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ORIGINAL PAPER

Study of continuous lead removal from aqueous solutions by marble wastes: efficiencies and mechanisms

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Abstract Lead removal from synthetic solutions and real wastewater by Bianco Gioia marble wastes as abundant, renewable and eco-friendly materials was studied under different experimental conditions in a continuous stirring tank reactor. These marble wastes were found to be very efficient in removing lead for several experimental situations. Indeed, for initial aqueous pH values higher than 3.6, a lead removal efficiency of about 100 % was achieved even for high aqueous concentrations (200 mg L^{-1}), important feeding flow rates (60 mL min^{-1}) and low marble waste dosage (2 g L^{-1}). The best removal capacity (175.7 mg g^{-1}) was obtained for an initial lead concentration of 200 mg L^{-1}, a marble waste dose of 5 g L^{-1} and an aqueous pH of 5. Even using the real wastewater with low aqueous pH (1.1), lead was also completely removed using 20 g L^{-1} of the tested marble wastes. According to the energy-dispersive spectroscopy and X-ray diffraction analyses, lead removal seems to be controlled by both precipitation as cerussite ($PbCO_3$) and hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), and adsorption onto the surface particles through cation exchange and complexation. The proposed low-cost material efficiently removes lead present in synthetic solutions and real wastewaters and constitutes an interesting environmental management option.

Keywords Dynamic mode · Mineral adsorbents · Precipitation · Wastes management · Water pollutants

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Introduction

Water resource pollution by heavy metals is considered as a serious environmental problem due to their toxic effects in water bodies (Cechinel et al. 2013). Lead, which is discharged in wastewaters from many industrial processes such as the manufactories of batteries, paint coatings, glass and dyes, is potentially toxic for both humans and the aquatic environment (Banerjee 2014). Indeed, even at low concentrations, lead can seriously damage the human liver, kidney, reproductive and nervous systems and also causes the poisoning of aquatic organisms and severe changes in the aquatic fauna and flora (Singh et al. 2014). Moreover, lead is non-biodegradable and tends to be highly accumulated by organisms as part of the food chain (Blazquez et al. 2010). In this context, the maximum lead concentration in the discharged wastewaters into receiving bodies allowed by Tunisian legislation is fixed to 0.1 mg L^{-1} and according to the USEPA standards, the current limit for drinking water is 0.015 mg L^{-1} (Momcilovic et al. 2011).

During the last decades, various technologies have been applied for heavy metal removal from industrial wastewaters with different degree of efficiency such as chemical precipitation, ion exchange, reverse osmosis and membrane filtration. However, these methods require considerable capital investment and maintenance costs for infrastructure and reagents. Adsorption onto natural materials is currently considered as an emerging and attractive technology because of its effectiveness and economy in heavy metals removal from wastewaters. Different raw and modified organic natural materials have been tested for heavy metals removal from aqueous solutions such as raw alga Anabaena sphaerica biomass (Abdel-Aty et al. 2013), raw Peganum harmala seeds (Zamani et al. 2013), modified Symphoricarpus albus biomass (Akar et al. 2012), modified olive tree pruning (Calero et al. 2013) and activated carbon from apple pulp (Depci et al. 2012). The main involved mechanisms were cation exchange and complexation with the active groups of the biomasses' constituents. Furthermore, the efficiency of some raw and modified inorganic materials for lead removal from aqueous solutions has been tested, such as natural zeolite (Calvo et al. 2009); raw illitic clays (Ozdes et al. 2011), palygorskite (Fan et al. 2009; Sheikhhosseini et al. 2013); sepiolite (Sheikhhosseini et al. 2013), dolomite (Irani et al. 2011), ore mine tailings wastes (Venalainen 2012), natural Greek bentonites (Bourliva et al. 2013) and modified attapulgite (Deng et al. 2013). The suggested corresponding mechanisms were adsorption by complex formation with hydroxyl groups as well as cation exchange. Calcite, which is the crystalline form of $CaCO_3$, has been also tested for heavy metals removal from aqueous solutions under static conditions (Chada et al. 2005; Ghazy and Ragab 2007; Ghazy and Gad, 2010; Rangel-Porras et al. 2010; Godelitsas et al. 2003). For example, Ghazy and Gad (2010) tested the use of Egyptian powdered marble wastes mainly formed by calcite and dolomite for lead removal from synthetic aqueous solutions in batch mode. They proved that this material is very efficient in removing lead under large experimental conditions with a maximum monolayer adsorption capacity of 101.6 mg g^{-1}. Although calcite materials have demonstrated a relatively high capacity for retention of some metals, the involved mechanisms and the surface process involved have not been explored in detail. Moreover, these removal capacities were evaluated under static flow conditions (batch mode), which are usually limited to the treatment of small quantities of synthetic solutions and present large difficulties for up scaling tasks. In order to find a solution to this problem, the application of dynamic-flow set ups (such as continuous stirring tank reactors (CSTRs)) can be considered as a good alternative. In fact, only few studies have focused on this approach regarding phosphorus removal from aqueous solutions by using powdered marble wastes (Jaouadi et al. 2014a) and acid mine drainage (Wei et al. 2008).

Therefore, the main purposes of the current study were (1) to evaluate lead removal efficiencies from synthetic aqueous solutions and real wastewater by abundant, renewable and eco-friendly calcitic materials (Bianco Gioia marble wastes (BGMW) in CSTR system) and (2) to assess the involved mechanisms through specific assays and analyses.

This research work has been performed at the Water Research and Technologies Centre (CERTE), Tunisia during 2012–2013.

Materials and methods

BGMW preparation and characterization

Marble wastes are freely available with relatively huge amounts in several countries. Indeed, around 70 % of this mineral resource is wasted in the mining, processing and polishing procedures (Aukour and Al-Qinna 2008). These wastes are always discharged into empty pits or landfills without any reuse. In this study, the used marble wastes were generated from the manufacturing of large stones of "Bianco Gioia" marble (BGMW) imported from Italy. They were collected, free of charge, as a dry powder at the vicinity of the cutting and polishing devices from a private marble processing workshop located in Borj Cedria city, which is situated at about 25 km at the south of Tunis, Tunisia. In this study, BGMW was sieved mechanically using a sieve with a mean diameter of 2 mm in order to remove any existing fragments. Then, it was washed with distilled water and dried in an oven at 40 °C for 48 h to a constant weight. The adsorbent characterization including the particle size distribution, the mineralogical analysis, the chemical composition and the pH of zero point charge was determined as indicated by Jaouadi et al. (2014b). They indicated that BGMW were constituted by fine solid particles with a mean diameter of about 22.6 µm. Furthermore, they were mainly formed by calcite with relatively high contents of calcium. Their pH_{ZPC} and BET were determined to 8.11 and 0.14 m^2 g^{-1}, respectively (Jaouadi et al. 2014b).

Preparation and analysis of synthetic lead solutions

Analytical grade of lead nitrate ($Pb(NO_3)_2$) was used in CSTR tests as the source of lead ions. A stock lead solution of 1,000 mg L^{-1} was prepared with distilled water and used throughout this study. The analysis of lead concentrations at the outlet of the CSTR was performed using an atomic absorption spectrometer (Perkin Elmer AAnalyst 200). During the assays, the pH values were adjusted with 0.1 M HNO_3 or 0.1 M NaOH. The pH measurements were performed using a pH meter (692 pH/ion meter, Metrohm).

CSTR lead removal studies

Laboratory CSTR presentation and experimental protocol

Continuous flow tests were carried out by a CSTR system for the removal of lead from synthetic solutions and real industrial wastewater (Fig. 1). The contact between BGMW and lead dissolved in aqueous solutions was ensured in a 1.2-L glass reactor. At the beginning of the

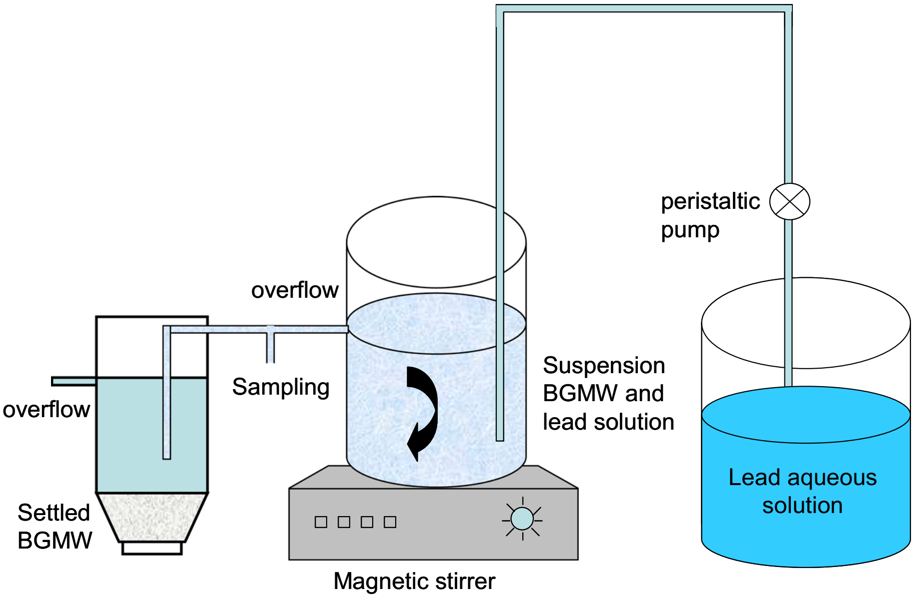


Fig. 1 Schematic representation of the CSTR used for the study of lead removal by BGMW

assays, the desired BGMW dosage was placed in the reactor, which is then rapidly filled with the aqueous lead solution at the desired concentration. Afterward, the lead-containing water was continuously fed from a 20-L-volume tank to the CSTR system with a variable flow pump (Masterflex, Cole-Parmer Instrument Company, USA) at different flow rates corresponding to the chosen contact times. The reactor was continuously stirred at 300 rpm using a magnetic stirrer (*Agimafic-S, IP. Selecta Company*) for several hours after reaching of the equilibrium. This state is characterized by a quasi stability of lead concentrations at the entrance of the settling setup.

The effluent was sampled at the entrance of the settling device at certain time intervals to determine the efficiency of this CSTR system for the removal of lead. For each aqueous sample (10 mL), the suspension (containing water and BGMW particles) was filtered through filter paper and then the filtrate was analyzed in order to determine its dissolved lead concentration. All assays, presented hereafter, were conducted in duplicate, and the mean values were reported.

Effect of influent lead concentration

The effect of influent lead concentration on its removal by BGMW was investigated using four synthetic concentrations 50, 100, 150 and 200 mg L^{-1}. This concentrations range was tested in order to determine the BGMW capacity regarding lead removal for other highly concentrated industrial wastewaters, where the related concentrations could reach 200–500 mg L^{-1} (Akar et al. 2012). The aqueous pH, BGMW dosage and flow rate were fixed to 3.6, 5 g L^{-1} and 20 mL min^{-1}, respectively.

Effect of the BGMW dosage

The impact of BGMW dosage onto lead removal was explored at a constant pH influent, concentration of synthetic solution and feeding flow rate of 3.6, 100 mg L^{-1} and 5 g L^{-1}, respectively. The tested BGMW dosages were fixed to 1, 2, 3 and 5 g L^{-1}.

Effect of the influent feeding flow rate

The effect of the contact time between BGMW particles and the lead synthetic solutions was determined for fixed feeding concentration, pH and BGMW dosage of 100 mg L^{-1}, 3.6 and 5 g L^{-1}, respectively. The tested flow rates were maintained constants at 20, 40 and 60 mL min^{-1} using the peristaltic pump. These flow rates correspond to theoretical hydraulic residence times in the reactor of 60, 30 and 20 min, respectively.

Effect of initial aqueous pH

The effect of initial aqueous pH on lead removal has been investigated for a synthetic solution feeding concentration, initial BGMW dosage and continuous feeding flow rate of 100 mg L^{-1}, 5 g L^{-1} and 20 mL min^{-1}, respectively. The tested initial pH values were fixed to 2, 3.6 and 5. Above pH 5, lead removal studies were not performed due to the possible precipitation of lead in the form of $Pb(OH)_2$ (Blazquez et al. 2010; Rangel-Porras et al. 2010).

Effect of ions competition

In order to assess the competing effect of the presence of other cations on lead removal by BGMW, a CSTR removal test of lead (50 mg L^{-1}) was performed following specific aqueous concentrations of some ions such as cadmium (10 mg L^{-1}), copper (10 mg L^{-1}) and zinc (30 mg L^{-1}). These concentrations were chosen on the basis of a previous study related to heavy metals repartition in Tunisian mines (Mlayah et al. 2009). Moreover, the BMGW dosage, aqueous pH and feeding flow rate were fixed to 5 g L^{-1}, 3.6 and 20 mL min^{-1}, respectively.

Validation with industrial wastewater

Industrial wastewater effluent from a battery manufacture in Grombalia city (North East of Tunisia) was used to study the effectiveness of the continuous flow system in treating real wastewater. This wastewater is a very acidic effluent with an average pH of 1.1 and has relatively high contents of lead and sulfates (Table 1). Three BGMW dosages were tested: 5, 10 and 20 g L^{-1} at a constant flow rate of 20 mL min^{-1}.

Lead removal parameters calculation

The lead removal by BGMW at equilibrium, q_e (mg removed lead g^{-1} BGMW), was calculated from mass balance equation as follows (Jaouadi et al. 2014a):

Table 1 Main chemical composition of the used real wastewater

Parameter	Concentration (mg/L)	Tunisian discharging norm (mg/L)
Suspended solids	76.5	30
pH(−)	1.1	6.5–8.5
Lead	5.4	0.1
Cadmium	0.12	0.005
Copper	0.55	0.5
Iron	3.03	1
Manganese	0.69	0.5
Nickel	0.34	0.2
Sodium	320	500
Potassium	7.5	50
Magnesium	4.29	200
Calcium	666	500
Chlorides	667	600
Sulfates	9,360	600

$$q_e = \frac{M_{t_0} + M_{\text{inj}} - M_{t_f} - M_{\text{recup}}}{M_{\text{BGMW}}} \tag{1}$$

where t_0 and t_f are the times corresponding to the start and the end of the experiment, respectively. M_{t_0}, M_{inj}, M_{t_f}, M_{recup} and M_{BGMW} are the initial lead mass existing inside the reactor before the start of the experiment, the injected mass in the reactor between the times t_0 and t_f, the existing mass inside the reactor at the end of the experiment, the recuperated mass at the outlet of the reactor during the same time period, and the used BGMW amount, respectively. These masses are calculated using the following equations:

$$M_{t_0} = C_0 V_r \tag{2}$$

$$M_{\text{inj}} = C_0 Q (t_f - t_0) \tag{3}$$

$$M_{t_f} = C_f V_r \tag{4}$$

$$M_{\text{recup}} = \int_0^{V_{\text{tot}}} C(t)\,\text{d}v \tag{5}$$

where C_0, $C(t)$ and C_f, are the aqueous lead concentration measured at the influent, at time t and final time at the reactor outlet, respectively. Q is the applied flow rate. V_r and V_{tot} are the reactor volume and the total solution volume recuperated at the outlet of the reactor.

Equation 5 was approximated using the trapeze method by the formula presented hereafter (Jellali et al. 2010):

$$M_{\text{recup}} = \frac{1}{2}\sum_{i=0}^{i=n} (C_{i+1} - C_i)(V_{i+1} - V_i) \tag{6}$$

where C_{i+1}, C_i and "V_{i+1}, V_i" are the lead aqueous concentrations and "recuperated volume at the outlet of the reactor" at the instants t_{i+1} and t_i, respectively.

The lead removal efficiency at equilibrium (ARE) is calculated from the relation:

$$\text{ARE}\,(\%) = \frac{(C_0 - C_{\text{eq}})}{C_0} \times 100 \tag{7}$$

where C_{eq} is the average measured lead concentration at the outlet of the reactor at the equilibrium state.

Lead removal mechanisms exploration

Energy-dispersive spectroscopy

Energy-dispersive spectroscopy (EDS) was used to analyze the chemical elemental composition of BGMW surface before and after lead removal by a Quanta-200-Fei apparatus. The used equipment is formed by three main components: an X-ray detector; a pulse processing circuitry, which determines the energy of the detected X-rays; and an analyzer equipment, which interprets the X-ray data and displays it on a computer screen.

X-ray diffraction

X-ray diffraction (XRD) was used to determine the main phases present in the raw BGMW and in the solid phase formed after contact between lead and aqueous filtered solution resulting from shaking of 1,000 mL of distilled water with 5 g of BGMW. These two crystalline phases were analyzed using an X-ray diffractometer CuKα radiation, PW 1710 Philips, and scans were conducted from 0° to 70° at a rate of 2° min^{-1}.

Replication of CSTR experiments

Each CSTR removal experiment cited above was performed twice to obtain reproductive results with an average error lower than 5 %. In the case of deviation larger than 5 %, more assays were conducted. Thus, all the data, presented hereafter, are the average values of minimum two tests.

Results and discussion

Dynamic experiments results

Removal efficiency of pollutants of CSTR is generally characterized by breakthrough curves which are composed of three stages. The first stage concerns the effluent concentrations decrease; the second is dealing with the equilibrium state (characterized by a plateau of concentrations); and the third presents the effluent concentration increase. The time taken to reach the equilibrium state, the duration of this plateau and the shape of the concentration time/volume profile are very important parameters in order to obtain the dynamical behavior of this kind of assays (Chakraborty et al. 2011).

Effect of influent lead concentration

The lead breakthrough curves show that BGMW is very efficient in lead removal from the synthetic solutions (Fig. 2). Indeed, even for a relatively high influent concentration (200 mg L^{-1}), the equilibrium effluent lead contents measured at the outlet of the CSTR were lower than the detection limit of the used apparatus (0.01 mg L^{-1}). Moreover, this equilibrium state that is characterized by a constant concentration at the outlet of the reactor has been reached very quickly: Only 1.5 min was sufficient for influent with concentrations of 50 and 100 mg L^{-1}. For the higher used concentrations (150 and 200 mg L^{-1}), a total removal of lead was obtained after only 3 min of the system operating (Fig. 2). This finding proves that BGMW can be considered as very attractive materials for lead removal from highly contaminated aqueous solutions. This relatively short-equilibrium time can be considered as a significant advantage for practical applications since the removal rate is extremely important for developing water treatment technology by low-cost materials. Relatively higher equilibrium times have been determined for several materials such as activated carbon from bovine bone (Cechinel et al. 2013), Symphoricarpus albus biomass (Akar et al. 2012) and modified attapulgite clay (Deng et al. 2013).

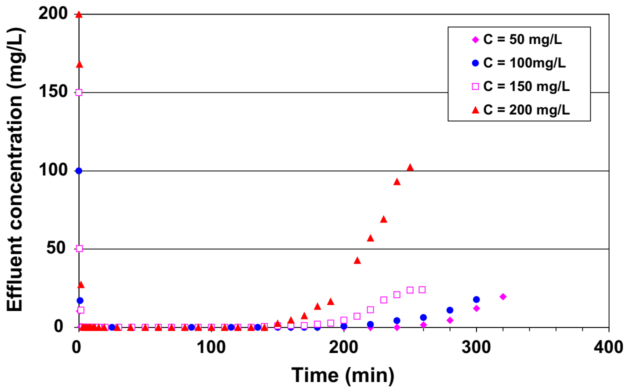


Fig. 2 Effect of influent aqueous concentrations on lead removal by BGMW (BGMW dosage = 5 g L^{-1}, temperature = 20 ± 2 °C, flow rate = 20 mL min^{-1} and initial pH 3.6)

Furthermore, the breakthrough times after the equilibrium plateau concentrations ($C/C_0 = 1$ %) increased with decreasing the influent concentrations. Indeed, these experimental times were evaluated to 246, 204, 175 and 148 min for aqueous influent concentrations of 50, 100, 150 and 200 mg L^{-1}, respectively (Fig. 2). This behavior is mainly due to the saturation of the active sorption sites of the used solid matrix particles and their continuous exit from the reactor (Jaouadi et al. 2014a). BGMW lead removal capacities increase with increasing the influent aqueous lead concentration. In fact, after 250 min of the beginning of the experiments, raising the influent lead concentration from 50 to 100, 150 and 200 mg L^{-1} allows the BGMW to increase their removal capacities from 51.3, 101.5, 146.7 and 175.7 mg g^{-1}, respectively. In this context, Cruz-Olivares et al. (2010) studied lead removal by de-oiled allspice husk (local Mexican lignocellulosic material) using glass laboratory columns (inside diameter of 1.78 cm and bed depth height of 15 cm) for a feeding flow rate of 40 mL min^{-1} and initial lead concentrations ranging from 5 to 25 mg L^{-1} at pH of 5. They showed that when the used initial concentration is higher, the time of column service is shorter, which is due to the rapidly saturation of their biosorbent. Furthermore, the sorption capacity of their biosorbent has tripled when the initial concentration increased from 5 to 25 mg L^{-1}.

Thus, the increase in BGMW' efficiencies in removing lead could be attributed to the fact that higher is the influent concentration, higher is the concentration gradient between aqueous solution and the solid phase. Moreover, increasing initial aqueous lead concentration provides an important initial force to overcome pollutant mass transfer resistances between the aqueous and BGMW particles resulting in more important diffusion rates. Furthermore, for higher initial aqueous concentrations, the contact probability between lead ions contained in the aqueous phase and the BGMW might be more privileged. Moreover, even at a fixed aqueous pH value, the precipitation of lead as $Pb(OH)_2$ or $PbCO_3$ should be favored with raising the initial aqueous concentrations since their solubility product were estimated to 1.2×10^{-15} and 7.4×10^{-14}, respectively (Dong et al. 2010; McQuarrie et al. 2000).

In order to compare the BGMW efficiency among the common used materials to remove lead from aqueous solutions, a comparison based on the adsorbed amount was conducted with some mineral materials under dynamic conditions (Table 2). It appears clearly that BGMW could be considered as promising materials to remove lead.

Table 2 Comparison of lead removal by BGMW with other materials adsorbents under dynamic and static conditions

Material	Study type	Experimental conditions	Lead removal capacity (mg/g)	References
Bianco Gioia marble wastes	CSTR	Glass reactor: 1.2 L; $C_0 = 200$ mg L^{-1}; pH 3.6; $D = 5$ g L^{-1}; flow rate = 20 mL min^{-1}	175.7	This study
Turkish clinoptilolite	Column	Plexiglass column (height = 100 cm; diameter = 3 cm); M = 370 g; $C_0 = 50$ mg L^{-1}; pH 7.1; flow rate = 70 mL min^{-1}	7.97	Turan et al. (2005)
Ecuadorianern heulandite Ecuadorianern clinoptilolite	Column	Glass column (height = 20 cm; diameter = 2 cm); M = 35 g; $C_0 = 428.9$ mg L^{-1}; pH 7–7.5; flow rate = 1 mL min^{-1}	8.6 40.4	Calvo et al. (2009)
Chemically modified Chinese zeolite	Column	Glass column (height = 30 cm; diameter = 1 cm); M = 20 g; $C_0 = 261$ mg L^{-1}; pH 5; flow rate = 7.69 mL min^{-1}	75.21	Han et al. (2006)
Mexican soil	Batch[a]	C_0: 10–400 mg L^{-1}; $D = 5$–10 g L^{-1}; pH 2–5.5;	0.5–8	Martinez-Villegas et al. (2004)
Thai Kaolinite Thai Illite	Batch[a]	C_0: 20–100 mg L^{-1}; $D = 20$ g L^{-1}; $T = 30$ °C.	1.41 4.29	Chantawong et al. (2003)
Egyptian powdered marble wastes	Batch[a]	C_0: 500–1,500 mg L^{-1}; $D = 1$ g L^{-1}; $T = 25$ °C; pH 7	101.6	Ghazy and Gad (2010)
Iranian perlite Iranian dolomite Iranian diatomite	Batch[a]	C_0: 10–500 mg L^{-1}; $D = 2$ g L^{-1}; $T = 25$ °C; pH 6	8.906 18.55 24.21	Irani et al. (2011)
Turkish illitic clay	Batch[a]	C_0: 50–1,200 mg L^{-1}; pH 4; $D = 10$ g L^{-1}; room temperature	53.76	Ozdes et al. (2011)
Chinese modified attapulgite	Batch[a]	C_0: 4–100 mg L^{-1}; $D = 1.2$ g L^{-1}; $T = 30$ °C; pH 5–5.3	128	Deng et al. (2013)

C_0 initial lead concentration, D solid material dosage, M solid material mass

[a] Langmuir's maximum monolayer adsorption capacity

Indeed, for an aqueous lead concentration of 200 mg L^{-1}, an adsorbent dosage of 5 g L^{-1} and at pH 3.6, the removal capacity of BGMW is relatively important compared with a Turkish clinoptilolite (Turan et al. 2005), Ecuadorian heulandites and clinoptilolite (Calvo et al. 2009) and chemically modified Chinese zeolite (Han et al. 2006). Because of the relative scarcity of dynamic assays, this comparison has been extended to batch systems. Even for a given material, the removed pollutant amounts in batch mode are generally more important than those obtained in dynamic mode (Dong et al. 2010) and the removed lead amount by BGMW in CSTR mode is much higher than the related ones determined for a Mexican soil (Martinez-Villegas et al. 2004), a Thai Kaolinite (Chantawong et al. 2003), an Iranian dolomite (Irani et al. 2011) and a Turkish illite clay (Ozdes et al. 2011).

Effect of BGMW dosage

The BMGW dosage is usually considered as an important factor conditioning pollutants removal from aqueous solutions under dynamic conditions. The impact of this parameter on lead removal efficiency has been determined with respect to the experimental conditions presented in section "Effect of the BGMW dosage." The related breakthrough curves indicated that for all the used BGMW dosages, the lead removal process is clearly time dependent (Fig. 3). Indeed, due to the presence of more adsorptive sites and the net increase in the aqueous pH, the higher is the BGMW dosage, the faster is the reaching of equilibrium. This state (minimum of C/C_0 values) was observed after 1.5, 12, 40 and 62 min for BGMW dosages of 5, 3, 2 and 1 g L^{-1}, respectively. This observed kinetic removal process could be explained by the fact that at the beginning, the lead ions were mainly precipitated as lead carbonates. This mechanism is more favored as the BGMW dosage increases since the aqueous pH become more important. The average pH values at equilibrium were determined to 5.34, 5.98, 6.1 and 6.64 for BGMW dosages of 1, 2, 3 and 5 g L^{-1}, respectively. Then, lead removal was ensured by both precipitation and adsorption onto active sorption sites. For this last mechanism, after the exterior surface sites saturation, the lead ions enter into the BGMW particles pores and were adsorbed by the interior surface of the particles which result in a slow removal rate (Ozdes et al. 2011; Cechinel et al. 2013).

Except for BGMW dosage of 1 g L^{-1}, where the measured minimum lead concentration was about 32 mg L^{-1} corresponding to a removal efficiency of 68 %, BGMW doses of 2, 3 and 5 g L^{-1} have permitted a complete lead removal from the synthetic aqueous solutions. Such trend is mainly attributed to both an increase in adsorption capacity (through an increase in the sorptive surface area and adsorption sites) and the availability of more favorable conditions of lead carbonates precipitation (due to the increase in the aqueous pH and to the dissolution of more HCO_3^- ions from BGMW into the aqueous solutions (Godelitsas et al. 2003; Rangel-Porras et al. 2010)). These very attractive lead removal efficiencies, even for relatively low BGMW dosages, could be considered as a promising result and should encourage the use of this kind of wastes as efficient materials for the treatment of real industrial wastewaters rich in heavy metals.

Effect of feeding flow rate

Figure 4 represents the lead breakthrough curves related to the impact of the feeding flow rate on lead removal from aqueous solutions for the experimental conditions mentioned in section "Effect of the influent feeding flow rate." On the basis of these breakthrough curves, it appears that lead removal efficiency is highly affected by the used flow

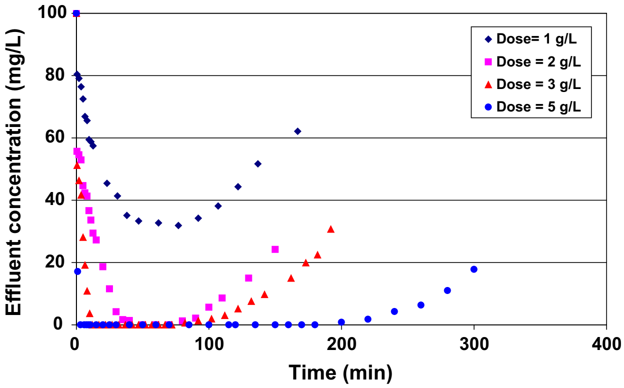


Fig. 3 Effect of BGMW dosage on lead removal from aqueous solutions (influent lead concentration = 100 mg L^{-1}, temperature = 20 ± 2 °C, flow rate = 20 mL min^{-1} and initial pH 3.6)

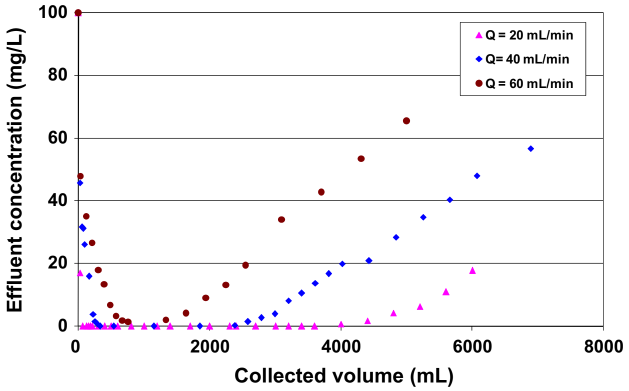


Fig. 4 Effect of influent feeding flow rate on lead removal by BGMW (influent lead concentration = 100 mg L^{-1}, BGMW dosage = 5 g L^{-1}, temperature = 20 ± 2 °C and initial pH 3.6)

rate. Indeed, relatively fast removal kinetic was observed as the flow rate decreases. The equilibrium state, which is characterized by relatively constant or unchanged concentrations at the outlet of the reactor, was obtained after 3, 8 and 12.5 min for used flow rates of 20, 40 and 60 mL min^{-1}, respectively. From these times, the lead ions were completely removed from the aqueous solutions for flow rates of 20 and 40 mL min^{-1} and at a percentage of 98.7 % for 60 mL min^{-1}. The duration of this equilibrium state corresponds to treated water volumes of 3,540, 1,571 and 760 mL for flow rates of 20, 40 and 60 mL min^{-1}, respectively. Thus, for the tested flow rate interval, higher is the contact time between the BGMW and aqueous lead solution, more effective is the lead removal (Fig. 4). This finding is comforted by the research work of Gupta et al. (2011) who studied lead removal by a synthesized composite (alumina-coated multi-wall carbon nanotubes material) using a relatively short bed depth column (1 cm). For an influent lead concentration of 20 mg L^{-1}, they demonstrated that when the flow rate was decreasing from 5 to 1 mL min^{-1}, more favorable adsorption conditions were achieved for lead. The breakthrough curves showed that the effluent solution concentration reached 5 % of its feed concentration at about 80, 200, 340 min residence times for 5, 3 and 1 mL min^{-1}, respectively (Fig. 4). The same trend has been observed by Han et al. (2006) when they followed lead removal by chemically modified Chinese zeolite in glass column mode.

This finding could be attributed to the fact that for relatively important flow rates, the corresponding residence times were not sufficient to ensure an equilibrium state between BGMW particles and the dissolved lead ions. Moreover, the use of lower flow rates had significantly increased the aqueous pH of the synthetic solutions which would result in the formation of more amounts of lead carbonates precipitate. However, when the flow rate decreases, the contact time between BGMW and lead ions in the CSTR is longer and consequently intra-particle diffusion becomes effective. Thus, the lead ions have more time to diffuse into the solid particles of BGMW, and better efficiencies removal is obtained. However, at a higher flow rate, probably lower diffusivity of lead ions into BGMW occurs which would result in a relatively rapid saturation of these solid particles. This trend has been observed by Akar et al. (2012) when studying lead removal by a chemically modified biomass in column mode. They found that lead biosorption yield was reduced from about 98.6–83.5 % when the flow rate was increased from 1.0 to 6.0 mL min^{-1}.

The average removed lead amounts were evaluated using Eq. 1, to 67.8, 89.9 and 101.5 mg g^{-1} for feeding flow rates of 60, 40 and 20 mL min^{-1}, respectively. This tendency has been also registered by Hasan et al. (2010) when they studied lead removal by a polysulfone immobilized Aeromonas hydrophila biomass using a laboratory column. For a bed height of 19 cm and an influent lead concentration of 103.6 mg L^{-1}, the removed lead amount decreased from about 54.5 to 49.3 mg g^{-1} when the applied flow rate increased from 2 to 10 mL min^{-1}.

Effect of initial aqueous pH

The pH is an important factor for determining the form of the lead species in the aqueous solutions. It influences the strength of the adsorption mechanism of lead ions as it determines the degree and sign of the charge on these ions (Blazquez et al. 2010; Jellali et al. 2011). For example, for an aqueous lead concentration of 100 mg L^{-1}, positively charged lead(II) species are dominant for pH values lower than 5.3. In case of higher pH values (pH 6–11), there are several lead species with different charges including $Pb(OH)^{+}$, $Pb_2(OH)^{3+}$ and $Pb(OH)_2$. Thus, the removal of lead is possibly accomplished by simultaneous precipitation of $Pb(OH)_2$ and sorption of $Pb(OH)^{+}$. For pH values higher than 11, besides $Pb(OH)_2$, lead ions can be present in the aqueous solutions as anions: $Pb(OH)_4^{2-}$ and $Pb(OH)_3^{-}$ (Blazquez et al. 2010).

The effectiveness of BGMW on lead removal from aqueous solutions versus pH has been carried out according to the experimental conditions cited in section "Effect of initial aqueous pH." The related breakthrough curves, depicted in Fig. 5, showed that the aqueous pH has a significant effect on lead removal. Indeed, it appears that lead removal was inhibited at low pH values. For the lowest tested aqueous pH (pH 2), the maximal removal efficiency was evaluated to be about 88 % during only 30 min time period. However, for initial aqueous pH values of 3.6 and 5, the measured lead concentrations at the outlet of the reactor were lower than the detection limit of the apparatus for a relatively long period (177 and 307 min,

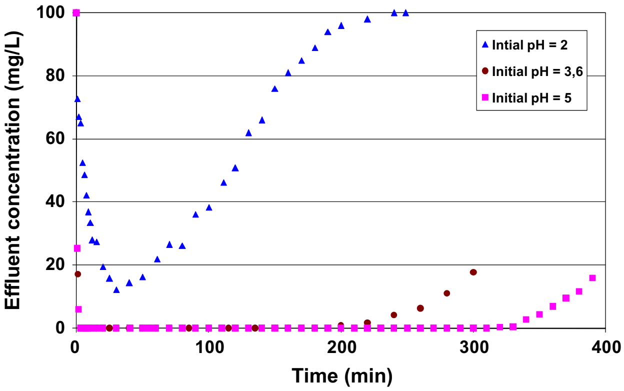


Fig. 5 Effect of initial influent pH on lead removal (influent lead concentration = 100 mg L^{-1}, BGMW dosage = 5 g L^{-1} and temperature = 20 ± 2 °C)

respectively). This equilibrium state, with minimum C/C_0 values of the breakthrough curves, corresponds to treated synthetic aqueous volume of about 3,540 and 6,386 mL for initial aqueous pH values of 3.6 and 5, respectively. This result was consistent with lead removal studies from synthetic solutions by modified Chinese attapulgite clay (Deng et al. 2013).

The removed lead amounts were determined using Eq. 1 to 34.5 mg g^{-1} for an initial pH of 2. This amount increases to 101.5 and 130.7 mg g^{-1} represented by increase percentages of 194 and 279 % for aqueous pH of 3.6 and 5, respectively. This finding is mainly caused by the fact that at lower pH, the concentration of positive charge (protons) increased on the sites of the solid particles surface, which limited the approach of lead ions because of charge-repulsion phenomenon. As aqueous pH values increase, the charge density on the BGMW surface becomes more negative and the protons concentrations decrease. This behavior will favor the removal of the positively charged lead ions onto the solid particles surface. On the other hand, the aqueous pH values of the solution in the reactor during the equilibrium phase become more important when increasing the initial pH solutions. Indeed, these equilibrium pH values were evaluated to 5.73, 6.64 and 6.68 for initial pH of 2,3.6 and 5, respectively. This result indicates that the precipitation phenomenon of lead (as lead carbonates) should be more favored as the initial aqueous pH values increased. This trend has been also pointed out by Rangel-Porras et al. (2010), where they studied lead removal using calcitic materials.

Effect of ions competition

Generally, several metal ions are ubiquitous in natural waters and industrial effluents, so it is important to study the sorption selectivity of BGMW toward target metal ions when assessing its technical applicability. In this regard, the impact of the presence of other heavy metals on lead removal from the synthetic aqueous solutions has been carried out according to the experimental conditions given in section "Effect of ions competition." The results indicated that maximal lead removal efficiency by BGMW (at equilibrium) has decreased due to the presence of other metals from 100 to 82.5 %. The observed decrease in the lead removal in the presence of the other metals could be explained by the adsorption competition between metal ions for the same sorption sites. The removal efficiencies of Cd, Zn and Cu were estimated to 4.9; 15.1 and 41.8 %, respectively (Fig. 6). They were relatively lower than the lead one which proves that for real wastewaters rich in mixture of heavy metals, lead ions will be preferentially removed. The same trend has been observed by Calvo et al. (2009) when they studied the removal of Pb^{2+}, Cu^{2+}, Zn^{2+}, H^+ and NH_4^+ by natural zeolite tuffs under dynamic mode using laboratory columns. Furthermore, Rangel-Porras et al. (2010) found that cadmium removal efficiency by three calcitic limestone materials from Mexico was much lower than lead. This, preferentiality to lead in comparison with the other metals, could be attributed to their physicochemical characteristics (size and electronegativity), their availability (the more available metal is better adsorbed onto the sorption sites) and the facility of the formation of the corresponding metal hydroxides complexes (Abdel-Aty et al. 2013). Furthermore, this sorption preference to lead may be also imputed to the fact that its hydration energy is lower than those of the other mentioned heavy metal ions (Rangel-Porras et al. 2010; Depci et al. 2012; Deng et al. 2013). In fact, the cations with the highest (absolute value) free energy of hydration should preferably remain in the solution phase where their hydration requirements may be better satisfied.

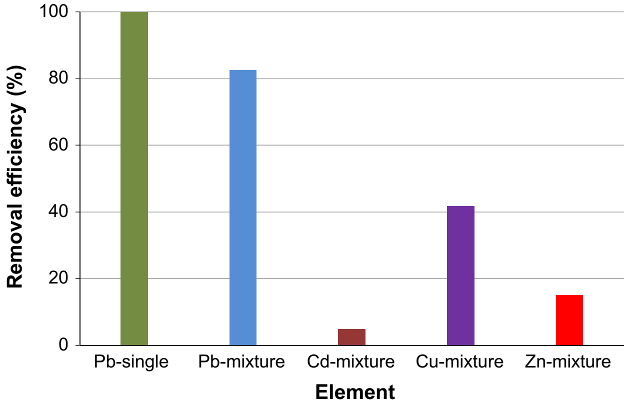


Fig. 6 Effect of the presence of other metals on lead removal (BGMW dosage = 5 g L^{-1}, pH 3.6 and temperature = 20 ± 2 °C)

CSTRs tests using secondary wastewater

The CSTR system has been used to study the efficiency of BGMW to remove lead from a real wastewater discharged by a battery manufacture. The main characteristics of this wastewater are presented in Table 1 (see section "Validation with industrial wastewater"). Figure 7 gives the variation of lead concentration at the outlet of the CSTR for BGMW doses of 5,10 and 20 g L^{-1}. Because of the relatively low initial aqueous pH value of the real wastewater (1.1), no significant removal of lead has been observed for a BGMW dose of 5 g L^{-1} since a quasi-constant lead concentration (relatively similar to the influent one) has been measured at the outlet of the reactor. The pH values of the aqueous samples collected at the outlet of the reactor were globally constants and equal to the initial value (1.1). Increasing the BGMW dose to 10 g L^{-1} has permitted a

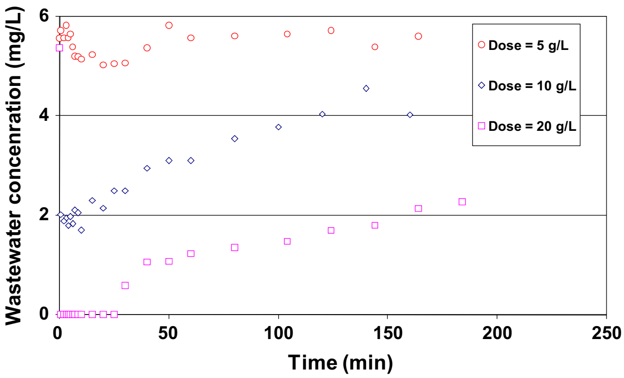


Fig. 7 Effect of BGMW dosage on lead removal from real wastewater (influent lead concentration = 5.4 mg L^{-1}, temperature = 20 ± 2 °C, flow rate = 20 mL min^{-1} and initial pH 1.1)

rapid decrease in the lead concentrations. Indeed, the measured average lead concentration during the period up to 10 min were evaluated to be about 1.9 mg L^{-1} corresponding to a removal efficiency of about 64 %. This is mainly due to the presence of more adsorption sites since the average effluent pH has not significantly increased (stabilized to about 1.2). However, a BGMW dose of 20 g L^{-1} has permitted a rapid and complete removal of lead for a time period of 25 min. This finding might be due to the combined effects of the presence of more adsorption sites and lead precipitation since the corresponding measured pH values during the first 10 min were higher than 6. After this time, a net decrease in the aqueous pH values and also the lead removal efficiencies were registered. This dosage is ten times higher than the one required for the synthetic solutions (see section "Effect of BGMW dosage"). This finding could be imputed to the very lower pH and the presence of relatively higher ions contents in the real wastewater.

Lead removal mechanisms exploration

Distinction between adsorption and precipitation

Lead removal from the aqueous solutions might occur by precipitation as lead carbonates or lead hydroxides complexes and also by adsorption onto the active sites of the surface of the BGMW particles. The precipitation of lead is instantaneous and very dependent on the aqueous pH values and the solutions contents of OH^-, HCO_3^- and Pb^{2+}. However, the adsorption phenomenon generally occurs in three steps: (1) transfer of lead from the aqueous solution to the sites of the adsorbent (boundary layer diffusion), (2) chemical complexation/ion exchange at the active sites of the adsorbent surface and (3) intra-particle diffusion of lead into the interior pores of the BGMW particles (Weber and Morris 1963).

In order to differentiate between these mechanisms cited above, specific batch assays have been carried out. In the first set of assays, aqueous lead at an initial concentration of 100 mg L^{-1} and initial pH of 3.6 was put in contact for 1 h with 5 g L^{-1} of BGMW. Thus, the lead removal was imputed to both adsorption and precipitation mechanisms. While, for the second set of experiments, the same lead concentration was introduced in contact for 1 h with a filtrate aqueous solution (using a 0.45 µm paper filter). This filtrate solution results from the shaking of 5 g L^{-1} BGMW in distilled water at the same initial pH (3.6). For this case, lead removal is exclusively due to precipitation. The experimental results show that in the first set of assays, adsorption and precipitation mechanisms succeed to completely remove lead from the aqueous solution. However, for the second type of assays, where only lead mechanism precipitation is present, the lead concentration has decreased from 100 to 42.97 mg L^{-1}, which corresponds to an average efficiency of 57 %. Therefore, under the experimental conditions cited above, lead removal from the synthetic aqueous solutions occurs by both precipitation and adsorption with an average contribution of about 57 and 43 %, respectively.

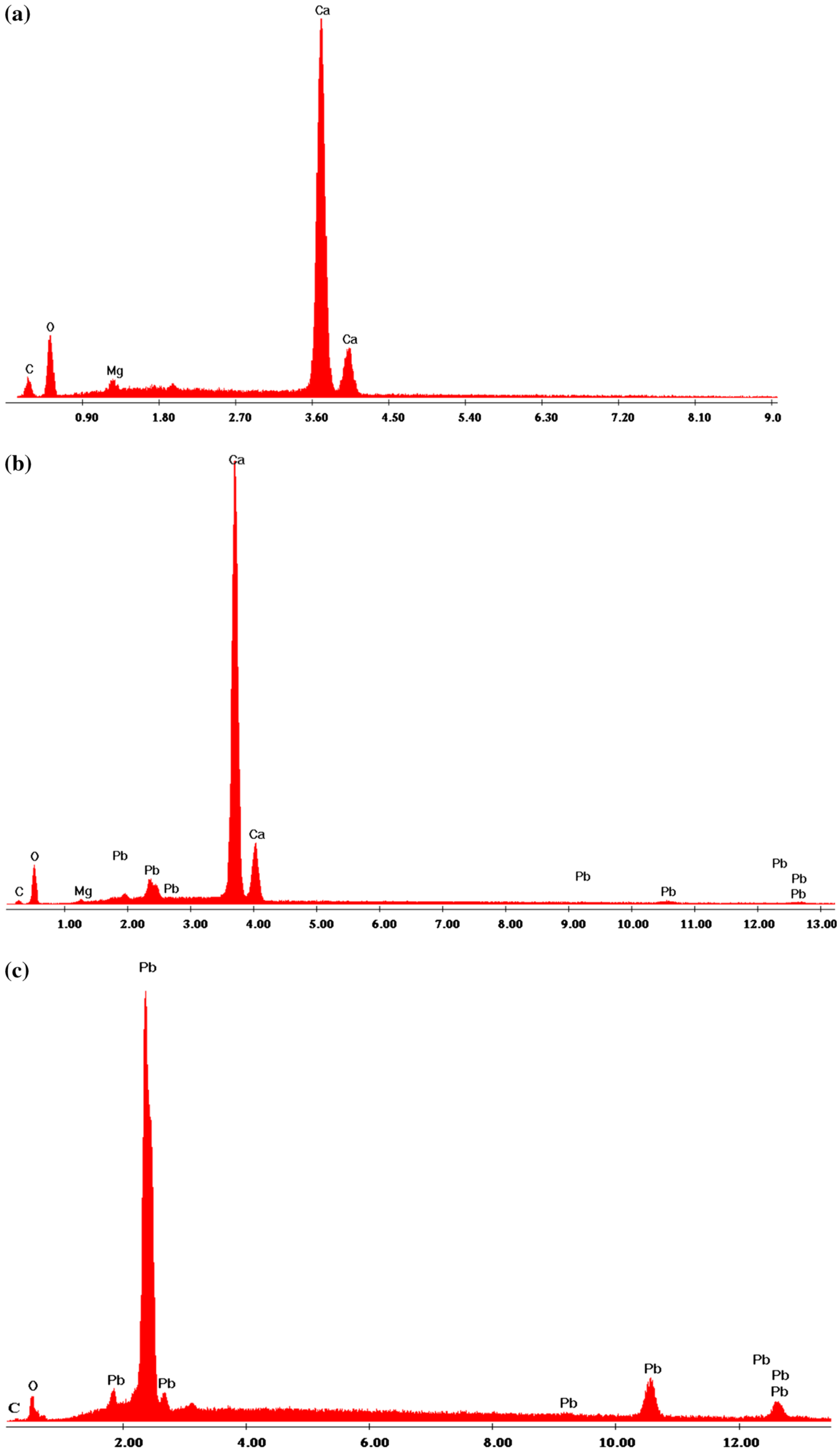
EDS analysis results

EDS spectra of BGMW samples before and after lead ions removal are shown in Fig. 8a, b. The EDS spectra of BGMW exhibit peaks for Ca, C, O and Mg, which are their main basic constituents (Fig. 8a). For the BGMW loaded lead ions sample, there are new peaks appearing in the EDAX spectrum, which are attributed to lead element (Fig. 8b). Therefore, the presence of a strong peak at 2.34 keV and small peaks at other locations in the EDS spectra provided an important evidence for lead adsorption on BGMW. On the other hand, EDS analysis of the solid phase formed as a consequence of lead precipitation (second set of assays: see section "Distinction between adsorption and precipitation") indicates that it is mainly formed by Pb, O and C (Fig. 8c).

XRD analysis results

XRD analysis has been done on the precipitated solid phase in order to determine the nature of this phase. The X-ray diffraction pattern (Fig. 9) indicates that this solid phase is formed by both cerussite ($PbCO_3$) and hydrocerussite ($(Pb_3(CO3)_2OH)_2$). This result is in concordance with the finding of Rangel-Porras et al. (2010), where they studied lead removal by calcitic materials. On the basis of the MINEQL software, hydrocerussite begins to appear at pH 5.0 and is the predominant species in the pH range between

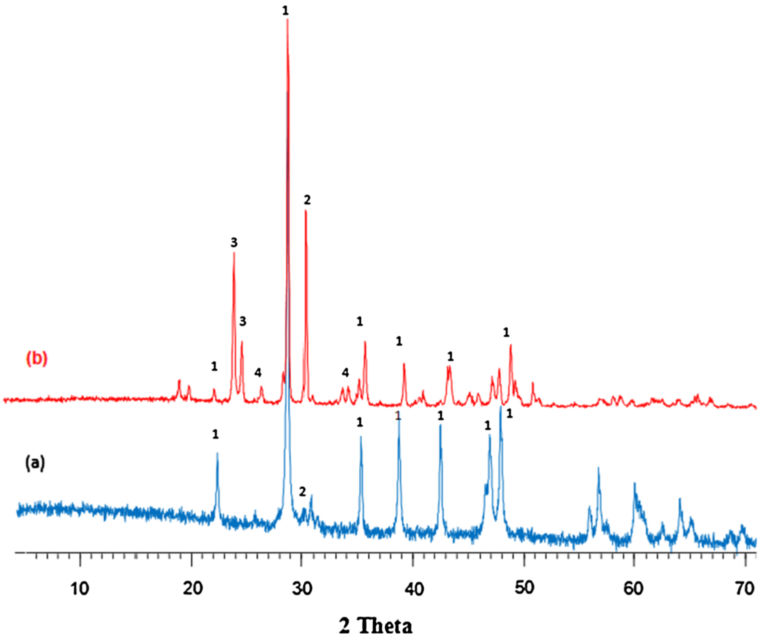
Fig. 8 EDS analysis results of raw BGMW (**a**), Pb-loaded BGMW (**b**) and lead precipitate solid phase (**c**)



5.5 and 7.5. However, cerussite could appear at lower pH (4.5), and it is predominating in the wide pH range above 8.0.

When BGMW particles are suspended in water, the main ions present in the system as a function of aqueous pH will be the following: Ca^{2+}, HCO_3^-, $CaHCO_3^+$,

Fig. 9 XRD analyses of raw BGMW (*a*), formed precipitate after contact between lead ions and filtered BGMW solution (*b*) (*1*: calcite, *2*: dolomite, *3*: cerussite and *4*: hydrocerussite)



$CaHO^+$, H^+ and OH^-. In presence of lead, the main species were Pb^{2+}, $Pb(CO_3)^+$, $Pb(NO_3)^+$, $Pb(CO_3)aq$ and $Pb(CO_3)_2^{2-}$. Therefore, lead removal can occur through precipitation in the form of $PbCO_3$ and $Pb(CO3)_2(OH)_2$ and their deposition at the BGMW surfaces as follows (Zhu 2002):

$$\equiv CaCO_3^0 + Pb^{2+} + HCO_3^- \leftrightarrow CaCO_3(s) + \equiv PbCO_3^0 + H^+ \tag{8}$$

$$\equiv PbCO_3^0 + Pb^{2+} + HCO_3^- \leftrightarrow PbCO_3(s) + \equiv PbCO_3^0 + H^+ \tag{9}$$

$$\equiv CaCO_3^0 + 3Pb^{2+} + 2HCO_3^- + 2OH^- \leftrightarrow CaCO_3(s) + \equiv (Pb_3(CO_3)_2(OH)_2)^0 + 2H^+ \tag{10}$$

$$\equiv (Pb(CO_3)_2(OH)_2)^0 + 3Pb^{2+} + 2HCO_3^- + 2OH^- \leftrightarrow Pb_3(CO_3)_2(OH)_2(s) + \equiv (Pb3CO_3(OH)_2)^0 + 2H^+ \tag{11}$$

On the other hand, it is worth to mention that for all assays' results mentioned above, the measured pH values at the outlet of the CSTR were significantly lower than the pH_{PZC} of the used BGMW, which has been evaluated to 8.11. Thus, the removal of lead ions has caused a net decrease in the aqueous pH values. This pH drop might be due to both OH^- ions consumption for lead carbonates (cerussite: $PbCO_3$ and hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) formation and also to the liberation of H^+ ions from the solid surface into the solution as a result of exchange with lead ions. As assumed by Dong et al. (2010) and Fan et al. (2009), when studying lead removal under static mode by hydroxyapatite/magnetite composite adsorbent and Chinese natural palygorskite, respectively, lead removal by BGMW particles could be ensured through the formation of inner-sphere complexes as follows:

$$BGMW - OH + Pb^{2+} \rightarrow BGMW - O - Pb^+ + H^+ \tag{12}$$

$$2BGMW - OH + Pb^{2+} \rightarrow (BGMW - O)_2 - Pb + 2H^+ \tag{13}$$

Lead removal from the aqueous solutions could occur also through cation-exchange mechanism with calcium ions:

$$Pb^{2+}BGMW\text{-}Ca \rightarrow Ca^{2+} + BGMW\text{-}Pb \tag{14}$$

This mechanism is also referred as outer-sphere complexation and does not involve formation of bonds between metal ions and the BGMW surface.

Conclusion

In the present work, Bianco Gioia marble wastes (BGMW), abundant and renewable wastes, have been tested under dynamic conditions as a low-cost material for lead removal from synthetic solutions and real wastewater. The experimental results confirm that BGMW can be considered as attractive and alternative materials for lead removal from synthetic aqueous solutions compared with various other materials. Indeed, even for relatively low doses (5 g L^{-1}), efficient removal of lead has been performed for a wide pH and aqueous concentrations ranges. BGMW application for lead removal from real wastewater showed that due to its very low pH (pH 1.1), a BGMW dose of 20 g L^{-1} was necessary to ensure a complete removal of lead. The main mechanisms involved in the lead removal were precipitation as cerussite and hydrocerussite, and adsorption through cation exchange and complexation.

The tested CSTR system could be up scaled and integrated in existing industrial wastewaters treatment plants with the added benefit of reducing derogatory environmental impacts of wastewaters discharge in water bodies.

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