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Potential of waste pumice and surface modified pumice for hexavalent chromium removal: Characterization, equilibrium, thermodynamic and kinetic study

Mohammad Noori Sepehr [a], Abdeltif Amrane [b], Kamal Aldin Karimaian [c], Mansur Zarrabi [a,*], Hamid Reza Ghaffari [d]

[a] Department of Environmental Health Engineering, Faculty of Health, Alborz University of Medical Sciences, Karaj, Iran
[b] Ecole Nationale Supérieure de Chimie de Rennes, Université Rennes 1, CNRS, UMR 6226, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France
[c] Department of Environmental Health Engineering, Faculty of Health, Kurdistan University of Medical Sciences, Sannandaj, Iran
[d] Department of Environmental Health, Faculty of Health, Hormozgan University of Medical Sciences, Bandar-e-Abbas, Iran

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ABSTRACT

The sorption potential of natural (NP) and surface modified pumice using $MgCl_2$ (MGMP) as an abundant and low cost geo-material for the removal of Cr(VI) ion was investigated. The influence of contact time, solution pH, initial metal concentration, amount of absorbents and solution temperature was studied. Natural and modified adsorbents were characterized by means of XRD, XRF, SEM and FTIR technologies. Maximum sorption was observed at pH 1 and 100 mg/L metal concentration. Equilibrium data were accurately fitted onto Langmuir, Freundlich and Temkin isotherms, showing the heterogeneous nature of the adsorbents; maximum sorption capacity according to the Langmuir isotherm were 87.72 mg/g and 105.43 mg/g for NP and MGMP, respectively, showing a high sorption potential if compared to adsorbents used for Cr(VI) removal. Intra-particle model demonstrated that film diffusion was the rate-limiting step instead of intra-particle diffusion, as confirmed from the analysis of pseudo-second order rate constants, showing an absence of limitation due to pore diffusion. Relevance of pumice was confirmed since high regeneration yields were obtained, 94.3% in acidic conditions (1 M HCl) for spent non-modified pumice and 91.3% in alkaline conditions (4 M NaOH) for spent modified pumice.

1. Introduction

In recent years, the rapid industrialization leads to increasing industrial discharges without any appropriate treatment of them [1]. Environmental pollution by industrial effluents especially those containing heavy metals was reported by many researchers [2]. Heavy metals are among the main environmental pollutants and the main source of this pollution is industrial activities [3]. Heavy metals are a general term applied to a metal or a metalloid, which has an atomic density greater than 4 g/cm^3 [4]. The presence of heavy metals in industrial and municipal effluents is an important problem related to the water resource pollution [5]. Heavy metals such as lead, mercury and chromium represent potential hazard to both environment and humans due to their carcinogenic and toxic effects [6,7]. Chromium is mainly originated from industrial activities such as metal plating, tanning industry, electroplating and so on [8,9]. In the environment, chromium exists in two oxidation states, namely hexavalent and trivalent forms. It is reported that Cr(VI) is more toxic than Cr(III) and also more soluble in soil and water [10]. Due to high toxicity of hexavalent chromium, its maximum level in aqueous environment should be below 0.1 mg/L [9]. Therefore, removal of chromium(VI) from effluents before their release is an important environmental issue. For this purpose, in recent years researchers tested several methods such as chemical precipitation, ion exchange, biological process and others for the removal of Cr(III) and Cr(VI) [11–14]. Among them, adsorption has received much attention to remove chromium ions, especially using activated carbon as an adsorbent. The economic issue and the need for the regeneration of the used adsorbents led researchers to investigate other inexpensive and economic adsorbents for the removal of chromium [15,16].

Geomaterials are low cost adsorbent resources showing frequent applications in the treatment of water and wastewater. They are mostly locally available and requirements before possible uses remain low [17,18]. In the series of geomaterials, pumice is a porous and amorphous material which mainly consists of SiO_2 and is traditionally used in the construction industry and bio-medicine

* Corresponding author at: P.O. Box No. 31485/561, Karaj, Iran.
Tel.: +98 2614336007/9; fax: +98 2614319188.
E-mail address: mansor62@gmail.com (M. Zarrabi).

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[19,20]. Besides traditional applications, pumice has been also investigated in the field of wastewater treatment for the removal of cadmium [21], the catalytic degradation of *p*-chloronitrobenzene in the presence of ozone [22], phenol and 4-chlorophenol [23], water softening [18,24] and so on. Iran is rich in pumice, which is mainly used in the construction industry. Due to the numerous advantages of pumice stone, its low cost and its accessibility in Iran, the purpose of this work was to investigate pumice waste for the removal of toxic Cr(VI).

Various methods have been tested for the modification of natural occurring materials, since it is believed that natural occurring materials has lower adsorption capacity; and hence appropriate modification with mineral or organic materials will improve natural adsorbent sorption capacity. A methylation process for the modification of biomass of *Spirulina platensis* [5], a poly 3-methyl thiophene polymer modification of chitosan [8], surfactant modified natural red clay for simultaneous adsorption of chromium(VI) and phenol [25] and Montmorillonite-supported magnetite nanoparticles [26] have been reported for the removal of chromium(VI), as well as chemically treated pumice with cationic surfactant for the removal of phenol and 4-chlorophenol [23]. Furthermore, many researchers tested magnesium modified adsorbent for the removal of various pollutants such as dyes [27] and fluoride [28]. However and to our knowledge, surface modified pumice with magnesium chloride solution has not been previously used for Cr(VI) removal. Recently, the potential of natural and chemically activated pumices by means of aqueous solution of magnesium chloride and hydrogen peroxide [17], as well as natural and alkali modified pumices have been examined for the removal of hardness agents from single and binary solution [18]. Therefore, in the present work, chemically activated pumice with aqueous solution of magnesium chloride was used and compared with natural pumice for the sorption of Cr(VI).

2. Materials and methods

2.1. Chemicals

All chemicals used in this work were obtained from Merck (Merck Co. Germany). 1 M H_2SO_4 and NaOH were used for pH adjustment and control (Jenway, Model 3510). $K_2Cr_2O_7$ of analytical grade (Merck) was used for the preparation of a stock solution using deionized water. This was further diluted to the desired concentration for practical use. Natural pumice stones were obtained from Tikmeh Dash Reign, East Azerbaijan province, Iran.

2.2. Analytical methods

The chromium concentration was measured by means of an UV/VIS spectrophotometer at 542 nm (model 1700, Shimadzu Japan) according to standards methods for the examination of water and wastewater using diphenylcarbazide method (method 3500-Cr D) [29]. This method is only used for the measurement of hexavalent chromium. For this purpose, a stock solution of diphenylcarbazide was prepared by adding 0.25 g 1,5-diphenylcarbazide onto 50 mL acetone. For the measurement of the hexavalent chromium concentration, 20 mL of chromium solution was transferred onto 50 mL beaker and then the pH was adjusted at 1 ± 0.3 with concentrate HNO_3. About 2 mL of prepared 1,5-diphenylcarbazide solution was then added to the beaker and after 10 min reaction time, the absorbance of the purple colored solution was read at 540 nm.

The adsorbent morphology was observed with a scanning electron microscope (SEM, Philips-XL30, Holland) equipped with energy dispersive X-ray microanalysis. The specific surface area of natural and modified adsorbent was measured using a nitrogen adsorption technique based on the Brunauer–Emmet–Teller isotherm model (Micromeretics/Gemini-2372). The functional groups on the surface of used adsorbents were analyzed using Fourier Transform Infrared spectroscopy at wavelengths in the range 400–4000 cm^{-1} (Bruker-VERTEX 70, Germany). The chemical compositions of the used adsorbents were determined by means of an X-ray fluorescence spectroscopy (XRF) instrument (Philips-Magix Pro, Netherlands). The crystalline structures of the used adsorbents were determined using an X ray diffractometer (XRD) which are collected by means of a PHILIPS Xpert pro with Cu Kα as radiation (1.54056 Å) generated at 40 kV and 40 mA instrument. The diffractograms wereobtained with a step width of 0.02° (2θ) and a scan rate of 8°/min.

2.3. Preparation of the adsorbent

Natural pumice stone was thoroughly washed several times with distilled water in order to remove any impurities until the turbidity value became lower than 0.1 NTU. The adsorbent was then treated with 1 M HCl to complete purification and remove any acid soluble impurities. It was then washed with deionized water to remove the excess of acid (pH 7). pumice was then dried at 55 °C for 24 h to remove the remaining water. The dried pumice was crushed and sieved to 10–30 mesh (2000 to 841 μm). The prepared adsorbent (about 100 g) was then introduced into 1 L beaker which was filled with 2 M $MgCl_2$ and left for 24 h at laboratory temperature to complete the modification. The beaker containing raw adsorbent and $MgCl_2$ was stirred for 24 h at 100 rpm for more impregnation. After 24 h, the adsorbent was removed from the beaker, filtered and kept in an electric furnace at 750 °C for 6 h (Lenton, England) to improve crystallization. After 6 h calcination, the adsorbent was washed several times with deionized water to remove the excess of $MgCl_2$. The modified adsorbent was then dried at 55 °C for 24 h and then used.

2.4. Batch experiments

All experiments were conducted in a batch mode in 250 mL conical flasks. Various experimental parameters, such as pH (1–9), temperature (10–50 °C), adsorbent mass (2–10 g/L), initial chromium concentration (10–100 mg/L) and contact time (10–300 min) were investigated. For the determination of the equilibrium time and the effect of the initial chromium concentration on the removal efficiency, adsorption properties were first studied by varying the contact time and the chromium concentration. A pH of 3 was considered and the adsorbent mass was 6 g/L based on the average adsorbent dosage. 6 g/L of natural or modified adsorbent was introduced into each conical flask containing the chromium ion at a concentration in the range 10–100 mg/L and the flask was shaken at 200 rpm (Hanna-Hi 190 M, Singapore). At a predetermined time interval, samples were taken, filtered (0.45 μm, Wathman), centrifuged (Sigma-301, Germany) and the chromium concentration was determined. Experiments were performed at room temperature. The removal efficiency was calculated by means of the following equation (Eq. (1)):

$$RE = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

where *RE* (%) is the percentage of chromium removed at equilibrium time; C_0 and C_e are the initial and equilibrium concentrations of chromium (mg/L), respectively.

After determination of the equilibrium time, 250 mL chromium solution containing 100 mg/L of solute was added to five 250 mL