Elimination of Hexavalent Chromium Ions in Water Using a Manganese-Coated Pumice Adsorbent

Puji Lestari[1*], Gani Purwiandono[2], Shike Pramayshela[1], Eko Siswoyo[1]

1 Department of Environmental Engineering, Faculty of Civil Engineering and Planning, Universitas Islam Indonesia, Jl. Kaliurang Km. 14.5, Yogyakarta 55584, Indonesia
2 Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Islam Indonesia, Jl. Kaliurang Km. 14.5, Yogyakarta 55584, Indonesia
* Corresponding author's e-mail: puji.lestari@uii.ac.id

ABSTRACT

A natural pumice stone stone coated with manganese (Mn) has been prepared and utilized to remove hexavalent chromium (Cr(VI)) ions in water via adsorption process. Prior to the application, the natural pumice was ground, sieved, and immerse in a dilute HCl solution. The coating of Mn on the acid-activated pumice was carried out by soaking the powder in 0.5 M $Mn(NO_3)_2$ solution for 72 h. The characterisation of the produced pumice adsorbent was performed with scanning electron microscopy and fourier-transform infrared spectroscopy instruments. The adsorption of Cr(VI) onto Mn-coated pumices was optimum at pH 3. Both the Langmuir and Freundlich isotherm models could be used to describe the adsorption process. The rate of adsorption followed the model for pseudo-second-order kinetics. The maximum adsorption capacity of Mn-coated pumice towards Cr(VI) ions was 1.94 mg/g.

Keywords*: adsorption, hexavalent chromium, isotherms, Mn-coated pumice.

INTRODUCTION

Heavy metals are known as metals with atomic number more than 20 and the density higher than 5 g/cm^3 (Tchounwou et al., 2012). Heavy metals are known for their toxicity and carcinogenic properties. Chromium, one type of heavy metal, can be found in the environment. It may originate from both natural and human-made sources such as various industries, predominantly the metallurgical industry (Ojembarrena et al., 2022). Chromium ions mainly occurs in 3+ and 6+ oxidation states. The trivalent chromium (Cr(III)) is found abundantly in the environment and has a relatively low toxicity. The hexavalent chromium (Cr(VI)) on the other hand, is known for its carcinogenic and mutagenic properties (Wise Jr. et al., 2022). The World Health Organization (WHO) has established specific thresholds for the presence of Cr(VI) in drinking water and industrial effluent. These thresholds are set at 0.05 mg/L and 0.1 mg/L, respectively (Zhang et al., 2020). Thus, the removal Cr(VI) from water is of an important environmental concern.

Numerous techniques have been implemented to eliminate heavy metal ions from water, with adsorption regarded as one of the most beneficial methods. Various adsorbents have been developed to remove Cr(VI). Nowadays, the development of adsorbents has shifted to the use of natural materials that are available abundantly from the local sources and require less processing, as well as non-toxic and environmentally friendly (Sepehr et al., 2013; Radoor et al., 2022). One alternative of the natural materials for adsorbent is the pumice which has specific surface areas of about 5–15 m^2/g. Pumice has high number of pores, especially micropores and consists mainly of silicate. Many studies have reported the use of pumice for environmental application such as adsorbent, media for filtration and catalyst support (Kitis et al., 2007, Kasraee et al., 2023). Application of geomaterials including pumice usually shows low adsorption capacity towards pollutant molecules. Thus, the activation of

the material is usually needed prior to the application as an adsorbent (Zhang et al., 2014).

In this study, the natural pumice powder was coated with manganese (Mn) and the material was used as an adsorbent to eliminate Cr(VI) from water. The investigation focused on several parameters that influence the adsorption process of Cr(VI) onto Mn-coated pumice. These parameters include the interaction time, initial concentration of Cr(VI), and pH.

METHODS

Materials

Pumices were collected from the area in Yogyakarta province, Indonesia. All chemicals in this study were directly used as received from the manufacturer. HCl, $Mn(NO_3)_2$, $K_2Cr_2O_7$, 0.1 M NaOH, and 0.1 M HCl were from Sigma Aldrich, Germany. All the solutions utilized in this investigation were prepared with deionized water. To produce a 1000 ppm Cr(VI) stock solution, 0.283 g of K2Cr2O7 was dissolved in water in a 100 mL volumetric flask.

Preparation of Mn-coated adsorbent

Prior to the use, pumices were dried at 105 °C to a constant weight to remove the moisture. After the drying process, pumices were ground and sieved using a 100 mesh-size sieve to obtain homogeneous powders. Prior to the coating with manganese (Mn), the pumice powder was immersed in 1% HCl for 24 h with a ratio of 1:3 (pumice:HCl, m/m). Following the soaking in HCl, pumice powder was washed using distilled water to neutral pH and was dried at 105 °C to a constant weight. The coating with Mn was carried out by immersing the HCl-activated pumice in 0.5 M $Mn(NO_3)_2$ solution for 72 h. After that, the powder was washed for three times using distilled water and dried at 105 °C to a constant weight. The Mn-coated pumice adsorbent was then characterized using Fourier Transform Infrared (FTIR) spectrophotometry (Shimadzu, IRTracer-100) and Scanning Electron Microscopy (SEM; Thermo Fisher Scientific, Phenom ProX).

Adsorption experiments

Adsorption processes were carried out in a batch system by interacting 25 mL of 10 ppm Cr(IV) solution with 50 mg of Mn-coated pumice adsorbent for 180 minutes. At pH values of 2, 3, 4, and 5, the impact of pH on the adsorption process was investigated. To modify the pH of the solution, dilute NaOH and HCl were utilized. To investigate the impact of initial Cr(VI) concentration on the adsorption process of Cr(VI) onto Mn-coated pumice, the initial concentration of Cr(VI) solution was varied while all other adsorption parameters remained constant. The initial concentration of Cr(VI) solution was varied from 10 to 50 ppm. The effect of time on adsorption process was studied by interacting 50 mL of Cr(VI) solution (pH 3) with 100 mg of the pumice adsorbent on orbital shaker at 150 rpm. The solution was sampled at time interval 10–180 min to measure the concentration of Cr(VI) in the solution. Following the adsorption procedure, the solution underwent filtration, and the concentration of Cr(VI) ions that remained in the solution was quantified at 542 nm using a UV-Visible Spectrophotometer Instruments (Shimadzu UV-1700 Pharmaspec). Eq. 1 was used to determine the removal efficiency of Cr(VI) by the adsorbent, whereas Eq. 2 was used to determine the quantity of Cr(VI) ions adsorbed on the Mn-coated pumice adsorbent.

$$\text{Removal (\%)} = \frac{C_i - C_t}{C_t} \times 100\% \qquad (1)$$

$$qt \left(\frac{mg}{g}\right) = \frac{(C_i - C_t)}{m} \times V \qquad (2)$$

The concentrations of Cr(VI) (mg/L) prior to and subsequent to the adsorption process are denoted as C_i and C_t, respectively. The quantity of Cr(VI) ions adsorbed on the pumice adsorbent is reported as qt (mg/g), the mass of the adsorbent is denoted as m (g), and the volume of the Cr(VI) solution is denoted as V (L).

A blank sample was run for each adsorption study. Each adsorption process was conducted in duplicates and the value reported in this study was the average of the duplicates.

RESULTS AND DISCUSSION

Characterization of Mn-coated pumice

Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) spectroscopy was utilized to examine the functional groups of Mn-coated pumice stone adsorbent. Figure 1 presented the FTIR spectra of natural pumice powder,
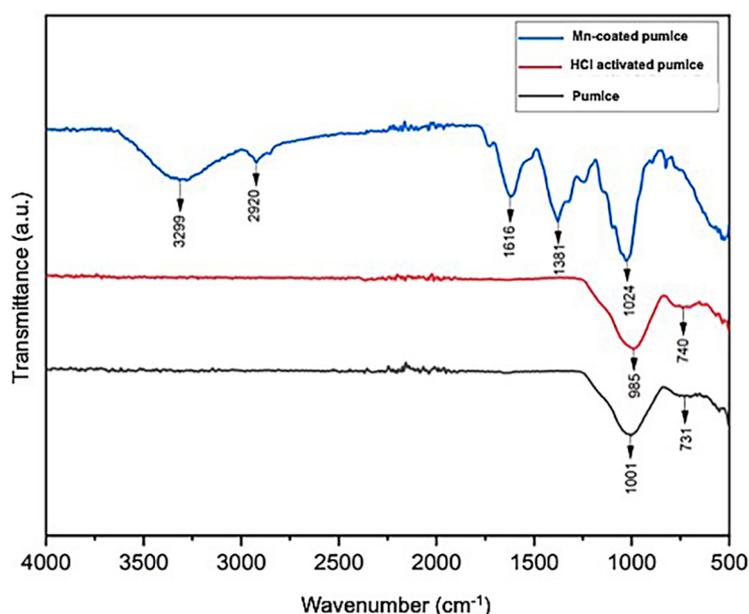
HCl-activated pumice, and Mn-coated pumice. The FTIR spectra On natural and HCl-activated pumice, the absorption at around 1001 and 985 cm^{-1} corresponded to the Si-O-Si stretching vibration while the absorption at 731 cm^{-1} and 740 cm^{-1} were assigned to Si-O-Al framework (Sepehr et al., 2013). It is known that pumice stone mainly consists of SiO$_2$ and Al$_2$O$_3$ (Safari et al., 2015). Further absorption peaks were detected at 3299 cm^{-1} and 1616 cm^{-1} after the application of the manganese coating. These peaks correspond to the bending vibration of the H-O-H bond and the -OH stretching vibration, respectively (Guler and Sarioglu, 2014). Figure 2 presented the surface images of the materials obtained from SEM analysis. It is seen that after the treatment of acid, the cavities on the pumice stone became larger. The treatment of acid aims at removing the impurities

that might clog the pores of the pumice as well as increasing the positive charges on the surface of the pumice.
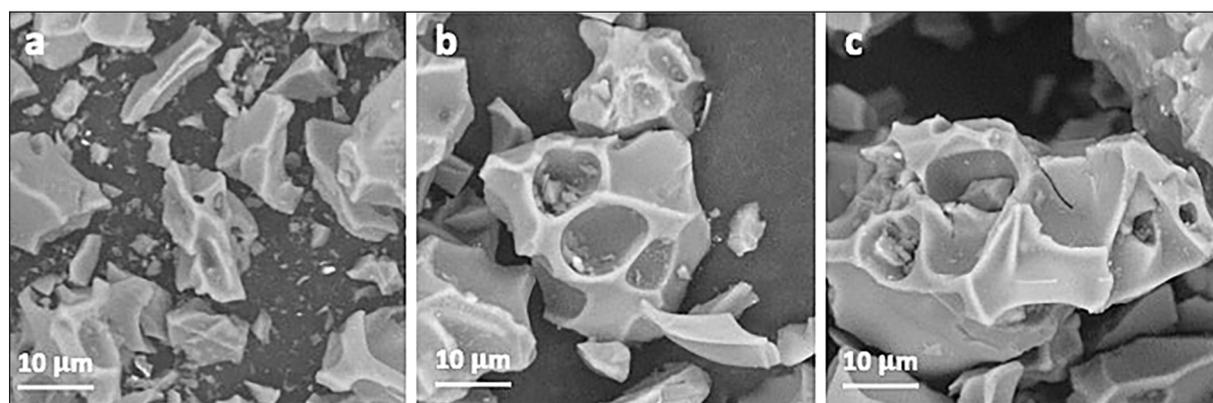
Effect of pH on adsorption process

The pH of the solution significantly influences the adsorption process and the adsorption capacity of an adsorbent is highly dependent on the pH of solution. The impact of pH was examined at pH values of 2, 3, 4, and 5, as the formation of CrOH$_3$ precipitates occurs at pH 6 (Unceta et al., 2010). The effect of pH on the adsorption of Cr(VI) on Mn-coated pumice was presented in Figure 3.

It is seen that the optimum pH of the adsorption process was pH 3. At pH 3, the functional groups of on Mn-coated adsorbent are likely to be protonated and the hexavalent chromium exist as the

Figure 1. Fourier Transform Infrared (FTIR) spectra of the materials in this study

Figure 2. Scanning Electron Microscopy (SEM) images of pumice (a), HCl-activated pumice (b), and Mn-coated pumice (c)
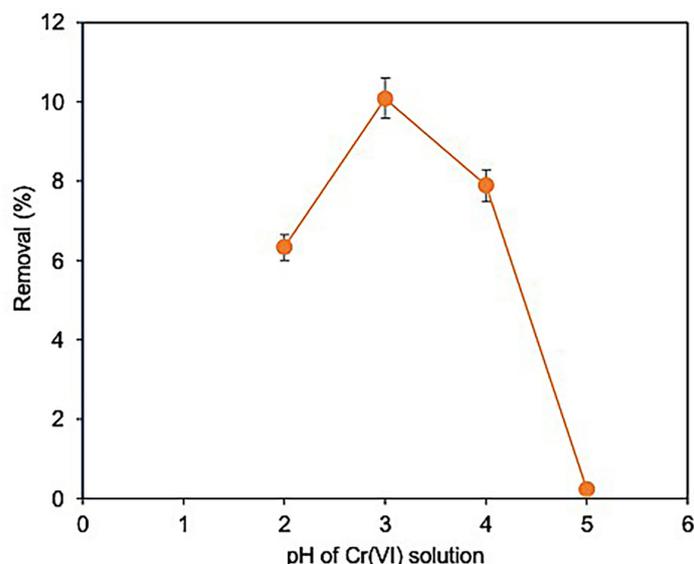
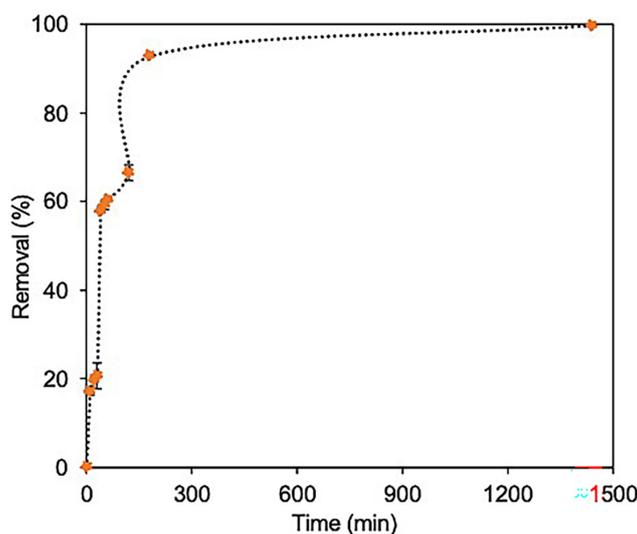**Figure 3.** Effect of pH on Cr(VI) adsorption onto Mn-coated pumice adsorbent

negatively charged $Cr_2O_7^{2-}$ and CrO_4^{2-} ions. Thus, making the adsorption process via electrostatic interaction to be more effective (Liu et al.2019). At pH 2, the hexavalent chromium is predominant as H_2CrO_4 which is a neutral species, consequently, the efficiency of the interaction between Cr(VI) in the form of H_2CrO_4 and the positively charged surface of the adsorbent was reduced. At pH values exceeding 3, the protonation of the adsorbent surface is expected to decrease, making the adsorption of Cr(VI) as $Cr_2O_7^{2-}$ and CrO_4^{2-} ions become less effective (Unceta et al., 2010).
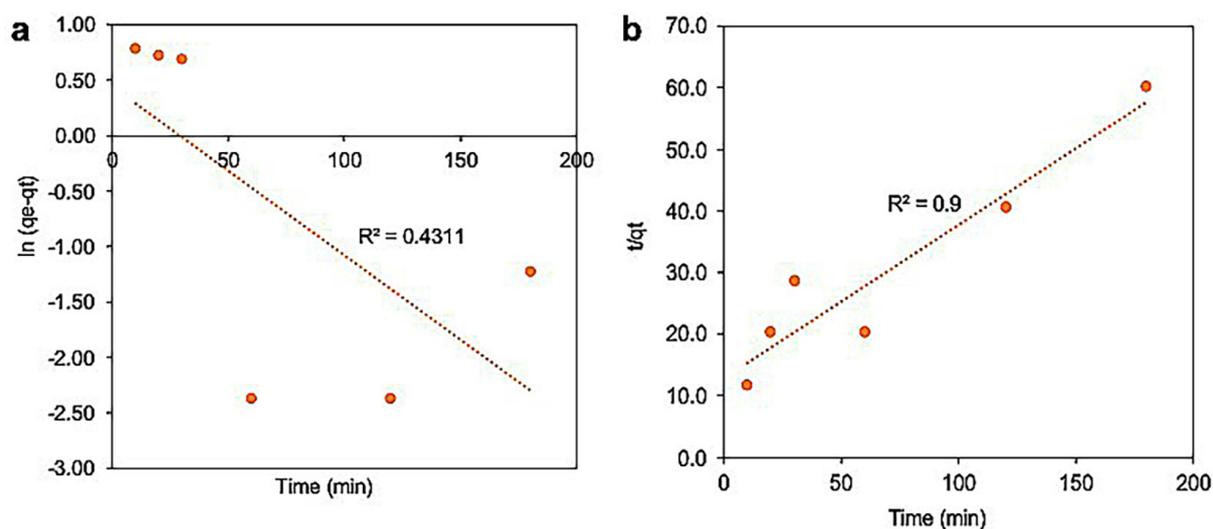
Adsorption kinetics

The effect of time on the removal efficiency of Cr(VI) using Mn-coated pumice was given in Figure 4. The removal of Cr(VI) using Mn-coated pumice increased with the increase of interaction time. At the initial phase of the adsorption process, the rate of adsorption was high, but it subsequently slowed as time passed. There are abundant adsorption sites on the adsorbent at the beginning of adsorption that are capable of interacting with Cr(VI) ions so that the adsorption process may occur (Rouhaninezhad et al., 2020).

The adsorption kinetics of Mn-coated pumice towards Cr(VI) was analyzed using pseudo-first order using the linear plot of ln(qe-qt) versus t and pseudo-second order kinetic model using the linear plot of t/qt versus t, as given in Figure 5. It was seen in that the adsorption of Cr(VI) onto Mn-coated pumice fitted the pseudo-second order

Figure 4. Effect of time on Cr(VI) adsorption onto Mn-coated pumice adsorbent

**Figure 5.** The graphs of time versus ln (qe-qt) (a) and time versus t/qt (b)

Table 1. Adsorption kinetics parameters

Kinetics model	Parameters	Values
Pseudo-first order	k_1 (min^{-1})	0.0152
	qe (mg/g)	1.55
	R^2	0.43
Pseudo-second order	k_2 (g/mg.min)	0.0049
	qe (mg/g)	4.00
	R^2	0.90

kinetics models which means that the rate-limiting step is a chemical interaction, and the rate of adsorption did not depend on the concentration of the Cr(VI) ions. The kinetics parameters of adsorption process in this study were summarized in Table 1.

Adsorption isotherms

Figure 6 illustrates the impact of the initial concentration of Cr(VI) on the adsorption process onto Mn-coated pumice. As the initial concentration of Cr(VI) rose from 5 to 50 mg/L, the
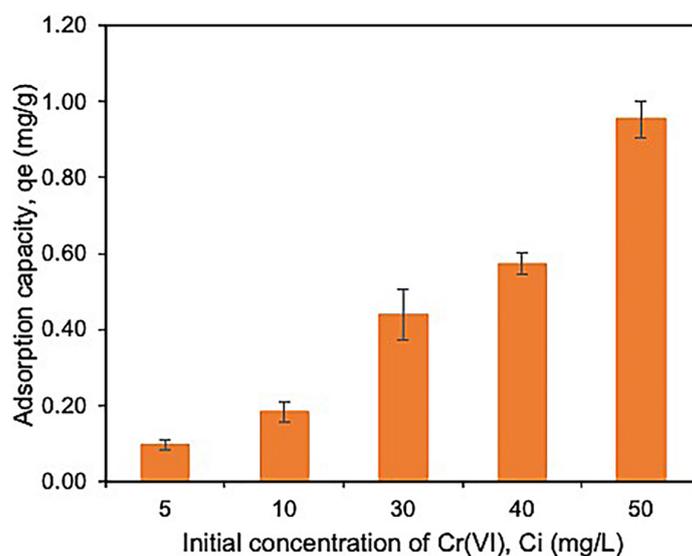
Figure 6. The graph of initial concentration of Cr(VI) versus adsorption capacity

Table 2. Adsorption isotherms parameters

Kinetics model	Parameters	Values
Langmuir isotherm model	q_{max}(mg/g)	1.94
	K_L	0.023
	R^2	0.99
Freundlich isotherm model	n	1.11
	K_F	0.025
	R^2	0.98

Table 3. Adsorption capacity of some pumice-based adsorbents to remove heavy metals in water

No.	Adsorbent	Heavy metal ions	Adsorption capacity (mg/g)	References
1.	Pumice	Cu(II)	1.43	Öztürk and Şahan, 2015
2.	Fe-coated pumice	As(V)	0.387	Far et al., 2012
3.	Mn-coated pumice	As(V)	0.072	Far et al., 2012
4.	Pumice	Pb(II)	7.46	Şahan and Öztürk, 2013
5.	Chitosan-pumice	As(V)	0.71	Asere et al., 2017
6.	Manganese-coated pumice	Cr(VI)	1.94	This study

adsorption capacity exhibited an increase from 0.10 to 0.95 mg/g. The likelihood of a collision between Cr(VI) and the adsorption sites of the adsorbent increases with the increasing concentration.

The analysis of the adsorption isotherms of Cr(VI) onto pumice coated with Mn involved the application of linearized Langmuir and Freundlich isotherm models. A summary of the adsorption isotherm parameters derived from both models is presented in Table 2. Cr(VI) adsorption onto Mn-coated pumice stone fitted both the Freundlich and Langmuir isotherm models. The findings suggest that the adsorption process might employ a hybrid configuration, combining both monolayer and multilayer adsorption mechanisms. The maximum adsorption capacity of Cr(VI) onto Mn-coated pumice stone adsorbent (q_{max}) was 1.94 mg/g. The 1/n value obtained from the linearized Freundlich isotherm was 0.899 which is between 0-1 suggesting that the adsorption of Cr(VI) onto Mn-coated pumice was favorable (Çifçi and Meriç, 2017). The comparison of the ability of some pumice-based adsorbents to remove heavy metals in water was given in Table 3. It can be seen that the maximum adsorption capacity of Mn-coated pumice toward the heavy metal ion Cr(VI) was relatively similar to some reported studies.

The results of this study indicated that the prepared Mn-coated pumice adsorbent is capable of eliminating the hexavalent chromium ions from water via adsorption process. However, the maximum adsorption capacity of the adsorbent toward Cr(VI) ions was relatively low. This disadvantage can be overcome by modifying and or increasing the surface are of the pumice stone, for example by decreasing the size to nano-size.

CONCLUSIONS

The Mn-coated pumice powder was prepared and was used to eliminate the hexavalent chromium, Cr(VI), in water via adsorption process. FTIR analysis showed the presence of Si-O-Si and Si-O-Al, as well as H-O-H bonding. The adsorption of Cr(VI) was most effective at a pH of 3, as this is where the predominant Cr(VI) forms, namely $Cr_2O_7^{2-}$ and CrO_4^{2-}, interact effectively with the positively charged surface of the pumice adsorbent coated with Mn. The adsorption process exhibited a rate constant of 0.0049 g/mg.min which was derived from the pseudo-second order model. The adsorption fitted both Langmuir and Freundlich isotherm models. The linearized Langmuir isotherm model predicted that the highest adsorption capacity of Cr(VI) onto Mn-coated pumice was 1.94 mg/g.

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