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Efficiency of perlite as a low cost adsorbent applied to removal of Pb and Cd from paint industry effluent

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ABSTRACT

Among the major environmental concerns worldwide is release of heavy metals in the environment. Different studies have demonstrated that natural volcanic glass has high capacity in removal of divalent heavy metal ions. Perlite is a volcanic rock with high porosity and specific surface area which costs much lower in comparison with the other adsorbents. In this study, the removal of lead and cadmium from Binalood paint industry (Kerman, Iran) effluent by perlite is investigated in batch conditions. Lead and cadmium measurements are carried out with atomic absorption spectrophotometeric methods adapted from standard methods applied to the examination of water and wastewaters. In this regard, the effect of pH, dosage and contact time is also determined and Langmuir and Freundlich isotherms are obtained. Results show that adsorption process follows Freundlich adsorption isotherm model. The maximum obtained removal efficiency at pH = 7 are close to 100% and 97.7% for lead and cadmium, respectively. These efficiencies are achieved in 10 g/l perlite and recommended contact time is 1.5 h. Finally, perlite is recommended as a low cost and accessible adsorbent to remove lead and cadmium from municipal and industrial wastewaters.

Keywords: Lead; Cadmium; Adsorption; Perlite; Paint industry

1. Introduction

Heavy metals are not biodegradable. Therefore, their accumulation in streams and lakes can lead to hazardous health problems in animals, plants and human beings [1,2].

Lead is a metal with no known biological benefit to humans. High concentration of this metal can damage various systems of the body. Among the physical effects of lead poisoning are damage of nervous, reproductive systems and the kidneys. In addition, high blood pressure, anemia, coma and finally death are remarkable results of lead exposure [2]. The health-based guideline of lead in drinking water was reported 0.01 mg/l [3].

Cadmium is an irritant for the respiratory tract. Exposure to this pollutant can lead to anemia, renal damage, osseous disease with the similar effects to osteoporosis and Itai-Itai disease [4,5].

People are exposed to these heavy metals through air, food and water. However, water is generally less effective in comparison with air and food. Paint industry effluent is one of the heavy metals sources that can cause adverse effects if it is discharged without any treatments to streams and lakes.

To date, several heavy metal removal techniques were developed. In recent years, adsorption techniques

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have become more popular due to their removal efficiencies especially for metal ions [6].

In last decade, many adsorbents, including natural zeolite, hydroxyapatite, peat, ash, rice husk, volcanic ash and pumice have been proposed for adsorption of heavy metal ions [7–13].

Current study investigates perlite as a low cost adsorbent for paint industries effluent treatment. Perlite is essentially a metastable amorphous aluminum silicate which can be considered as mixed oxide containing mainly SiO_2 and Al_2O_3. Obsidian, quartz, feldspar, biotite and magnetite are the major minerals that occur in the glassy matrix of perlite [14]. Surface layer of perlite has negative charges due to interlaying of silica by aluminum in silica tetrahedra [15]. Perlite is greatly expanded in 860–1200 °C, because water trapped in the structure of the material vaporizes and escapes and this causes the expansion of the material to 4–20 times more than original volume [16]. Dogan and Alkan [17] investigated electro-kinetic properties of expanded and unexpanded perlite, reporting negative zeta potential value at all pH conditions. They related this change to interlaying of silica by alumina, defects in crystal lattice, broken particle edge, and structural hydroxyl groups [17]. Antonacci et al. [18] studied the adsorption of some organic solution on modified perlite. They found that perlite was quite effective in extraction of organic solute from water [18]. In another study, expanded and unexpanded perlite has also been used as an adsorbent for the adsorption of methyleneblue from aqueous solution. Results showed that unexpanded perlite is more effective than the expanded one [19]. Mathialagan et al. (2002) studied the removal efficiency of expanded perlite as adsorbent of Cd from aqueous solution and concluded that perlite can be considered as a potential adsorbent for this purpose. Their results showed that the maximum removal of Cd obtained from batch study was 55% [20]. The aim of this study is to detect the efficiency of Miane (Northwest of Iran) unexpanded perlite for adsorption of Cd and Pb in paint industries effluent.

2. Material and methods

2.1. Adsorbent preparation

Perlite tephra extracted from Miane mines (Northwest of Iran) was selected as adsorbent. The word tephra is used as a collective term for unconsolidated fragmental material, produced during explosive volcanism [21]. It includes all airborne material such as ashes, pumice and perlite. Perlite rhyolitic tephra consists mostly of silicic glass with a variable content of crystals of several minerals distributed in the glassy matrix. Table 1 shows the characteristics of Miane perlite.

Table 1
Typical characteristics of Miane perlite mine ore [22]

Elements/compounds (wt. %)	Value
Al_2O_3	12.85
SiO_2	68.33
CaO	1.73
Fe_2O_3	1.50
K_2O	2.20
MgO	10.67
Na_2O	1.26
FeO	0.01

Perlite was crashed and sieved through #30 and #20 sieves, and then crashed materials were washed several times to remove fines and undesirable materials with deionized water and dried in oven at 105 °C for 24 h.

2.2. Effluent samples characteristics and samples preparation

Binalood paint industry with 70 tons/month paint productions approximately produces 200 m^3/mo wastewater commonly containing Cd, Pb, Cu, Ni and Cr. Samples were taken from equalization tank effluent. After pH and temperature measurements, samples were transferred to the laboratory. In order to remove supernatant and unwanted suspended materials, each sample was settled one hour and filtered through 0.45 μm Polycarbonate filter. To preserve metals content, by adding acid lowered pH until it reached to less than 2 and kept at 4 °C. In order to determine raw wastewater characterization, prepared samples were analyzed with nonflame atomic absorption techniques. Moreover, test methods were adapted from 19th Edition of standard methods for the examination of water and wastewater [23]. The effect of different conditions (contact time, pH and adsorbent dosage) was investigated according to similar studies [24–26]. Meanwhile, for evaluation of perlite efficiency in peak condition, Pb and Cd content has been increased to higher concentration (two fold) by adding metal standard solutions (Pb $(NO_3)_2$ and Cd $(NO_3)_2$. The mentioned metals concentration was 11 mg/l Pb and 2.6 mg/l Cd.

2.3. pH study

To determine the effects of different pH values on the adsorption rate, prepared sample was influenced by standard HCl and NaOH solution. Then, sample pH adjusted to 3, 7 and 10. Afterward, 10 g perlite was added to each 1 l sample, stirred at 200 rpm and every 10 min. A 10 ml sample was withdrawn, filtered through 0.45 µm polycarbonate filter and Pb and Cd contents were measured. Then optimum pH was determined for next steps. In order to determine pH effect on metal settlement in alkaline condition, one blank sample without perlite at pH = 10 was obtained. The amount of metal sorbed by perlite (q) and the removal efficiency were calculated by the following equations:

$$q = V(C_0 - C_e)/\mathrm{m} \quad (1)$$

$$\text{Removal (\%)} = [(C_0 - C_e)/C_0] \times 100 \quad (2)$$

where, C_0 is the initial concentration (mg/l), C_e is the equilibrium concentration (mg/l), V is solution volume (l) and m is the amount of adsorbent (g). If there were any settlement in blank sample, it was considered at calculation.

2.4. Contact time

In order to determine optimum contact time, 10 g perlite was added to 1L beaker containing effluent with 11 mg/l Pb and 2.6 mg/l Cd. During the reaction, the effluent was stirred with a mechanical mixer to 200 rpm and every 10 min, 10 ml sample was withdrawn and filtered and Pb and Cd content was measured until reached to equilibrium state.

2.5. Adsorbent dosage

By adding different dosages of absorbent (1–10 g/l) to metal solution with the same concentration, the effect of different quantities of adsorbent was determined. The optimal pH and contact time conditions achieved previously were also applied.

2.6. Adsorption isotherm

In this study, experimental data were modeled by Langmuir and Freundlich isotherms according to Metculf & Eddy [27]. The adsorption isotherm models measured in 25 °C ± 1, pH = 7 and fixed concentration of Pb and Cd. Different dosages of adsorbent (1–10 g/l) were added to beakers, containing 11 samples with fixed concentration of Pb and Cd. Then mixed with a mechanical mixer to 200 rpm speed the resulted sample was filtered. Every 10 min, Pb and Cd measurements were done for the withdrawn samples until reached equilibrium.

To control any leaching interference during the test period, a sample was prepared by adding perlite to 1000 ml of deionized water as a blank sample.

2.7. Analytical method

Pb and Cd measurements were taken with atomic absorption spectrophotometeric methods and test methods were adapted from standard methods for the examination of water and wastewater [23]. pH was measured by digital pH meter, Hanna instruments.

3. Results and discussion

The average Pb and Cd concentrations of ten raw wastewater samples were 5.6 and 1.8 mg/l, respectively, after transferring to the laboratory. The reported quantities are more than maximum contaminant level (MCLS) for wastewater used in agricultural irrigation (Cd: 0.01 mg/l and Pb: 5 mg/l) and propounded as the most important environmental problem, due to their toxicities, accumulation and inhibition for plant cell growth [28].

3.1. Effect of pH

The results of pH effect on the adsorption rate of Cd and Pb on perlite are illustrated in Figs. 1 and 2. Fig. 1 shows the removal efficiency for Pb at various ranges of pH from 3 to 10. pH variations showed a negligible effect on the adsorption rate. At lower pH condition, the adsorption rate decreases but there exist no significant differences between the average Pb removal in different $\mathrm{pH_s}$ (sig = 0.628). However, as shown in Fig. 2, effect of pH on Cd adsorption is considerable and in alkaline condition the Cd removal increases. The silicon atoms at the surface of perlite tend to "maintain their tetrahedral coordination with oxygen completed at room temperature by attachment to monovalent Hydroxyl groups, forming Silanol groups". Adsorption

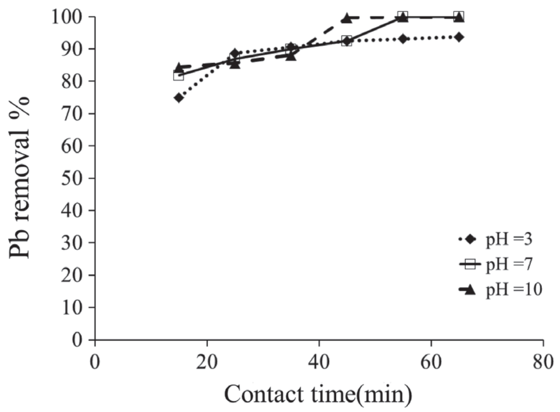

Fig. 1. Effect of pH on Pb adsorption using perlite, M = 10 g, C_{Pb} = 11 mg/l.

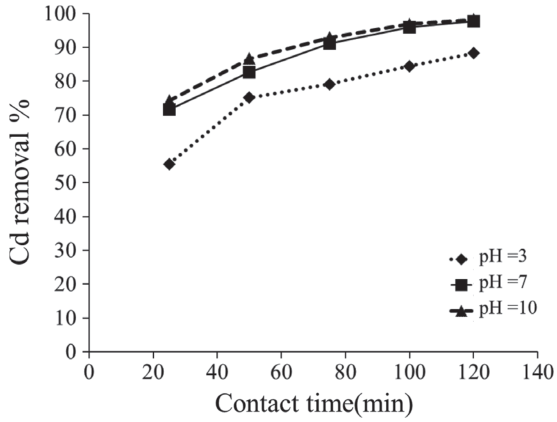

Fig. 2. Effect of pH on Cd adsorption using perlite, M = 10 g and C_{Cd} = 2.6 mg/l.

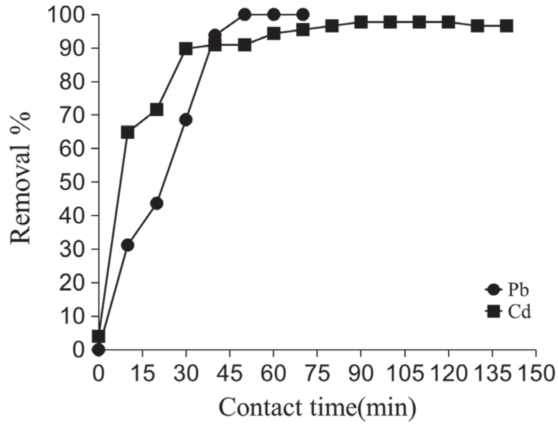

Fig. 3. Effect of contact time on Cd and Pb adsorption by 10 g perlite and at pH = 7.

capacity of perlite is related to silanole groups on the surface of perlite [29]. In alkaline condition Cd^{++} and Pb^{++} tend to settle and become insoluble and also produce more negative charge on the perlite surface. These results are in accordance with Viraraghavan et al. [26]. Statistical analysis showed that in adsorption of Cd, there is a significant difference between the means of Cd removal at pH = 3 with pH = 7 and 10 (sig = 0.019). There is not any significant differences at pH = 7 and 10 (sig = 0.908). According to limitations in discharge of acidic and alkaline effluents to the environment, neutral pH is logical and acceptable in the removal process. The optimum pH (pH = 7) was selected for further experiments.

3.2. Effect of contact time

Fig. 3 shows removal percentage of Pb and Cd (ions) as a function of contact time at the optimum pH of 7.0. From this figure it can be seen that the adsorption of Pb and Cd increases by contact time and equilibrium was reached within 60 min and 90–120 min, respectively. It is evident from Fig. 3 that the uptake rate of Cd and Pb by perlite was rapid within first 20 min. The removal rate of Cd and Pb graduately decreased with increase of contact time. Initially, the removal rate of Cd and Pb were higher because all sites on perlite were vacant and solute concentration was high, but decreasing in sorption sites reduced the uptake rates. Removal efficiencies for Pb and Cd at the same conditions were closed to 100% and 97.7%, respectively. Compared with the results of similar studies about perlite efficiency for removing heavy metals, this study showed higher efficiencies which is due to different type and origin of perlite [20]. Therefore, concerning the technical and economical aspects, 1.5 h contact time is recommended for Pb and Cd removal from wastewater by perlite adsorption and these results were generally in agreement with those of previous studies [25].

3.3. Effect of perlite dosage

Study of different dosages of perlite showed that the increasing amount of adsorbent, providing more adsorption capacity has a great role in adsorption of Cd and Pb (Fig. 4). As amount of perlite increases, the metal adsorption increases significantly. Results showed that at pH = 7 and using 10 g/l of perlite the maximum Pb and Cd adsorptions were about 100% and 97%, respectively.

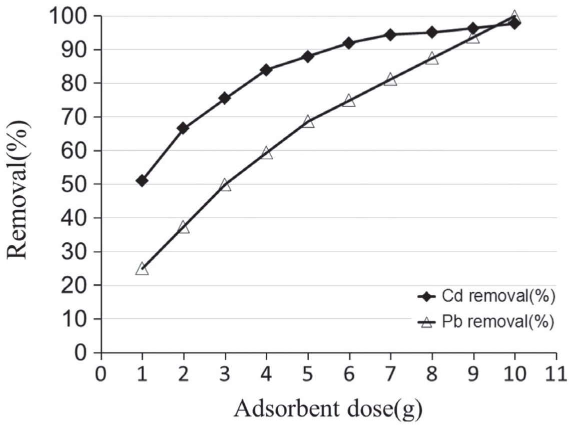

Fig. 4. Effect of different doses of adsorbent on Cd and Pb removal.

3.4. Adsorption models

For modeling heavy metals adsorption from wastewater, two models (Langmuir and Freundlich) were used. The simplest equation for adsorption under equilibrium conditions was derived by Langmuir using kinetic theory. The Langmuir model considered a surface with a specific number of binding sites that are identical and can adsorb one molecule. The Freundlich equation is one of the first equations purposed to relate the amount of material adsorbed to the concentration of material in solution. The Langmuir and Freundlich equations are:

Langmuir model $q = [q_m.K_L.C]/[1 + K_L.C]$ (3)

Freundlich model $q = K_F.C^{1/n}$ (4)

where q: the amount of metal ions adsorbed per specific amount of adsorbent (mg/g); C: equilibrium concentration (mg/l or mmol/l); q_m: the amount of metal ions required to form a monolayer (mg/g); K_L: Langmuir equilibrium constant; K_F and $1/n$: indicative isotherm parameters of sorption capacity and intensity, respectively [29]. The values of Freundlich and Langmuir constants are reported in Table 2. In Freundlich model, the value of 1/n was between 0 and 1, indicating that the sorption of metal ions onto perlite was favorable under the mentioned conditions [30].

Figs. 5 and 6 shows that Freundlich isotherm model fits experimental results better than Langmuir model, in agreement with the results reported by Matialagan et al. [20]. However, there are controversial results in the literature as other previous studies [30–33] reported that Cu, Cd and Pb sorption fitted well the Langmuir model. The Freundlich isotherm has an assumption that sorption takes place at a heterogeneous surface with non uniform distribution [34].

As a consequence, the Freundlich isotherms for Pb removal by raw perlite can be represented by the following empirical formula:

Table 2
Freundlich and Langmuir model parameters

Freundlich model components	Pb	Cd
K_F	0.94	0.79
$1/n$	0.35	0.468
R^2	0.98	0.981
Langmuir model components	Pb	Cd
$q_{m(mg/g)}$	2.47	1.148
K_L	0.59	2.55
R^2	0.85	0.923

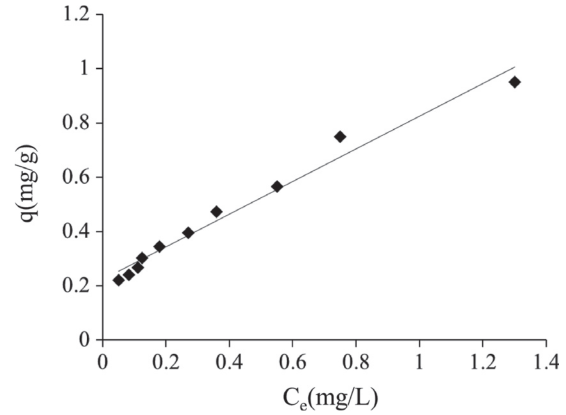

Fig. 5. Freundlich equation for Cd adsorption by perlite, pH = 7, T = 25 °C, C_e: Equilibrium metal concentration (mg/l).

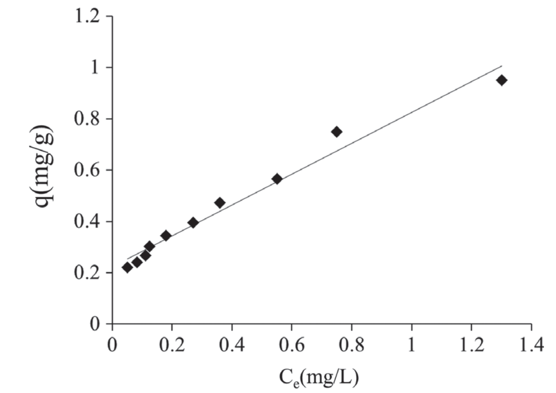

Fig. 6. Freundlich equation for Pb adsorption by perlite, at pH = 7, T = 25 °C, C_e: Equilibrium metal concentration (mg/l).

$Q = 0.94\ x^{0.35}$ (5)

Cd removal by raw perlite can be represented as:

$Q = 0.79\ x^{0.468}$ (6)

Regarding monolayer adsorption capacity of perlite for Pb, Sari et al. (2007) determined higher q_m(13.39mg/g) [33].

In Table 3, removal efficiency of different adsorbents was compared. Perlite has lower adsorption capacity than clinoptilolite related to Cd, but it could be a competitive adsorbent related to montmorillonite for Cd adsorption.

Table 3 shows that perlite has a high adsorption capacity related to Pb and it could be a selective adsorbant for Pb removal from effluents.

Table 3
Comparison of different supports

Sorbent support	q (mg/g)		Removal %		Ref.
	Cd	Pb	Cd	Pb	
Perlite	0.20 – 0.95	0.20 – 2.0	97.7	≈100	Current results
Perlite	0.42	–	55	–	[20]
Leca	0.22 – 0.75	1.41 – 3.0	89.7	93.7	[35]
Fly ash	–	–	93	–	[26]
Wood ash	–	–	–	96.1	[25]
Bio mass					
Crab shell	–	19.83 ± 0.29	–	–	[24]
Area shell	–	18.33 ± 0.44	–	–	[36]
Clinoptilolite	2.40	1.60	–	–	[37]
Montmorilonite	0.72	0.68	–	–	[38]

4. Conclusion

This study demonstrates the potential of perlite for removal of $Pb^{(++)}$ and $Cd^{(++)}$ from paint industry effluent.

- With the gradual increase of the adsorbent amount, adsorption rate has been increased and finally with 10 g/l of adsorbent and at pH = 7 this rate reached to maximum level of 100% for Pb and 97.7% for Cd.
- The data obtained from batch studies were applied to Langmuir and Freundlich isotherm. The latter showed better correlation coefficient value compared to Langmuir isotherm.
- The best results were obtained (100% for Pb and 97.7% for Cd) under optimized condition of 1 h and 1.5 h for Pb and Cd of shaking time using perlite as adsorbent, respectively. Overall, the recommended contact time was 1.5 h.
- Adsorption of Pb and Cd by perlite was favored in alkaline condition, but because there is not any significant differences between the pH = 7 and pH = 10, the pH = 7 is favorite one.
- The affinity of Pb and Cd for perlite at constant and non constant pH was Cd < Pb.

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