements in natural pumice from Sungai Pasak, as shown in Table 1 as determined by EDX. Other elements, except K, Ca, Na and Mg were present in relatively smaller amounts (less than 3%). The elemental compositions of the pumice also indicate the absence of hazardous or carcinogenic substances, thus the pumice are considered appropriate as adsorbent to treat polluted water. The SEM image showed the surface morphology of natural pumice from Sungai Pasak, West Sumatra was displayed in Figure 1. The image denoted that the pumice had a highly porous, cellular, smooth surface, and irregular texture with larger cavities, which serves suitable sites for adsorption.

3.2 Effect of pH
Many studies have proved that pH is one of the most important parameters having an influence on the adsorption capacity of adsorbent for heavy metal ions removal from the aqueous solutions. The effect of pH on the adsorption of total chromium onto the natural pumice was studied in the range of 2 - 6. Figure 2 shows the total chromium uptake increased from 0.084 mg/g to 0.101 mg/g as pH increased from 2 to 3. The highest total chromium uptake was recorded at pH 3 and the total chromium uptake decreased as pH increased to 6. The result
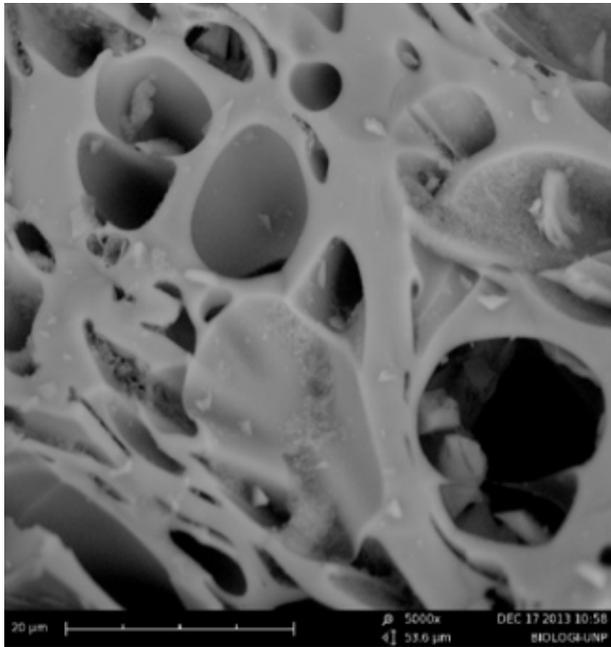
Figure 1. SEM micrograph of pumice from Sungai Pasak, West Sumatra, Indonesia

Table 1. Elemental and oxide composition of natural pumice from Sungai Pasak, West Sumatra, Indonesia

Element	% weight
Na	0.49
Mg	0.06
Al	3.89
Si	32.56
K	2.41
Ca	1.2
Fe	3

revealed the removal of total chromium from aqueous solution by adsorption is highly dependent on the pH of the solution, which affects the surface charge of the adsorbent. At low pH, the surface of the natural pumice becomes protonated favoring the strong electrostatic attraction between the adsorbent and chromium anions. However, at higher pH, the binding sites of adsorbent are deprotonated and causes the increasing negatively charged sites on the adsorbent surface and this is no longer favorable to anionic chromium adsorption. Thus, the optimum pH for adsorption of total chromium onto the natural pumice was observed at pH 3. Similar finding on pH trend has been reported in adsorption of chromium studies by other researchers (Sepehr et al., 2014; Tytłak et al., 2014). Above all the following experiments were carried out with pH values of 3.
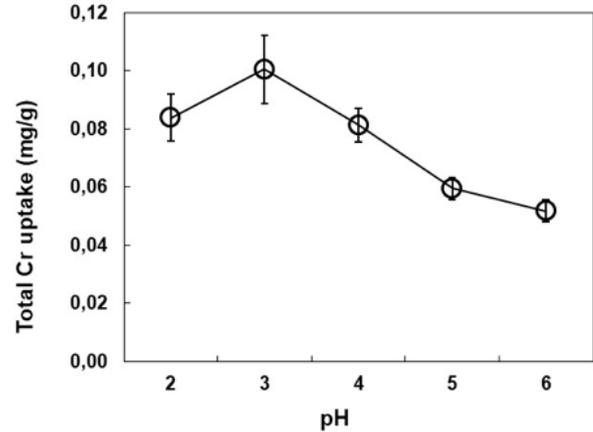
Figure 2. Effect of pH on total Cr uptake onto pumice (chromium concentration = 0.05 mg/L; adsorbent dose = 0.3 g/L; diameter of adsorbent = < 63 μm; contact time = 60 min). Data represent averages of triplicates ± SE.

3.3 Effect of Adsorbent Dose

The different doses of the pumice (0.3, 1.0, 3.0, 10 and 30 g/L) were studied to study the effect on chromium adsorption. The experiment was performed at room temperature, 3 of pH, 60 minutes of contact time and the initial concentration of chromium was fixed as 0.05 mg/L (Figure 3). The results revealed that the chromium uptake decreased as the adsorbent dose increased. The total chromium uptake decreased from 0.043 mg/g to 0.001 mg/g by increasing the adsorbent dose from 0.3 to 30 g/L. As the adsorbent dose increased, the sorption sites remain unsaturated during the adsorption reaction and the agglomeration of adsorbent particles may occur that reducing the available external surface area and an increase in diffusional path length both of which contribute to decrease in amount adsorbed per unit mass. It is in accordance with our previous study and also confirms observations by other investigators (Indah et al., 2017; Dhanakumar et al., 2007; Yu et al., 2003). A maximum adsorption uptake at equilibrium of 0.043 mg Cr/g was obtained for a pumice dose of 0.3 g/L. Therefore, 0.3 g/L of adsorbent dose was determined to be the optimum dose in this study and above all the following experiments were carried out with this dose.

3.4 Effect of Contact Time

Figure 4 depicts the effect of contact time on the adsorption of chromium onto natural pumice from aqueous solution. It was observed that the total Cr uptake increased with increase in contact time up to 60 min. At this time, Cr uptake reached 0.101 mg Cr/g. However, at 90, 120 and 150 min of contact time, the Cr uptake decreased to 0.09, 0.083 and 0.054 mg Cr/g. The result indicated that the adsorption of total chromium is most rapid in the initial stages and gradually decreases until the equilibrium is reached. A large number of vacant surface sites of pumice that available for adsorption resulted the increasing

Cr uptake during the initial stage of sorption. After an interval in time, due to repulsive forces between the solute molecules on the adsorbent surface and the bulk phase, the remaining vacant surface sites of pumice were occupied (Wongjunda and Saueprasea, 2010). Therefore, the equilibrium time for the removal of total chromium from aqueous solution by natural pumice is taken as 60 min and applied for further experiments.

3.5 Effect of Diameter of Adsorbent

To study the effect of particle sizes of natural pumice on the adsorption of total chromium, 5 variations of diameter of adsorbent representing the variation of particle size of adsorbent were applied. Figure 5 shows that the increasing in the diameter of adsorbent resulted the decreasing in total Cr uptake. The total Cr uptake was decrease from 0.103 to 0.053 mg Cr/g as diameter of adsorbent increase from <63 to 500-600 μm. The results revealed that the adsorption capacity depends on the size of adsorbent; as the diameter of adsorbent decreases, the adsorption capacity increases due to the wider exchange surface provided for the adsorption of the chromium ions. Similar results were also documented in in the literature using other adsorbent [2, 17] (Wang et al., 2014; Lopez-Nuñez et al., 2014). Therefore <63 µm, as the smallest diameter of the 5 variations, was defined as the optimum diameter of adsorption and were applied for the further experiments.

3.6 Effect of Initial Concentration

The effect of initial concentration on total chromium adsorption onto natural pumice was investigated in the range 0.01-1 mg/L. As shown in Figure 6, the total Cr uptake increased from 0.012 to 2.226 mg Cr/g, as the concentration was increased from 0.01 to 1 mg/L. It indicated that the actual amount of chromium ions adsorbed per unit mass of the natural pumice was increased with increasing in chromium ions concentra-
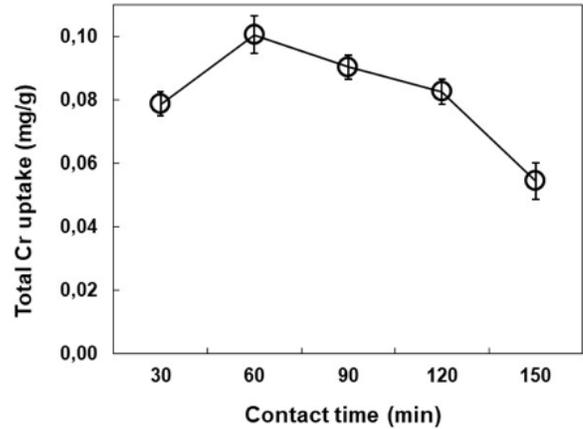
Figure 4. Effect of contact time on total Cr uptake onto pumice (chromium concentration = 0.05 mg/L; diameter of adsorbent = < 63 μm; pH = 3; adsorbent dose = 0.3 g/L). Data represent averages of triplicates ± SE.

tion in the aqueous solution. An increase in initial chromium concentration may cause higher availability of chromium ions in the solution for removal and increase concentration gradient, which provides a stronger driving force to overcome mass transfer resistance of chromium ions between the aqueous and solid phases, resulting in higher probability of collision between chromium ions and active sites of natural pumice, thus leading to a higher total chromium uptake. The results clarified that higher initial concentration of chromium can enhance the adsorption process and the interaction between chromium and pumice as adsorbent. The result is consistent with the finding by other researchers (Malarvizhi et al., 2010; Puentes-Cárdenas et al., 2012). From the results it was also evident that the adsorption of total chromium onto natural pumice is dependent on initial metal concentration. Under the conditions tested in this study, the highest total chromium uptake was 2.226 mg Cr/g.

3.7 Adsorption Isotherm Models

The adsorption isotherm usually shows how the molecules are distributed between the liquid and the solid phases, at equilibrium during the adsorption process. A number of isotherm models have been developed to describe equilibrium relationships. Linear forms of the Langmuir, Freundlich and Elovich adsorption isotherm models ((3), (4) and (5), respectively) were used to verify the adsorption data:
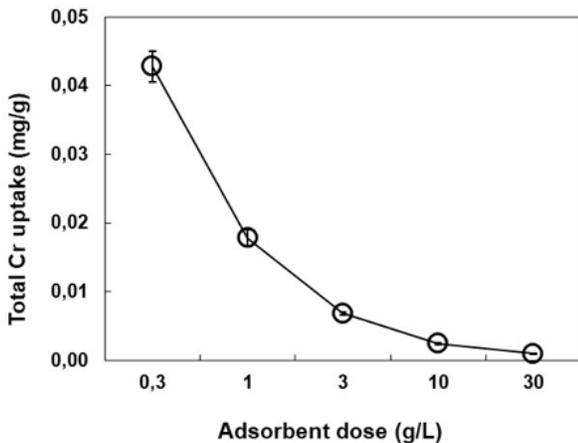
Figure 3. Effect of adsorbent dose on total Cr uptake onto pumice (chromium concentration = 0.05 mg/L; diameter of adsorbent = < 63 μm; pH = 3; contact time = 60 min). Data represent averages of triplicates ± SE

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}} \qquad (3)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (4)$$
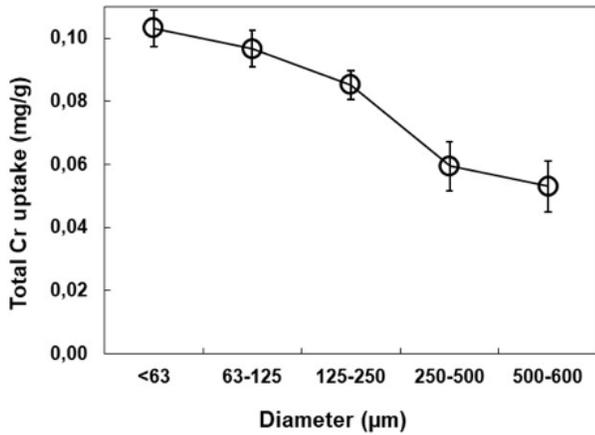
Figure 5. Effect of diameter of absorbent on total Cr uptake onto pumice (chromium concentration = 0.05 mg/L; pH = 3; adsorbent dose = 0.3 g/L; contact time = 60 min). Data represent averages of triplicates ± SE.
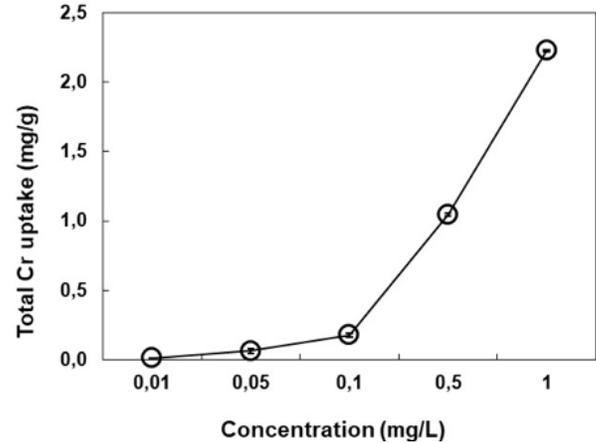
$$\ln \frac{q_e}{C_e} = \ln K_E q_{max} - \frac{q_e}{q_{max}} \qquad (5)$$

where C_e is the equilibrium concentration, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent, q_{max} is the maximum adsorption capacity, K_L is the Langmuir constant related to the adsorption rate, K_F is the Freundlich isotherm constant related to adsorption capacity, n is the Freundlich isotherm constant related to adsorption intensity (indicating the favourability of the adsorption process) and K_E is the Elovich equilibrium constant.

The Langmuir model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate along the plane of the surface. From the slopes and the intercepts, a linear fit to the Langmuir equation yields Langmuir constant (K_L) and the maximum adsorption capacity (q_{max}), respectively (Low, 1960). The Freundlich model is based on the assumption that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases. The linear form of the Freundlich isotherm model yields a straight line. The slope and intercept of the obtained fit are used to calculate the Freundlich constants $1/n$ and K_F (Freundlich, 1907). The Elovich model is based on a kinetic principle assuming that the adsorption sites increase exponentially with adsorption, which implies a multilayer adsorption. The Elovich maximum adsorption capacity and Elovich constant can be calculated from the slopes and the intercepts of the plot of $\ln(q_e/C_e)$ versus q_e (Elovich and Larinov, 1962). The applicability of the isotherm equations to describe the adsorption process was judged based on the maximum value of adsorption and correlation coefficients (R^2) which are a measure of goodness of fit.

To determine the adsorption isotherm of total chromium adsorption onto natural pumice, the initial total chromium

Figure 6. Effect of initial concentration on total Cr uptake onto pumice (pH = 3; adsorbent dose = 0.3 g/L; contact time = 60 min; diameter of adsorbent = < 63 μm). Data represent averages of triplicates ± SE.

Table 2. Isotherm model constants for adsorption of total chromium onto natural pumice

Isotherm	Constants		R^2
Langmuir	q_{max} (mg/g) -1	K_L (L/mg) -2.31	0.687
Freundlich	$1/n$ 1.33	K_F (L/g) 9.25	0.99
Elovich	q_{max} (mg/g) -1.98	K_E (L/mg) 0.63	0.746

concentration was varied in the interval ranging from 0.01 to 1 mg/L with 3 of pH and 0.3 g/L of adsorbent dose. Figure 7 shows the Langmuir, Freundlich and Elovich isotherm plots and Table 2 presents the isotherm model constants for the adsorption. Data in Table 2 show that the Freundlich isotherm model presents the highest R^2 value (0.990) indicated the model fitted well with the equilibrium data, compared with Langmuir and Elovich isotherm models. It revealed that the adsorption of total chromium onto natural pumice is multilayer sorption and the adsorption occurred on the heterogeneous surface of pumice and the active sites of pumice have different energy, as the Freundlich isotherm model's assumption [20].

As shown in Table 2, for the Langmuir model, the maximal value of adsorption q_{max} was negative, which reflects the inadequacy of this model for explaining the adsorption process (Alshabanat et al., 2013). From the Freundlich isotherm model, the adsorption of total chromium onto natural pumice from Sungai Pasak resulted 9.25 mg Cr/g of K_F as adsorption capacity and 1.33 of $1/n$. The $1/n$ value derived from the Freundlich equation serves to describe the linearity of adsorption. Typically, $1/n$ values range from 1 downwards. A higher value of n (smaller value of $1/n$) implies an effective interac-
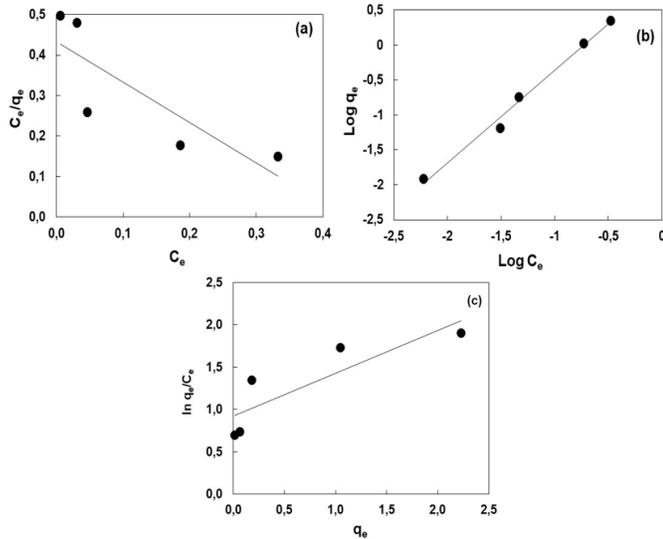
Figure 7. Langmuir (a), Freundlich (b) and Elovich (c) isotherm plots for the adsorption of Cr onto natural pumice (Cr concentration: 0.01-1 g/L; adsorbent dose: 0.3 g/L; contact time: 60 min; pH: 3)

Figure 8. Adsorption and desorption efficiencies as well as total Cr uptake onto pumice at 3 cycles of adsorption-desorption (pH = 3; adsorbent dose = 0.3 g/L; contact time = 60 min; diameter of adsorbent = <63 μm; chromium concentration = 1 mg/L). Data represent averages of triplicates ± SE

tion between the adsorbent and adsorbate. When $1/n < 1$, it corresponds a normal L-type Langmuir adsorption isotherm, while $1/n > 1$ reflects a co-operative adsorption (Guo et al., 2016). Since the value of 1/n from this study is 1.33, it indicate that co-operative adsorption may occur in the system, where adsorbed adsorbate has an effect on the adsorption of "new" adsorbate molecules. Moreover, $1/n$ values of > 1 are indicative of S-type isotherms, according to the Giles et al. (Giles et al., 1960) classification, indicating that adsorption becomes easier for increasing concentration. The S-type characterized first by a weak adsorption which then gradually increases suggests a weak surface interaction and competitive adsorbate-adsorbate interactions. The S curve of the adsorption isotherm generally reflects strong competition between the solvent and the adsorbed species for the adsorbent surface sites. For this study, in order to make a stronger interaction between natural pumice as adsorbent and adsorbate, more attempts could be made, such as modify the surface of the adsorbent physically or chemically using thermal treatment, protonation or metal oxides impregnation (Sepehr et al., 2014).

3.8 Desorption Study

Batch desorption experiments were conducted in order to investigate the mechanism of metal ion removal and recovery from metal-loaded adsorbent and also for the regeneration and recycling of spent adsorbents, which in turn may reduce operational cost and protect the environment from the problem of residues of the adsorbent. In addition, efficient removal of loaded metal from the natural pumice was necessary to ensure its long term use for repeated adsorption-desorption cycles. The regeneration of the adsorbent is likely to be a key factor in
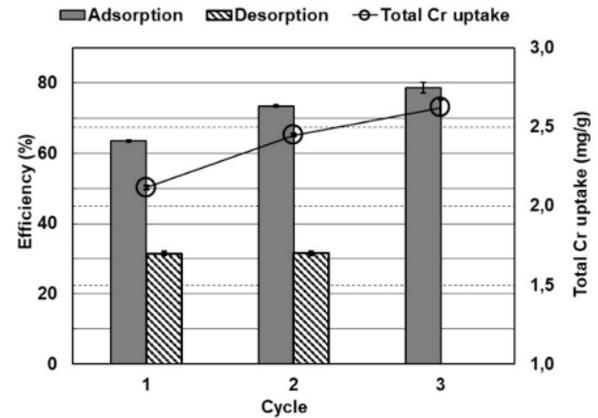
accessing the potential of the adsorbent for commercial application. The capacity of natural pumice to adsorb total chromium ions was determined by repeating the adsorption-desorption experiments in three consecutive cycles by using 0.1 M HCl as desorbing agent.

Figure 8 shows the desorption efficiencies for total chromium ions by using 0.1 M HCl as desorbing agent were in the range of 31-32%. A slight increase in desorption efficiencies was observed (approximately 1 %) at the second desorption cycle (desorption 2) may due to the accumulation of total chromium ions that could not release at the second adsorption (adsorption 2). Although complete desorption were not achieved, the result confirmed that HCl can be used as desorbing and recovery agent. In desorption process, the residence time is very essential because the higher the residence time, the longer the contact between the desorbing agent and the metal loaded adsorbent, so that the desorption efficiency may increase (D Wankasi, 2005). Desorption efficiency of Cr(VI) ion from natural pumice obtained from Tikmeh Dash Reign, East Azerbaijan, Iran reached 94.3% after 300 min contact time with 1 M HCl (Sepehr et al., 2014). In this study, the desorption time was 60 min. If the contact time is extended, it may be possible to reach 100% desorption.

As shown in Figure 8, the reuse of the remaining natural pumice in a second and third adsorption cycle increased the removal efficiency of total chromium ions from 63.50% (adsorption 1) to 73.47% (adsorption 2) and 78.66% (adsorption 3). These results may be related to chemical changes in the natural pumice produced by acid solution (HCl) that used as desorbing agent. Many researchers notified that the interaction between acid solution like HCl and adsorbents can modify the adsorbents and improve their adsorption capacity. The acid solution can removal of impurities on the adsorbent surface,

decrease the organic content, increase the porosity, breakdown of the cell wall or generation of new sorption active sites of the adsorbents (Sepehr et al., 2014). These results define that natural pumice from Sungai Pasak, West Sumatra, Indonesia can be sufficiently reused up to 3 cycles of adsorption- desorption.

4. CONCLUSIONS

Natural pumice from Sungai Pasak, West Sumatra, Indonesia, which is available in a great abundance, as by-product of the process of sand mining in that area, was examined to become an alternative low-cost adsorbent for the removal of total chromium in water. The natural pumice has a highly porous, smooth surface, cellular and irregular texture with larger cavities, which provides suitable sites for adsorption. From the batch experiments which were performed at ambient temperature (25°C) and 100 rpm of agitation speed, it was found that the optimum condition of total chromium removal by natural pumice were 3 of pH solution, 0.3 g/L of adsorbent dose, 60 min of contact time of adsorption, <63 μm of diameter of adsorbent, and 1 mg/L of total Cr concentration with 2.226 mg Cr/g pumice of adsorption capacity. The result also revealed that the Freundlich isotherm model fitted well with the equilibrium data within the concentration range studied as it presents higher R^2 value than that of the Langmuir and Elovich isotherms. It denoted that the adsorption of total chromium onto natural pumice is multilayer sorption, the adsorption occurred on the heterogeneous surface of pumice and the active sites of pumice have different energy. To maximize function and capability of adsorbent used and make the process environmental friendly, the regeneration and reuse of adsorbent were studied by desorption experiment. It was confirmed that the exhausted natural pumice could be desorbed 31-32% by 0.1 M HCl. The used natural pumice also could be regenerated and reused up to three successive adsorption-desorption cycles with increasing trend in total Cr uptake that may due to the surface modification of natural pumice caused by HCl as acidic medium. Overall study revealed that pumice from Sungai Pasak could be a promising adsorbent for total chromium removal from water.

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