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ACID MINE DRAINAGE TREATMENT BY PERLITE NANOMINERAL, BATCH AND CONTINUOUS SYSTEMS

OCZYSZCZANIE KWAŚNYCH WÓD KOPALNIANYCH PRZY WYKORZYSTANIU NANOMINERAŁU PERLITU – SYSTEMY DZIAŁANIA CIĄGŁEGO I OKRESOWEGO

In this paper the adsorption activity of perlite nanoparticles for removal of Cu^{2+}, Fe^{2+} and Mn^{2+} ions at Iran Sarcheshmeh copper acid mine drainage was discussed. Thus, raw perlite that provided from internal resource was modified and prepared via particles size reduction to nano scale and characterized by X-ray diffraction, X-ray fluorescence, scanning electron microscopy, transmission electron microscopy, Fourier transforms infrared and BET specific surface area analysis. The results of acid mine drainage show that pH of acid mine drainage is 5.1 and Cu^{2+}, Fe^{2+} and Mn^{2+} ions are 10.5, 4.1 and 8.3 ppm, respectively. Firstly in the batch system the influence of adsorbent dose and temperature parameters were considered and then isothermal and kinetic models were investigated. According to the results the Langmuir isotherm and pseudo-second order kinetic model showed better correlation with the experimental data than other isotherm and kinetic models. Obtained thermodynamic parameters such as $\Delta G°$, $\Delta H°$ and $\Delta S°$ show that the Cu^{2+}, Fe^{2+} and Mn^{2+} ions adsorption from acid mine drainage is spontaneous and endothermic. Finally, perlite nanoparticles adsorbent was packed inside a glass column and used for the removal of heavy metals in 1, 3, 5 ml/min acid mine drainage flow rates, the breakthrough curves show that the column was saturated at 180, 240 and 315 min for different flow rates, respectively. According to the obtained results, this abundant, locally available and cheap silicate mineral showed a great efficiency for the removal of heavy metal pollutants from acid mine drainage and can be utilized for much volume of acid mine drainage or industrial scale.

Keywords: Acid mine drainage, Perlite nanoparticles, Cu^{2+}, Fe^{2+} and Mn^{2+} ions adsorption, Sarcheshmeh porphyry copper mine, batch and continuous systems

W pracy omówiono zdolności adsorpcyjne nano-cząsteczek perlitu wykorzystywanych o usuwania jonów $Cu^{2+,}$ Fe^{2+} i Mn^{2+} z kwaśnych wód kopalniach w kopalni miedzi w Sarcheshmeh w Iranie. Surowy perlit pozyskiwany ze źródeł własnych został zmodyfikowany i odpowiednio spreparowany poprzez zre-

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dukowanie cząsteczek do rozmiarów rzędu nano- cząsteczek. Perlit poddany został następnie badaniom z wykorzystaniem dyfrakcji promieniowania rentgenowskiego, rentgenowskiej analizy fluorescencyjnej, skaningowej mikroskopii elektronowej, transmisyjnej mikroskopii elektronowej, spektroskopii w podczerwieni z transformatą Fouriera. Przeprowadzono także badania powierzchni właściwej w oparciu o równanie BET. Wyniki badań kwaśnych wód kopalnianych wykazują ich kwasowość na poziomie 5.1, a zawartość jonów $Cu^{2+,}$ Fe^{2+} i Mn^2 wynosi odpowiednio 10.5, 4.1, 8.3 ppm. W pierwszym etapie analizowano system działania okresowego, zbadano wpływ następujących parametrów: ilości czynnika absorbującego i temperatury. Następnie przebadano modele izotermiczne i kinetyczne. Na podstawie uzyskanych wyników wykazano, że izoterma Langmuira oraz model pseudo-kinetycznego drugiego rzędu wykazują lepszą zgodność z danymi eksperymentalnymi niż pozostałe modele izotermiczne i kinetyczne. Uzyskane parametry termodynamiczne: $\Delta G°$, $\Delta H°$ i $\Delta S°$ wskazują, że adsorpcja jonów $Cu^{2+,}$ Fe^{2+} i Mn^2 z kwaśnych wód kopalnianych przebiega spontanicznie i jest procesem endotermicznym. W końcowym etapie badania nanocząsteczki perlitu- adsorbentu zostały umieszczone wewnątrz szklanej kolumny i wykorzystane do usuwania jonów metali ciężkich z kwaśnych wód kopalnianych podawanych z prędkością przepływu 1, 3, 5 ml/min. Krzywe przebicia wskazują, że kolumna została nasycona odpowiednio po 180, 240 i 315 dla odpowiednich prędkości przepływu. Uzyskane wyniki wskazują, że ten występujący lokalnie w dużych ilościach, tani i łatwo dostępny minerał krzemianowy wykazuje wysoką skuteczność w usuwaniu z kwaśnych wód kopalniach zanieczyszczeń w postaci metali ciężkich, dlatego też może być z powodzeniem wykorzystany do oczyszczania znacznych ilości wód a także na skalę przemysłową.

Słowa kluczowe: nanocząsteczki perlitu, adsorpcja jonów $Cu^{2+,}$ Fe^{2+} i Mn^2, kopalnia miedzi i porfirów Sarcheshmeh, systemy działania ciągłego i okresowego

1. Introduction

Contamination of water by heavy metals is a global problem (Danil de Namor et al., 2012), as, heavy metal ions consist of iron, lead, manganese, zinc, copper, chromium, nickel and cadmium and so on lead to many problems for human and air/soil/water environment. In the environment two main sources of heavy metals are natural background that derived from parent rocks and anthropogenic contamination including mineral industrial wastes, tailing damps of sulfide mines, agrochemicals and other output of industrial activities and factories (Li et al., 2012). Several conventional methodologies such as precipitation (Martin et al., 2010), ion exchange (Yuan et al., 2010), filtration membrane technology (Song et al., 2011), electrochemical processes (Karami, 2013) and adsorption process (Chiban et al., 2011) are available for heavy metal removal and other pollutants from wastewaters. Generally, they are expensive or ineffective sometimes, especially when the metal concentration is higher than 100 ppm (Schiewer and Volesky, 1995; Miretzky et al., 2006). Among all the treatments proposed, adsorption process is a popular method. It is now recognized as an effective, efficient and economic method for water decontamination applications and for separation to pilot purpose (Niu et al., 2007). Nowadays, the adsorption of pollutants by natural materials has been widely reported such as diatomite (Caliskan et al., 2011), perlite (Ghassabzadeh et al., 2010), red mud (Lopez et al., 2012), chitosan (Kyzas et al., 2013) , orange skin (Lugo et al., 2012), soy meal hull (Badii et al., 2008), almond skin (Doulati Ardejani et al., 2008), dead fungi biomass (Seifpanahi et al., 2011), sawdust (Pehlivan & Altun, 2008), zeolite (Egashira et al., 2012) and clay (Sheikhhosseini et al., 2013), these adsorbents have natural base and they are environmental friendly and it is possible to be regenerated most of them or be applied in different products, and also was used for synthetic wastewaters, usually. Acid mine drainage generation at Sarcheshmeh mine was happened and this acid drainage that caused many problems, was entered to surface and groundwater's. So, in this paper treatment of acid mine drainage consist of heavy metal ions by natural adsorbents with nanoscale particles size was

done. So, the objective of the present study is focused on the development perlite nanoparticles for removal of heavy metal ions consist of Cu^{2+}, Fe^{2+} and Mn^{2+} ions from Sarcheshmeh porphyry copper acid mine drainage.

2. Materials and Methods

In this research the raw perlite samples were obtained from internal sources, Zanjan mine at North West of Iran (Fig. 1).

Fig. 1. Perlite reservoirs in the Zanjan mines (N-W of Iran) and Sarcheshmeh copper mine (S-E of Iran)

The Sarcheshmeh copper mine is located at the South East part of Iran (Fig. 1). In this mine the results of acid mine drainage chemical analysis that was entered to Shur River, were showed at Table 1.

TABLE 1

The results of acid mine drainage chemical analysis

Ion	Fe^{2+}	Mn^{2+}	Cu^{2+}	Al^{3+}	Mo^{2+}	Pb^{2+}	Ni^{2+}	Ag^{2+}
Concentration (ppm)	4.1	8.3	10.5	0.24	0.29	0.65	0.003	0.057
SDWR (USEPA, 2011)	0.3	0.05	1	0.05-0.2	0.04	0	0.01	0.1

According to Table 1 the Cu^{2+}, Fe^{2+} and Mn^{2+} ions have very higher range than Secondary Drinking Water Regulation (SDWR) of United State Environmental Protection Agency (USEPA). So for removal of Cu^{2+}, Fe^{2+} and Mn^{2+} ions from Sarcheshmeh acid mine drainage the perlite nanoadsorbent was used.

In assessing the potential applications of perlite as nano for the removal of heavy metal ions from acid mine drainage, the modification of the material is an important issue to address. A variety of methodologies can be used to modify the perlite surface such as calcinations (Ghassabzadeh et al., 2010; Ediz et al., 2010; Jing et al., 2011), functionalization (Thanh et al., 2011; Fowler et al., 2007). So, raw perlite five times was washed with deionized water and then dried at 100°C for 8h. Next the samples were crushed by laboratory planetary ball mill (Fritsch Pulverisette 6 model) consist of distilled water in 250 rpm for 5h. Finally, slurry samples were dehumidifying by spray dryer (B-290 model) in 180°C and prepared for investigation the adsorption processes of heavy metal ions and characterization.

The chemical composition of the modified perlite nanoparticles which were determined by XRF 1800 model is given in Table 2.

TABLE 2

The chemical analysis of modified perlite nanoparticles

Constituent	Modified perlite nanoparticles (wt. %)
SiO_2	56.87
K_2O	17.70
Al_2O_3	18.36
Na_2O	2.61
Fe_2O_3	2.53
CaO	0.96
ZrO_2	0.19
MgO	0.20
SO_3	0.27
TiO_2	0.17
MnO_2	0.13

According to Table 2, modified perlite nanoparticles are mainly composed of silica as SiO_2. The hydroxyl species on perlite structure were identified as a function for adsorption process. Thus various hydroxyl species including isolated hydroxyl groups, H-bonded hydroxyl groups and water uptake have been identified for perlite (Yuan et al., 2004). Generally, the hydroxyl groups are classified according to their coordination to the silicon atom that was showed as Fig. 2.

The BET specific surface area analysis Quantachrome 2200e model was done for modified perlite nanoparticles and raw perlite is show in Table 3.

TABLE 3

BET Specific surface area of modified perlite nanoparticles and raw unmodified perlite

Material	Specific surface area (m^2/gr)
Modified perlite nanoparticles	89.7
Raw perlite	3.5

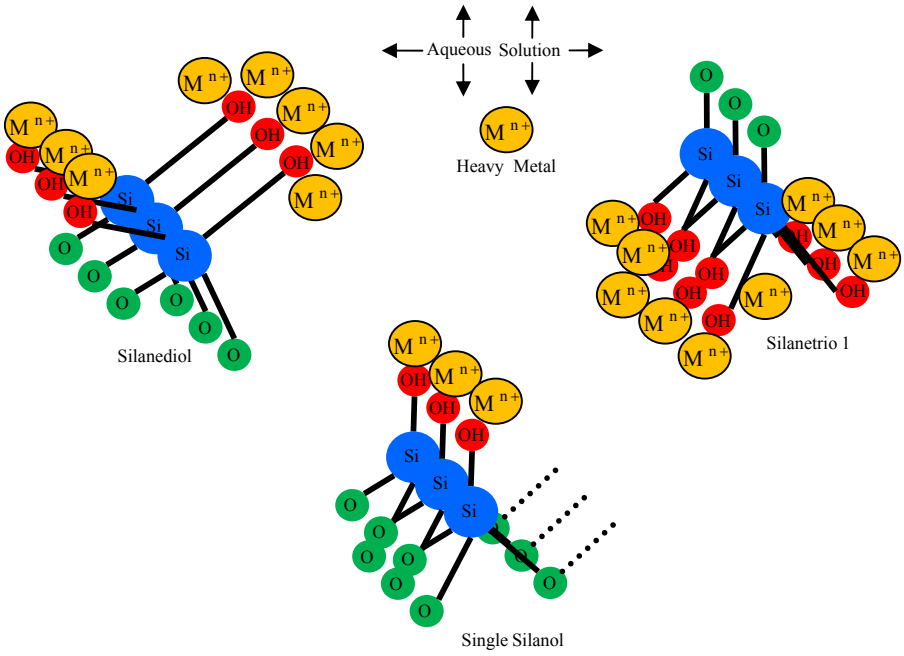

Fig. 2. The various arrays of hydroxyl groups that show for SiO_2 (Danil de Namor et al., 2012)

According to Muller (2010) researches the increase in surface area by decreasing the particle size of the perlite resulted in a higher uptake of heavy metal ions by the smaller particles relative to the larger ones (Muller, 2010).

The X-ray diffraction (XRD) patterns for modified perlite nanoparticles were obtained by XMD300-Unisantis X-ray diffractometer is show in Fig. 3.

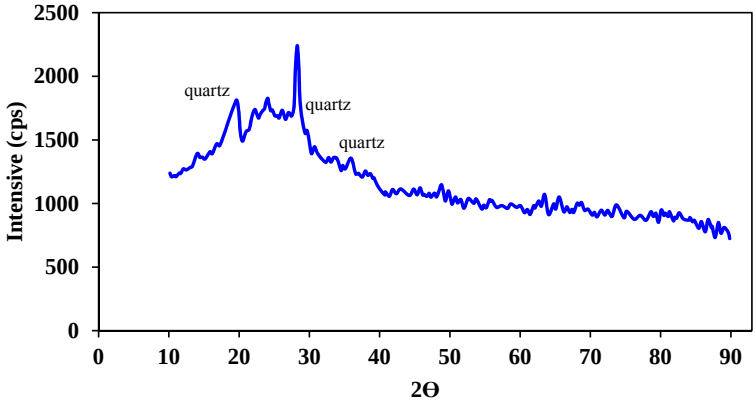

Fig. 3. XRD pattern of modified perlite nanoparticles

Scanning electron microscopy (SEM) LEO-1455VP model and the transmission electron microscope (TEM) PHILIPS CM120 model were used to study the morphology and homogeneity of the modified perlite nanoparticles.

The SEM (Fig. 4A) and TEM (Fig. 4B) images show the pure modified perlite nanoparticles. Generally, Fig. 4 shows the modified perlite nanoparticles that has an amorphous (Fig. 4A) granular (Fig. 4B) morphology with an average diameter of 150-200 nm.

The FT-IR technique is one of the most important characterization techniques used to elucidate the changes in chemical structures. FT-IR spectra of modified perlite nanoparticles for 1 min are shown in Fig. 5.

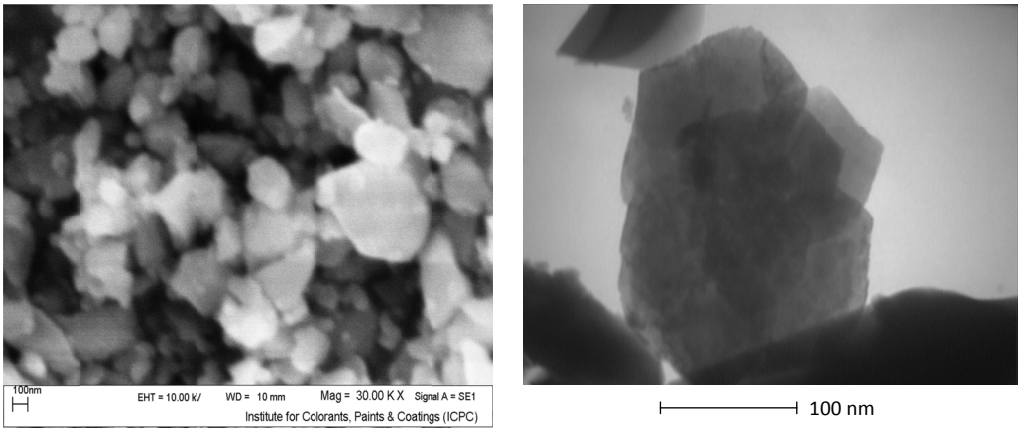

Fig. 4. SEM (A) and TEM (B) images for modified perlite nanoparticles

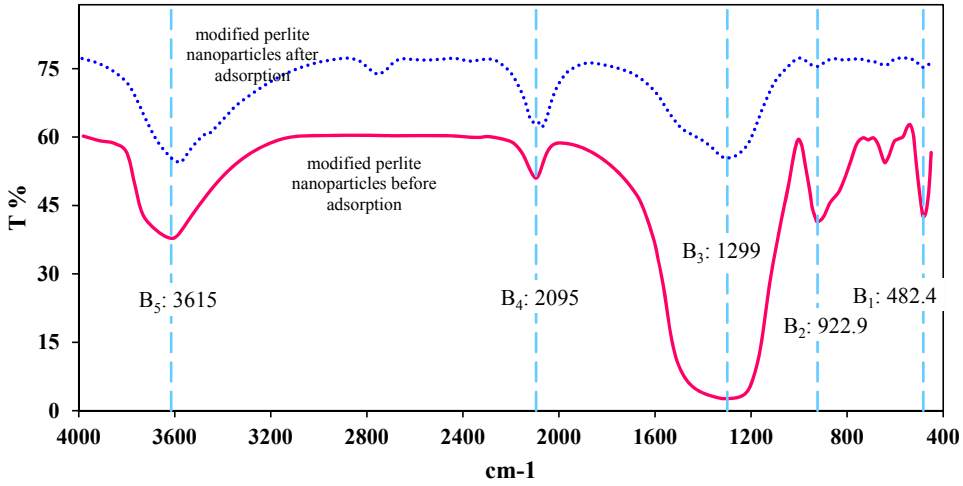

Fig. 5. FT-IR spectrum of the modified perlite nanoparticles before (————) and after (.....) ions adsorption process from acid mine drainage

According to Fig. 5, modified perlite nanoparticles five main absorption bands are observed at 482.4 cm^{-1} (B_1), 922.9 cm^{-1} (B_2), 1299 cm^{-1} (B_3), 2095 cm^{-1} (B_4) and 3615 cm^{-1} (B_5). Bands B_1 and B_2 are attributed to the Si–O stretching vibrations of Si–O–Si and Si–O–Al, respectively (Sodeyama et al., 1999). Band B_3 is the deformation band of molecular water (Roulia et al., 2006; Varuzhanyan et al., 2006). Band B_4 is attributed to molecular adsorbed water (Sodeyama et al., 1999). Band B_5 is attributed to the combination of OH stretching arising from hydrogen-bonded and free Si–OH (Hong and Minoru, 1994; Sodeyama et al., 1999). The intensities of bands B_3, B_4 and B_5 are closely related to the water content, similar to other silicate materials and minerals, such as volcanic tuffs and zeolites. Development of the silicate network has been attributed to de-hydroxylation of mainly Si–OH (see Fig. 2) groups during any thermal and chemical treatment, including those treatments that do not lead to modification (Roulia et al., 2006). On the other hand in Fig. 5, the FT-IR spectra of modified perlite nanoparticles before and after ions adsorption from acid mine drainage was showed. As is obvious the band B_5 was OH weaken after ions adsorption from acid mine drainage than before adsorption that due to OH function saturating by Cu^{2+}, Fe^{2+} and Mn^{2+} ions and so on.

2. Environmental application

2.1. Batch mode adsorption studies

Acid mine drainage solutions were prepared from Sarcheshmeh copper porphyry mine and followed by batch adsorption studies at 25°C on a multi stirrer hot plate to investigate the sorption processes. Known mass of modified perlite nanoparticles was added to a 25 mL of acid mine drainage solution, thoroughly mixed, and allowing sufficient time for equilibrium. Fast filtration followed and remaining metal ion concentrations were determined directly in the supernatant solution by flame atomic absorption spectrometry PG-990 model. The percentage adsorption of Cu^{2+}, Fe^{2+} and Mn^{2+} heavy metals from aqueous solution was computed as follows:

$$\text{Adsorption } (\%) = ((C_0 - C_t)/C_0) * 100 \tag{1}$$

Where, C_0 and C_t are the initial concentration of Cu^{2+}, Fe^{2+} and Mn^{2+} ions (see Table 1) and concentration at time t, respectively. So, in Fig. 6 the residual concentration of Cu^{2+}, Fe^{2+} and Mn^{2+} ions in mine drainage solution for known mass of modified perlite nanoparticles were showed.

The effect of temperature on Cu^{2+}, Fe^{2+} and Mn^{2+} ions removal from aqueous solution was considered for three temperatures 25, 45 and 65°C. The results of temperature changes were showed in Fig. 7. With observing Fig. 7, it is obvious that by increasing in temperature the removal of heavy metal pollutants increased.

The amount of adsorption at equilibrium q_e (mg/g) was calculated according to the expression:

$$q_e(mg/gr) = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where, C_0 and C_e are the initial and equilibrium concentrations (mg/L), V the volume of solution (L), m the weight of modified perlite nanoparticles adsorbents (gr). Different masses of adsorbent, m, were dosed to 25 ml of the system investigated and then the system was agitated until the equilibrium was reached. The sorption time needed to reach the equilibrium increased when m was increased. The dependences of equilibrium amounts of sorbed Cu^{2+}, Fe^{2+} and Mn^{2+} ions on the adsorption time for different masses of adsorbent are shown in Fig. 8.

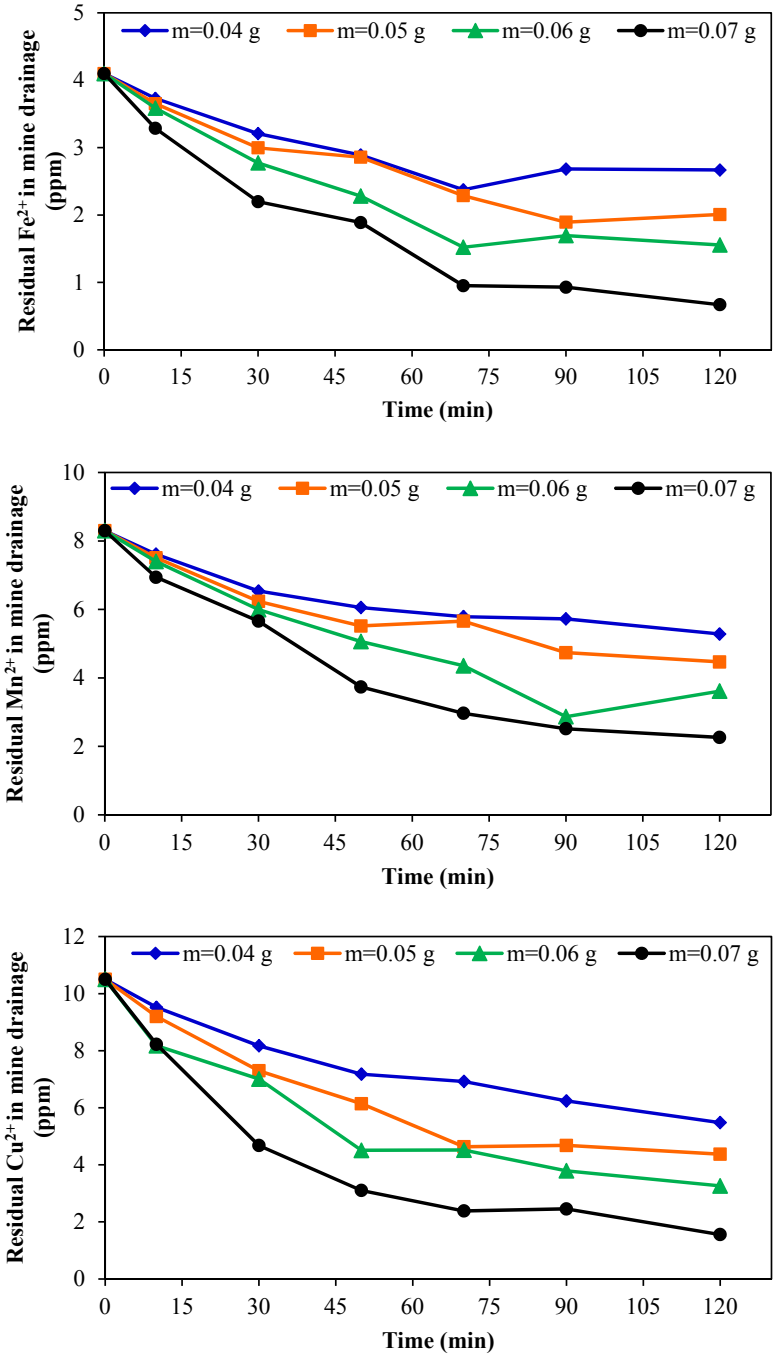

Fig. 6. Effect of adsorbent dose on the adsorption of Fe^{2+}, Mn^{2+} and Cu^{2+} heavy metals by modified perlite nanoparticles for $pH = 5.1$, $C_{0\text{-}Cu}{}^{2+} = 10.5$ ppm, $C_{0\text{-}Fe}{}^{2+} = 4.1$ ppm, $C_{0\text{-}Mn}{}^{2+} = 8.3$ ppm, $C_{0\text{-other ions}} = 1.24$ ppm, $V = 25$ ml and Temperature = 25°C and m = mass g

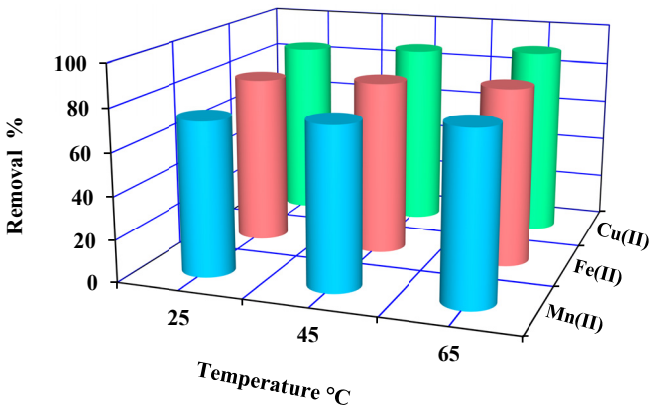

Fig. 7. Effect of temperature on the adsorption of heavy metal pollutants by modified perlite nanoparticles from acid mine drainage for *pH* = 5.1, adsorbent dose = 0.07 gr and Volume = 25 ml

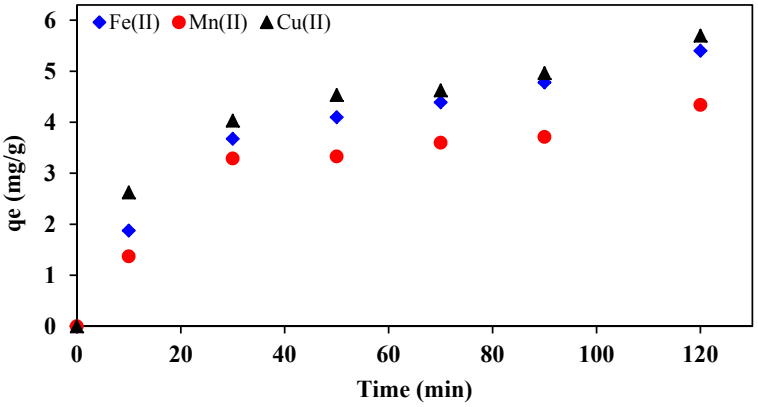

Fig. 8. The dependences of equilibrium amounts of sorbed Cu^{2+}, Fe^{2+} and Mn^{2+} ions on the adsorption time for different adsorbents masses, m

2.2. Isotherms and kinetics of heavy metal pollutants adsorption from acid mine drainage

2.2.1. Sorption isotherm

Generally, adsorption isotherms provide vital information in optimizing the use of adsorbents. Descriptions on affinity between sorbates and sorbents, bond energy and adsorption capacity, to mention a few, can be extracted from isotherm equilibrium models applicable to adsorption processes (Ijagbemi et al., 2009). The equilibrium data were analyzed in accordance with the Langmuir, Frundlich and Temkin isotherm models. All of the models are listed in Table 4.

TABLE 4

Isotherm models, their linear forms and respective coefficients (Zheng et al., 2009)

Isotherm model	Equation	Linear form	Plot
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e$	$\frac{C_e}{q_e}$ *VS.* C_e
Frundlich	$q_e = K_F C_e^{1/n}$	$\ln(q_e) = \ln K_F + \frac{1}{n} \ln C_e$	$\ln q_e$ *VS.* $\ln C_e$
Temkin	$q_e = \frac{RT}{b} \ln(K_T C_e)$	$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$	q_e *VS.* $\ln C_e$

where, in Table 4, in Langmuir isotherm q_m is a constant related to the area occupied by a monolayer of adsorbate, reflecting the maximum adsorption capacity (mg/g), C_e is the equilibrium concentration of solution (mg/l), K_L is a direct measure of the intensity of adsorption (l/mg) and q_e is the amount adsorbed at equilibrium (mg/g). In Frundlich isotherm, K_F ((mg/g)(l/mg)$^{1/n}$) and n (dimensionless) are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity, respectively. In Tempkin isotherm R is the gas constant (8.314 J/mol K), T is the absolute temperature (K) and b is the Temkin constant related to heat of sorption (J/mol).

Isotherm parameters for various two parameters adsorption isotherms for the adsorption of Cu^{2+}, Fe^{2+} and Mn^{2+} ions onto modified perlite nanoparticles adsorbents at 25.0°C were showed in Table 5. It was found that the Langmuir isotherm showed better correlation with the experimental data than other isotherms.

TABLE 5

Langmuir, Freundlich and Tempkin isotherm constants for the adsorption of Cu^{2+}, Fe^{2+} and Mn^{2+} ions onto modified perlite nanoparticles adsorbent

Isotherm model	Parameters	Three ions
		$Cu^{2+} + Fe^{2+} + Mn^{2+}$
Langmuir	q_m (mg g^{-1})	5.13
	K_L	0.63
	R^2	**0.986**
Freundlich	K_F	9.17
	n	5.85
	R^2	0.819
Tempkin	$B1$	1.06
	K_t	3423.05
	R^2	0.841

Square of correlation coefficient of the fit to experimental data (R^2) showed that the uptake of $Cu^{2+} + Fe^{2+} + Mn^{2+}$ ions onto modified perlite nanoparticles adsorbent could be described by the Langmuir model.

2.2.2. Sorption kinetic

The kinetic of the adsorption process was analyzed using the pseudo-first-order and pseudo-second-order equations and intra-particle diffusion model to model the kinetics of Cu^{2+} + Fe^{2+} + Mn^{2+} ions adsorption onto modified perlite nanoparticles adsorbent. Three kinetic models are listed in Table6.

TABLE 6

Kinetic models, their linear forms and respective coefficients (Najafi et al., 2011)

Kinetic model	Equation	Linear form	Plot
Pseudo first-order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$\ln(q_e - q_t)\ VS.\ t$
Pseudo-second-order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	$\frac{t}{q_t} = \frac{1}{k_2\ q_e^{\ 2}} + \frac{1}{q_e}t$	$\frac{t}{q_t}\ VS.\ t$
intra-particle diffusion model	$q_t = \frac{K_i}{m}t^{(0.5)}$	$q_t = \frac{K_i}{m}t^{(0.5)}$	$q_t\ VS.\ t^{(0.5)}$

Where in Table 6 q_e and q_t are the amounts of metal ions adsorbed on the adsorbent (mg g^{-1}) at equilibrium and at time t, respectively, k_1 is the rate constant of the first-order adsorption in min^{-1} and k_2 is the rate constant of second-order adsorption in (g mg^{-1} min^{-1}), also for intra-particle diffusion model m is the mass of sorbent (g), q_t the amount of solute adsorbed at time t (mg/g) and K_i is the initial rate of intra-particle diffusion (mg/l $s^{-1/2}$). The values of parameters obtained by different kinetic and intra-particle diffusion model for the adsorption of Cu^{2+} + Fe^{2+} + Mn^{2+} ions adsorption onto modified perlite nanoparticles adsorbent were showed in Table 7.

TABLE 7

The values of parameters obtained by different kinetic models for the adsorption of Cu^{2+}, Fe^{2+} and Mn^{2+} ions adsorption onto modified perlite nanoparticles adsorbent

Kinetic model	Parameters	Ions
		Cu^{2+} + Fe^{2+} + Mn^{2+}
Pseudo-first order	K_1 (min^{-1})	0.03
	q_e (mg g^{-1})	0.3
	R^2	0.792
Pseudo-second order	K_2 (g mg^{-1} min^{-1})	0.05
	q_e (mg g^{-1})	8.27
	R^2	0.969
intra-particle diffusion model	K_i	0.688
	R^2	0.882

The correlation coefficient for the pseudo-second-order kinetic model for modified perlite nanoparticles is 0.969. The high correlation coefficients and the agreement of calculated and

experimental q_e both demonstrated that the adsorption kinetics of Cu^{2+}, Fe^{2+} and Mn^{2+} ions adsorption onto modified perlite nanoparticles adsorbent followed the pseudo-second-order kinetic model. Therefore, the rate-limiting step may be chemical sorption or chemisorptions through sharing or exchange of electrons between sorbent and adsorbate.

2.2.3. Thermodynamic parameters

The amounts of Cu^{2+}, Fe^{2+} and Mn^{2+} ions uptakes at 298.15, 318.15 and 338.15 K temperatures were calculated to obtain the thermodynamic parameters which were evaluated using the Van't Hoff equation (Urano and Tachikawa, 1991):

$$\log K_d = \frac{\Delta S^\circ}{2.303\,R} - \frac{\Delta H^\circ}{2.303\,RT} \tag{3}$$

The values of log K_d were defined as follow:

$$K_d = \frac{a}{1-a} \tag{4}$$

where, $\Delta S°$ and $\Delta H°$ are entropy (kJ/mol K) and enthalpy (kJ/mol) change of adsorption, respectively, R is universal gas constant (8.314 J/mol K), and T is the absolute temperature (K), K_d is the equilibrium constant and a is uptake percentage of adsorbate at equilibrium. The values of $\Delta H°$ and $\Delta S°$ were calculated from the slope and intercept of linear regression of $\ln(K_d)$ vs. (1/T). Values of $\Delta G°$ were estimated by:

$$\Delta G = -RT \ln K_d \tag{5}$$

Calculated thermodynamic parameters such as $\Delta H°$, $\Delta S°$ and $\Delta G°$ are given in Table 8.

TABLE 8

Values of thermodynamic parameters for the adsorption of $Cu^{2+} + Fe^{2+} + Mn^{2+}$ ions on modified perlite nanoparticles adsorbents

Ions	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔG (kJ mol^{-1})		
			298.15°K	318.15°K	338.15°K
$Cu^{2+} + Fe^{2+} + Mn^{2+}$	0.108089	0.033258	–9.80778	–10.4729	–11.1381

The negative values of $\Delta G°$ indicate that the sorption of $Cu^{2+} + Fe^{2+} + Mn^{2+}$ ions from acid mine drainage onto modified perlite nanoparticles adsorbent were spontaneous processes. Change in enthalpy ($\Delta H°$) values is positive, showing that the sorption of Cu^{2+}, Fe^{2+} and Mn^{2+} ions are endothermic in nature. All ions uptake increased with the increasing of temperature (see Fig. 7). The sorption of all ions also require a diffusion process, which is an endothermic process; i.e., the rise of temperatures favors Cu^{2+}, Fe^{2+} and Mn^{2+} ions transport within the particles of modified perlite nanoparticles. In another aspect, the exchanges of the metal ions with H^+ need first the bond breaking of OH, which is one of the possible existing forms of proton in modified perlite nanoparticles. The bond breaking is also an endothermic process. The $\Delta H°$ of Cu^{2+}, Fe^{2+} and Mn^{2+} ions uptake by modified perlite nanoparticles is as Cu^{2+}, Fe^{2+} and Mn^{2+} ions, that implying, temperature has a more important influence on Mn^{2+}, Fe^{2+} and Cu^{2+} uptake, respectively. The

positive low values of $\Delta S°$ indicate low randomness at the solid/solution interface during the uptake of Cu^{2+}, Fe^{2+} and Mn^{2+} ions onto modified perlite nanoparticles adsorbent.

Since, $\Delta H > 0$ and $\Delta S > 0$, thus enthalpy and entropy are unfavorable and favorable agent, respectively, scilicet entropy cause to the adsorption processes was done to more adsorption and enthalpy cause to the adsorption processes was done to less adsorption. So, theses adsorption processes are bilateral and can be done spontaneous. Also, at the reactions that enthalpy and entropy is inversely, the temperature is determinant agent, hence at the high temperatures the entropy is predominant agent and at the low temperatures the enthalpy is effective agent.

2.3. Continuous mode adsorption studies

After characterization, preparation and batch mode adsorption studies, the adsorbent was packed inside a glass column, where it was used for the adsorption/removal of Cu^{2+}, Fe^{2+} and Mn^{2+} ions from Srcheshmeh acid mine drainage. A schematic view of glass column was showed in Fig. 9.

The length and diameter of glass column are 20 cm and 2 cm, respectively. A known amount of nanoadsorbent was packed inside a glass column and Cu^{2+}, Fe^{2+} and Mn^{2+} ions solution were allowed to flow inside the column with a certain flow rate. The metal ions concentration was determined before and after the treatment using atomic absorption spectroscopy PG-990 model.

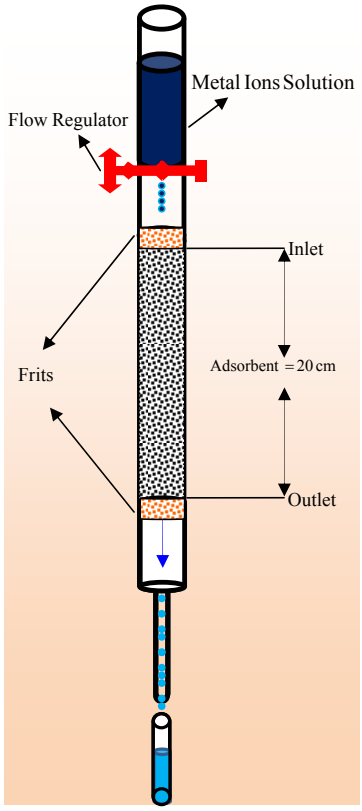

Fig. 9. Modified perlite nanoparticles adsorbent packed inside a glass column

So, the column of adsorbent were tested for all ions and obtaining the breakthrough curves. The breakthrough curves that obtained for Cu^{2+} + Fe^{2+} + Mn^{2+} ions adsorption by modified perlite nanoparticles adsorbent was showed in Fig. 10.

In the breakthrough curve if C_{inlet} (ion concentration at inlet or initial concentration) = C_{outlet} (ion concentration at outlet), therefore the saturation of adsorbent at column is occurs. The saturation time that occurs for ions adsorption onto modified perlite nanoparticles adsorbent for 1, 3 and 5 ml/min are 180, 240 and 315 min, respectively.

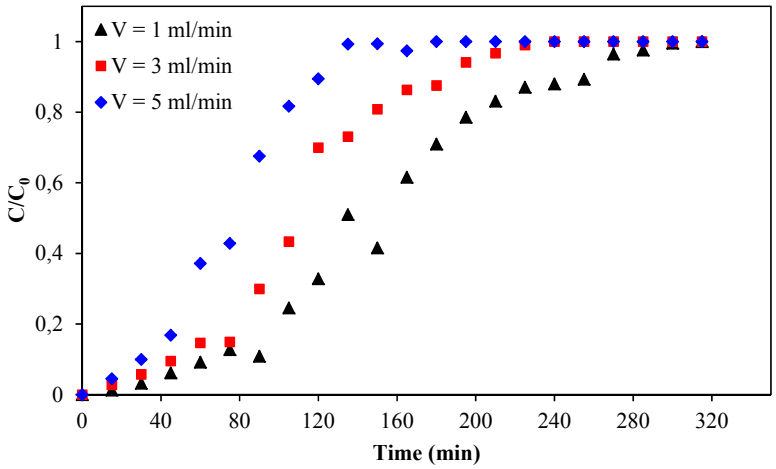

Fig. 10. The breakthrough curves of Cu^{2+} + Fe^{2+} + Mn^{2+} ions adsorption by modified perlite nanoparticles adsorbent

3. Conclusions

The surface properties and potential use of modified perlite nanoparticles as an adsorbent for iron (II), manganese (II) and copper (II) from Sarcheshmeh copper acid mine drainage was studied. Thus modified perlite nanoparticles that were prepared from internal resource (Zanjan mine, North West of Iran) firstly were modified and then characterized by XRD, XRF, SEM, TEM, FT-IR and BET analysis. XRD and XRF show that the main component is SiO_2 (Nearly 60%). The FT-IR shows the positive effect of OH function in SiO_2, also in Fig. 6 the FT-IR spectra of modified perlite nanoparticles before and after Fe(II), Mn(II) and Cu(II) ions adsorption processes from acid drainage it is obvious the band B_5 was OH weaken after Fe(II), Mn(II) and Cu(II) ions adsorption processes than before adsorption that due to OH function saturating by Fe(II), Mn(II) and Cu(II) ions. The BET analysis shows specific surface area 89.7m^2/gr and 3.5 m^2/gr for modified perlite nanoparticles and raw perlite, respectively. In batch mode after the consideration of adsorbent dosage, the results of isotherm and kinetic studies show that the Longmuir isotherm and pseudo-second order kinetic have a good correlation with adsorption processes. Also, the maximum adsorption value for modified perlite nanoparticles is 5.13(mg/g). Calculations of thermodynamic parameters show that the negative $\Delta G°$ values at three different temperatures

suggest that the sorption of all metal ions from acid mine drainage were spontaneous. Change in enthalpy ($\Delta H°$) for all ions show the endothermic process, as ion uptake increased with increase in temperature. Values of $\Delta S°$ indicate low randomness at the solid/solution interface during the uptake of both all ions by adsorbents. In the long run, the modified perlite nanoparticles was packed inside a glass column and used for the removal of four ions from aqueous solution in several flow rates and obtaining the breakthrough curves. The saturation time that occurs for ions adsorption onto modified perlite nanoparticles adsorbent for 1, 3 and 5 ml/min are 180, 240 and 315 min, respectively. All results show that the ions affinity to adsorption onto adsorbents is as: Cu (II) > Fe (II) > Mn (II). The high selectivity in the bonding of iron (II), manganese (II) and copper (II) suggests modified perlite nanoparticles may be useful for removal of these toxic heavy metal ions and probably other heavy metal ions from other mining wastewaters. This ability can be explored in treatment technologies since perlite are cheap, abundant, and locally available resource.

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