REVIEW ARTICLE

Re-evaluation of several heavy metals removal by natural limestones

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Abstract Different treatment technologies have been efficiently applied to remove heavy metals from wastewater. Efforts have been made to find out the most economic water treatment technology by using low cost and easily accessible natural materials. On the other hand, heavy metals are the most threatening groundwater contaminants because of their toxicity and harmful effects on human and biota. This review discusses the use of natural geological materials for heavy metal removal in aqueous systems. Special attention has been devoted to natural limestone through a systematic inventory of relevant published reports. The removal of toxic metals may include different mechanisms (e.g., physisorption, chemisorptions, precipitation, etc.), depending on the physico-chemical properties of the material and the removed metal. Sorption of toxic metals (e.g., Pb, Cu, Cd, Zn, Cr, Hg, etc.) onto natural limestone involved precipitation of metal carbonate as a predominant removal process, but often subordinated by adsorption and ion exchange, depending on the physico-chemical properties of the studied limestone.

Keywords limestone, heavy metals, sorption, wastewater, passive treatment technology

1 Introduction

Rapid industrialization and urbanization have resulted in the deterioration of water, air and land quality [1]. Various industrial activities including textile dyeing, fertilizer production and mining activities generate high volume of contaminated wastewater [2–4]. The tremendous increase in the use of heavy metals over the past few decades has eventually resulted in an increased flux of metallic substances in the environment. Heavy metals are of special concern because they are non-degradable and therefore persistent [5].

Commonly encountered metals of concern include Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, etc. These metals are toxic in both their chemically combined forms as well as the elemental form [6]. Exposure to these contaminants present even in low concentration in the environment can prove to be harmful to the human health; excessive concentrations of those metals exert adverse effects on living organisms [7]. Therefore, it is necessary to seek for an easy to use and applicable method to solve the problem of heavy metal pollution [3]. It is well known that liquid effluents are usually treated before being discharged in the environment in order to reduce the concentration of environmental pollutants such as heavy metals and organic compounds, as prescribed by relevant environmental regulations [8,9]. Various methods were proposed for heavy metals removal from wastewater including ion exchange [10,11], solvent extraction [12], electrochemical treatment [13], and biosorption [14,15]. Among those techniques, adsorption was the most preferred technique due to its simplicity and relatively low cost [16–19].

The above-mentioned in place treatment technologies available for the removal of heavy metal ions from aqueous solutions are preferred when huge volume of contaminated wastewater is treated [20]. Other existing methods, despite their high efficiency, showed drawbacks such as high capital cost and the treatment of small volumes.

2 Heavy metals in the environment: fate and mobility

Fate and transport of a metal in soil and groundwater depends significantly on the chemical form and speciation of the metal [21]. Mobility of metals in ground-water systems is hindered by reactions that cause metals to adsorb or precipitate. These mechanisms can retard the movement of metals and also provide a long-term source of

metal contaminants [22]. While various metals undergo similar reactions in a number of aspects, the extent and nature of these reactions varies under particular conditions.

Chemical form and speciation of some of the more threatening metals found in contaminated sites are discussed below. The influence of chemical form on fate and mobility of these compounds is also discussed.

2.1   Lead

The primary industrial sources of lead (Pb) contamination include metal smelting and processing, secondary metal production, lead battery manufacturing, pigment and chemical manufacturing, and lead-contaminated wastes [1,2,23–25]. Widespread contamination due to the former use of lead in gasoline is also of concern. Lead released to groundwater, surface water and land is usually in the form of elemental lead, lead oxides and hydroxides, and lead metal oxyanion complexes [26].

Lead occurs most commonly with an oxidation state of 0 or +2. Pb^{2+} is the more common and reactive form of lead; it forms mononuclear and polynuclear oxides, and hydroxides.

Under most conditions, Pb^{2+} and lead-hydroxy complexes are the most stable forms of lead [26]. Low solubility compounds are formed by complexation with inorganic (Cl^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}) and organic ligands (humic and fulvic acids, amino acids) [27]. Lead carbonate solids form above pH 6 and PbS is the most stable solid when high sulfide concentrations are present under reducing conditions [4,24,28–30].

Most lead released to the environment is retained in the soil [2,31–34]. The primary processes influencing the fate of lead in soil include adsorption, ion exchange, precipitation, and complexation with sorbed organic matter. These processes limit the amount of lead that can be transported into the surface water or groundwater [17,31,35]. The relatively volatile organolead compound tetramethyl lead may form in anaerobic sediments as a result of alkylation by microorganisms [26].

The amount of dissolved lead in surface water and groundwater depends on pH and the concentration of dissolved salts and the types of mineral surfaces present. In surface water and ground-water systems, a significant fraction of lead occurs as precipitates ($PbCO_3$, Pb_2O, $Pb(OH)_2$, $PbSO_4$), sorbed ions or surface coatings on minerals, or as suspended organic matter.

2.2   Chromium

The distribution of compounds containing chromium(III) and chromium(VI) depends on redox potential, pH, the presence of oxidizing or reducing compounds, kinetics of the redox reactions, formation of chromium(III) complexes or insoluble chromium(III) salts, and total chromium concentration [36]. Chromium is one of the less common elements and does not occur naturally in elemental form, but only in compounds [37]. Chromium is mined as a primary ore product in the form of the mineral chromite, $FeCr_2O_4$. Major sources of Cr contamination include releases from electroplating processes and the disposal of chromium containing wastes [26,38]. Cr^{6+} is the form of chromium commonly found in contaminated sites. Chromium can also occur in the + 3 oxidation state, depending on pH and redox conditions [39,40]. Cr^{6+} can be reduced to Cr^{3+} by soil organic matter, S^{2-} and Fe^{2+} ions under anaerobic conditions often encountered in deeper groundwater [41,42]. Major Cr^{6+} species include chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) which precipitate readily in the presence of metal cations (especially Ba^{2+}, Pb^{2+}, and Ag^+). Chromate and dichromate also adsorb on soil surfaces, especially iron and aluminum oxides. Cr^{3+} is the dominant form of chromium at low pH (< 4). Cr^{3+} forms solution complexes with NH_3, OH^-, Cl^-, F^-, CN^-, SO_4^{2-}, and soluble organic ligands. Cr^{6+} is the most toxic and mobile form of chromium and is also more mobile [37,43–45]. Cr^{3+} mobility is decreased by adsorption to clays and oxide minerals below pH 5 and low solubility above pH 5 due to the formation of $Cr(OH)_3(s)$ [46].

Chromium mobility depends on sorption characteristics of the soil, including clay content, iron oxide content and the amount of organic matter present. It can be transported by surface runoff to surface water in its soluble or precipitated form. Soluble and unadsorbed chromium complexes can leach from soil into groundwater. The leachability of Cr^{6+} increases as soil pH increases [47,48]. Most of chromium released into natural waters is particle associated, however, and is ultimately deposited into the sediment [26,38].

2.3   Zinc

Zinc occur naturally as sulfates, with sphalerite ZnS as the most known natural mineral ores [49]. Zinc is usually extracted from sphalerite to prepare zinc oxide, used as a corrosion-resistant coating for iron or steel [26]. Zinc is one of the most mobile heavy metals in surface waters and groundwater because it is present as soluble compounds at neutral and acidic pH [50]. At higher pH, zinc can form carbonate and hydroxide complexes which control zinc solubility [30,51]. Excessive concentrations of zinc generate its precipitation in highly polluted systems, and may coprecipitate with hydrous oxides of iron or manganese [26]. It is noteworthy that co-precipitation of zinc is favored in the presence of lead [3]. This is a further proof for the coexistence of zinc and lead in the abundant Pb-Zn deposits [52,53].

The primary fate of zinc cations in aquatic systems involves its sorption to the surface of various natural materials, including hydrous iron and manganese oxides,

clay minerals, and organic matter. The efficiency of the sorption was found to increase when the solution pH increase [54].

2.4   Cadmium

Cadmium originates from both natural and anthropogenic sources, usually in the form of CdS or $CdCO_3$. It is mainly recovered, in its natural form, from the mining of sulfide ores of lead, zinc and copper. Anthropogenic sources of cadmium include plating operations and the disposal of cadmium-containing wastes [12,26,55,56]. Cadmium is usually encountered in different forms, depending on the solution and soil chemistry. The most common forms of cadmium include Cd^{2+}, cadmium-cyanide complexes, or $Cd(OH)_2$ solid sludge [26]. Hydroxide ($Cd(OH)_2$) and carbonate ($CdCO_3$) solids dominate at high pH whereas Cd^{2+} and aqueous sulfate species are the dominant forms of cadmium at lower pH (< 8) [13,57]. Cadmium is relatively mobile in surface water and ground-water systems and exists primarily as hydrated ions or as complexes with humic acids and other organic ligands [58]. It is usually removed from aqueous solutions by precipitation and sorption to mineral surfaces, especially oxide minerals and mesoporous aluminosilica, at high pH values ($> pH\ 6$) [58]. It is well known that sorption of metal cations is influenced by various physico-chemical parameters including the cation exchange capacity of clays, carbonate minerals, and other competing metals present in soils and sediments, as discussed later in this paper [26,59].

2.5   Copper

Mining activities are the major source of copper contamination in groundwater and surface waters. Other sources of copper include algicides, chromated copper arsenate [60], pressure treated lumber, and copper pipes.

It is well known that soil chemistry strongly influence the speciation of copper in ground-water systems [41,61]. In alkaline conditions, copper carbonates ($CuCO_3$) constitute the dominant species that are commonly subordinated by hydroxide complexes such as $CuOH^+$ and $Cu(OH)_2$. Copper forms strong complexes with humic acids, especially at high pH and low ionic strength [62]. Furthermore, copper could be easily adsorbed to mineral surface over a wide range of pH [30,63]. In terms of toxicity, the cupric ion (Cu^{2+}) is the most toxic form of copper; $CuOH^+$ and $Cu_2(OH)_2^{2+}$ are also toxic, but to a lower extent [64].

2.6   Mercury

Like other divalent cations, the primary natural source of mercury is sulfide ore, as a by-product of ore processing [26]. Anthropogenic activities, such as coal combustion and measuring devices are also the major source of mercury contamination. The release of mercury from manometers in pressure measuring stations and other pipelines also contribute to this contamination. World Health Organization (WHO) revised the guideline for mercury of less than $1\ \mu g \cdot L^{-1}$. According to WHO, drinking-water is considered to be a minor source of exposure to mercury, except in circumstances of significant pollution [36]. It is well-known that the redox potential and pH of the system determine the stable forms of mercury that will be present, of which alkylated forms are the most toxic because of their solubility in water and volatilization in air [26]. Sorption of divalent mercury cations to soils, sediments, and other natural materials is an important mechanism for the removal of mercury from solution. Mercury may also be removed from solution by coprecipitation with sulfides [26]. In addition, Hg^{2+} forms strong complexes with a variety of both inorganic and organic ligands, making it very soluble in oxidized aquatic systems [27].

3   Metals leaching in mining activities

Cravotta III and Trahan [65] mentioned that acid mine drainage (AMD) and metal dissolution are the primary problems associated with pollution from mining activities. They are usually contaminated with dissolved and particulate matters, the chemistry of which is relatively complicated, depending on the geochemistry and physical characteristics that can vary greatly from site to another [66].
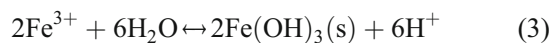
In mining areas, when pyrite (FeS_2) is oxidized under acidic conditions, acid generation and metals dissolution will start ubiquitously. This oxidation process occurs in undisturbed rock at a slow rate, rendering the streaming water to buffer the acid generated. Water natural buffering capacities will be easily overwhelmed as mining activities increase the excavated surface area of these sulfur-bearing rocks, allowing the excess acid generation:
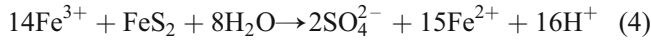
$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{3+} + 4SO_4^{2-} + 4H^+ \quad (1)$$
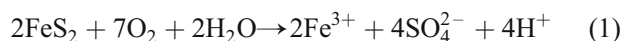
It is also possible to observe the transformation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) via oxidation through the sufficient oxygen dissolution in the water, especially when water is abundantly aerated with atmospheric oxygen.
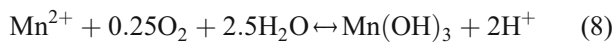
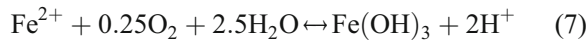$$2Fe^{2+} + 1/2O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O \quad (2)$$
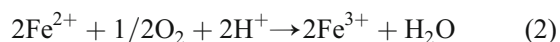
Those ferric ions (Fe^{3+}) usually precipitate as $Fe(OH)_3$, specific for waters affected by acid mine drainage; they can also interact with pre-existing pyrite to produce more ferrous iron and acidity [67].
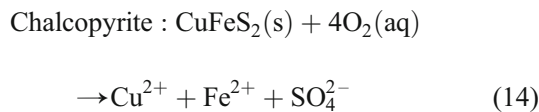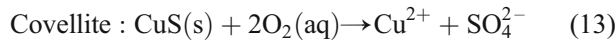
$$2Fe^{3+} + 6H_2O \leftrightarrow 2Fe(OH)_3(s) + 6H^+ \quad (3)$$

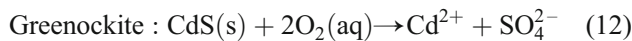$$14Fe^{3+} + FeS_2 + 8H_2O \rightarrow 2SO_4^{2-} + 15Fe^{2+} + 16H^+ \quad (4)$$
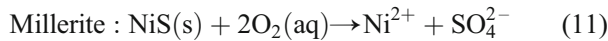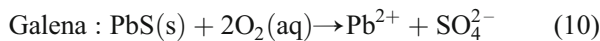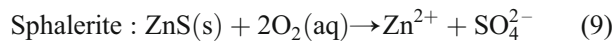
Without dissolved oxygen, water will be laden with ferrous iron because of the interaction between pyrite and ferric iron, leading to the release of more proton ions [68]. This should be the main source of acidity. Furthermore, the generation of additional hydrogen ions, when certain metals precipitate, is a subordinate source of acidity that have to be considered in the preparation treatment strategies.

$$Al^{3+} + 3H_2O \leftrightarrow Al(OH)_3 + 3H^+ \quad (5)$$

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+ \quad (6)$$

$$Fe^{2+} + 0.25O_2 + 2.5H_2O \leftrightarrow Fe(OH)_3 + 2H^+ \quad (7)$$

$$Mn^{2+} + 0.25O_2 + 2.5H_2O \leftrightarrow Mn(OH)_3 + 2H^+ \quad (8)$$

Other metals commonly found in mine drainage waters exist because they are present in the rocks, similar to pyrite. For example, there are a variety of other metal sulfides that may release metal ions into solution, but may not generate acidity, the reasons for this are not clear [68]. Among those metal sulfides, the following minerals can be cited [69]:

$$\text{Sphalerite}: ZnS(s) + 2O_2(aq) \rightarrow Zn^{2+} + SO_4^{2-} \quad (9)$$

$$\text{Galena}: PbS(s) + 2O_2(aq) \rightarrow Pb^{2+} + SO_4^{2-} \quad (10)$$

$$\text{Millerite}: NiS(s) + 2O_2(aq) \rightarrow Ni^{2+} + SO_4^{2-} \quad (11)$$

$$\text{Greenockite}: CdS(s) + 2O_2(aq) \rightarrow Cd^{2+} + SO_4^{2-} \quad (12)$$

$$\text{Covellite}: CuS(s) + 2O_2(aq) \rightarrow Cu^{2+} + SO_4^{2-} \quad (13)$$

$$\text{Chalcopyrite}: CuFeS_2(s) + 4O_2(aq)$$

$$\rightarrow Cu^{2+} + Fe^{2+} + SO_4^{2-} \quad (14)$$

4 Uses of limestone in heavy metal removal

Natural limestone beds have been widely excavated for dimension stone, cement, glass manufacturing, painting materials and pharmaceutical products [70–72]. Several specialized factories are also using this limestone as a raw material for manufacturing pure calcium carbonate [70–72]. Limestone is mainly composed of calcite, but it often contains variable impurities (e.g., clay minerals, silt and sand) that strongly influence its physical and chemical properties. The assessment of those properties is fundamentally important for the choice of the most auspicious

industrial application [73,74]. One of the famous applications of natural limestone is the use of its lime form for the softening and clarification of municipal water, the removal of harmful bacteria, and as a neutralizing agent in acid-mine and industrial discharges. Limestone and marble are very reactive to acid solutions, making acid rain a significant threat for statues and building surfaces which may suffer severe damage. However, the reactive property with acid water was the cornerstone for the development of viable technologies (e.g., passive treatment technology, active treatment technology, batch sorption) to neutralize acidic soil conditions.
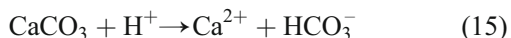
4.1 Passive treatment technology

Active chemical treatment of AMD to remove metals and acidity is often expensive and a long term liability [75], therefore, a variety of passive treatment systems have been developed to allow naturally occurring chemical and biological processes to clean contaminated mine waters. The most important passive treatment technologies include constructed wetlands, anoxic limestone drains (ALDs), limestone ponds, and open limestone channels (OLCs) [76].

Natural wetlands are characterized by water-saturated soils or sediments with supporting vegetation adapted to reducing conditions in their rhizosphere. Constructed wetlands are man-made ecosystems where the promotion of oxidation and hydrolysis in the surface water of the wetland is speeded up. In anaerobic conditions (i.e., anaerobic wetlands), the metabolic products of sulfate-reducing bacteria and limestone, are major reactants in raising pH and precipitating metals as sulfides, hydroxides and/or carbonates [77]. ALDs consist mainly of buried limestone beds that generate bicarbonate alkalinity when water flows through. Limestone ponds are built over the upwelling of a seep, which are filled with limestone for treatment. Passive systems can be implemented as a single permanent solution for many types of AMD at a much lower cost than active treatment. Relative to active chemical treatment, passive systems generally require longer retention times and greater space, but markedly reduce long-term costs. Many passive systems have realized successful short term implementation in the field and have substantially reduced or eliminated water treatment costs in many mine sites [78]. The selection and design of an appropriate passive system depends on water chemistry, flow rate and local topography and site characteristics [79]. These systems are used when the water has net acidity, so alkalinity must be generated in the wetland and introduced to the net acid water in order to accomplish significant precipitation of dissolved metals. Limestone reacts with acidity in the wetland to generate alkalinity:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \qquad (15)$$

Limestone continues to react when kept in an anaerobic environment because ferrous iron is relatively soluble at pH 7 in anoxic water. Limestone dissolution produces water with higher pH and therefore bicarbonate alkalinity for metal removal. Caraballo et al. [80] developed a field multi-step limestone and MgO passive system to treat acid mine drainage with high metal concentrations. Their system consisted of two tanks filled with 3 m³ of limestone and wood shavings, and one tank (1 m³) of caustic magnesia powder and wood shavings separated by several oxidation cascades and decantation ponds. This system achieved high removal (about 100%) of Al, Cu, As, Pb and Fe within 9-month operation. The main precipitates were schwertmannite, hydrobasaluminite, amorphous Al(OH)₃ and gypsum. Similarly, Silva et al. [81] assessed the removal of manganese from aqueous solutions by natural calcites in batch and continuous systems, concluding that calcite limestone can be used to remove more than $15.5 \ mg \cdot L^{-1}$ out of $16.5 \ mg \cdot L^{-1}$ of manganese from industrial effluents. Lee et al. [82] have investigated the retention of trace metals onto precipitates formed by neutralization of 3 natural waters contaminated with AMD. They found that the laboratory scale neutralization of the AMD-contaminated waters caused the formation of ferrihydrite and schwertmannite, depending on solution pH. In addition, the removal of trace metals (e.g., Zn, Cu, Ni, Co, Pb and Cd) was directly related to the precipitation of those metals compounds. For instance, the pH-dependent sequence of sorption edges is Pb > Cu > Zn ≈ Cd > Co, which is in agreement with precipitation pH of those metals carbonates. Lead carbonate (PbCO₃) precipitates at pH 5.3, whereas otavite (CdCO₃) forms at pH 8.5 [83]. Huminicki and Rimstidt [84] measured the effect of hydrodynamics and gypsum coatings, eventually sulfates, on calcite neutralization rates. They developed a numerical model to simulate the efficiency of anoxic limestone drains (ALD) to buffer the AMD-contaminated waters pH, which lead to the precipitation of metals [83]. Skousen et al. [85] summarized the main passive treatment technologies. They mentioned that limestone ponds are a new passive treatment idea in which a pond is constructed on the upwelling of an AMD seep or underground water discharge point [85,86]. Limestone is placed in the bottom of the pond and the water flows upward through the

limestone bed [78]. Based on the topography of the area and the geometry of the discharge zone, the water can be from 1 to 3 m deep, containing 0.3 to 1 m of limestone immediately overlying the seep (Fig. 1). The pond is sized and designed to retain the water for 1 or 2 days for limestone dissolution, and to keep the seep and limestone under water [84]. Another easy technique commonly used to produce alkalinity is open limestone channel (OLC) that introduces alkalinity to acid water by in place addition of limestone [87]. Acid water introduced to the channel is treated by limestone dissolution, leading to precipitation of metal carbonates at high pH [4]. Field experiments showed efficient treatment by OLCs, but studies are needed to clarify the possible mechanisms [84]. It is also relevant to investigate the behavior of OLCs in waters of different pH and high heavy metal loads, possible interactions with water chemistry, and the importance of limestone purity. An open limestone channel was successfully designed by Green et al. [88] within an existing drain to treat the acidic and metal-rich drainage waters. They concluded that the main problem, faced during the early operation stage, was the accumulation of sediment over the limestone, preventing contact of limestone with acidic water and therefore leading to the reduction of alkalinity and calcium released into solution. They recommended continuous agitation of the limestone to produce an equivalent or even greater amount of alkalinity; therefore more metals could be removed from solution compared to fresh limestone. Thus, the removal of different metals from the water was attributed to the increase in pH produced by limestone dissolutions in addition to sorption reactions.

Bamforth et al. [89] constructed a reactor to assess the effect of substrate-type on Mn sequestration. They tested pure materials (all of grain size 1–2 mm) to treat the mine water in small reactors that contained one carbonates (i.e., limestone, dolomite or magnesite; Fig. 2) using Quartzite as a carbonate free control. Results of laboratory experiments highlighted the potential importance of Mn carbonates for the immobilization of Mn in man-made water treatment systems. It was also demonstrated that Mn carbonates and Mn oxyhydroxides provided additional sinks for Mn. They also suggested that the chemical nature of natural aggregates used as substrates may not be important as drivers of precipitation [89].

Akcil and Koldas [69] cited many factors that determine the rate of acid generation. Those factors included pH,
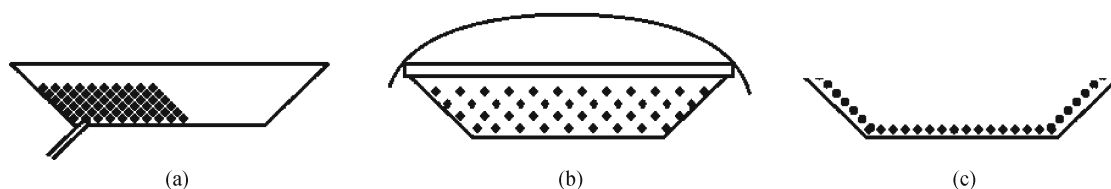

Fig. 1 Schematic presentation of passive treatment by limestone. (a) Limestone ponds, (b) anoxic limestone drain and (c) open limestone channel. This was prepared after the modification of Ziemkiewicz [87]
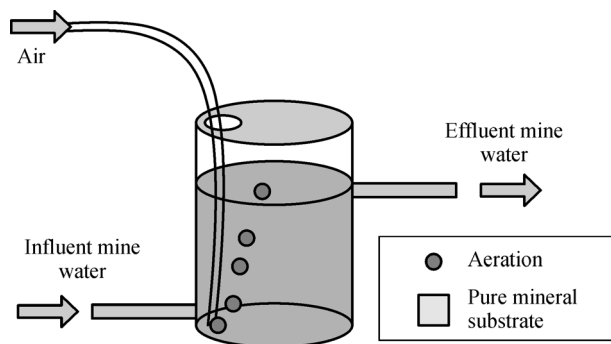
Fig. 2   Representation of laboratory reactors [89]

Fig. 3   Acid mine drainage from an old metalliferous mine showing the dark reddish water [69]

temperature, chemical activity of Fe^{3+}, surface area of exposed metal sulfide, chemical activation energy required to initiate acid generation, etc. The same authors stated that AMD releases usually have low pH, high specific conductivity, high concentrations of iron, aluminum, and manganese, and low concentrations of toxic heavy metals. They indicated that AMD is often left without treatment because of the inadequate or expensive treatment technologies. The reactions of acid generation are best illustrated by examining the oxidation of pyrite (FeS_2), which is one of the most common sulfide minerals. The first important reaction is the oxidation of sulfide mineral into dissolved iron, sulfate and hydrogen [69]. Johnson and Hallberg [75] reviewed the effects of acid mine drainage on the environment and the corresponding available technologies. They attested that various options are available for remediating AMD, among them "passive" treatment technologies (require relatively little resource input once in operation). They described new and emerging technologies (i.e., anoxic lime drain "ALD", active treatment process and biological remediation strategies, and reducing and alkalinity producing systems; Figs. 2–4).

4.2   Removal of heavy metals in batch method

Batch sorption is usually utilized as an appropriate technique to evaluate the efficiency of a given adsorbent in removing the desired solute under static conditions [4,83], especially from wastewater. In typical conditions, known amount of limestone sample is mixed with appropriate volume of metal ion solution of known concentration and pH, and shaken under a controlled temperature to reach equilibrium. The removal of toxic metals by natural limestones has been investigated by various researchers [4,30,90–94], pointing out that limestones could be an efficient natural geological material for the treatment of heavy metals in contaminated water. Karageorgiou et al. [95] found that the dissolution of calcite in water is a fast process that initiates the interactive reaction of metal cations at the surface of limestone. Sdiri et al. [3,4,30] and Sdiri and Higashi [83] demonstrated that

calcite dissolution under acidic conditions (pH 3) constituted the first step for heavy metals sorption because of metal carbonate formation to the surface of natural limestones, as was further confirmed in other relevant studies [77,93,95,96].

It was also found that the sorption of lead ions onto limestone was very fast compared to other metal ions [4,30,51,83]. Godelitsas et al. [28] confirmed those results when studying the removal of Pb ($10 \text{ mg} \cdot \text{L}^{-1}$) by calcite in aqueous solution; they found that lead was completely removed within 1 min interaction. Thus, according to the above-mentioned studies, the removal process is predominantly governed by the precipitation of lead carbonate due to the low precipitation pH of $PbCO_3$ (pH 5.3) and the solubility product constant ($K_{sp} = 7.4 \times 10^{-14}$ at 25 °C) [1,97]. Above that pH, $PbCO_3$ solid phase should be formed, leading to high removal capacity, because the solution is neutralized (pH $\approx$ 7) after the addition of limestone [4]. Several previous works confirmed that carbonate precipitation was especially effective for the removal of lead [24,28].

Theoretical precipitation of $CdCO_3$ ($K_{sp} = 1 \times 10^{-12}$ at 25 °C) begins at pH 8.5, but an initial chemisorption step could be suggested as a possible removal mechanism at lower pH [98]. Our previous investigations showed that higher removal efficiency was completed by the lower grade limestone samples because of the high specific surface area and the high amounts of impurities [4,83]. In addition, it was found that cadmium may exert an inhibitory effect on calcite dissolution resulting in the reduction of the available site for metal sorption [4,83,99,100]. Similar findings were reported by Alkattan et al. [101] and Cubillas et al. [92] when studying the effect of metal sorption on calcite dissolution. These results may explain the lowest removal of cadmium by the pure limestone, despite the fact that cadmium is the metal cation
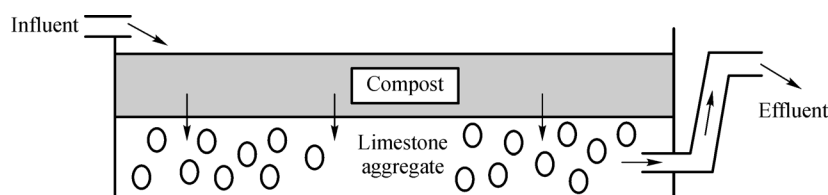
Fig. 4   Reducing and alkalinity producing system [75]

which replaces more easily Ca^{2+}, due to the similarity of their ionic radii [35,93]. Sdiri et al. [4] found that the removal of cadmium by Tunisian limestone varied between 14.57% and 95.34%, after shaking for 60 min. They also found a copper removal efficiency of 37.68% to 91%, indicating that pure limestone had better affinity to this element in comparison with cadmium. In addition, they found that high purity limestone achieved low removal capacity of zinc (c.a., 7%), whereas low grade samples removed more than 70% in most cases. According to Sanchez and Ayuso [93], and Pickering [98], the available sites for Zn exchange represent less than 10%. Moreover, Zn^{2+} was quickly removed by low grade limestone, indicating the predominance of chemisorption process as a possible removal mechanism. According to many authors [4,25,29,90,91,93], longer equilibration time is indicative of physical adsorption, while shorter contact time favors chemisorption. This is a further confirmation of chemisorption process.

The adsorption capacities of seven inorganic sorbents (i.e., solid wastes) for Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Cr^{3+} were studied in detail by Zhou and Haynes [102] at two different concentrations (10 and 100 mg·L^{-1}) and an equilibrium pH of 6.0. The results indicated that calcareous materials showed a very pronounced decline in the adsorption of Pb and Cd after acid treatment. This was attributed to the effects of residual surface alkalinity which enhanced the adsorptive capacity of the calcareous materials (i.e., blast furnace slag and red mud), but acid pre-treatment neutralized most of this alkalinity.

The effect of contact time on the sorption was kinetically analyzed by applying the pseudo first and second order kinetic model to study the sorption of various metal ions (e.g., Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}) from aqueous solutions by natural geological materials [3,4,11,16,37,103–106]. The retention process was also examined in terms of diffusion of metal ion in the solution in order to evaluate the extent of the rate-limiting step [39,107]. Wankasi et al. [25] reported several consecutive steps in the metal retention process including sorption on the external surface and intra-particle diffusion along the pore walls, as well as their combination for the rate-controlling factor. However, the intra-particle diffusion model may not the only rate limiting step, as mentioned by Sdiri et al. [4] and Wu et al. [108]. They mentioned chemisorption as a predominant interactive process that

was subordinated by physisorption. As for lead, the removal by carbonaceous sorbents is very quick, hindering any possible kinetics [4,24,45,94].

Conventional chemical coagulation, sedimentation and filtration can remove up to 80% of inorganic mercury, but only 20%–40% of organic mercury. Ferric sulfate is more effective than aluminium sulfate, and the removal is more effective in the presence of high concentrations of suspended solids. Powdered activated carbon is effective for the removal of inorganic and organic mercury and can be used to enhance removal during coagulation. Ion exchange could be an alternative method [109]. It should, therefore, be possible to achieve a concentration below 1 µg·L^{-1} by treatment of raw waters that are not grossly contaminated with mercury [36].

4.3   Comparison of removal efficiencies studies by limestones

Based on the published research, the amount (%) of heavy metals removed by limestone originating from several different locations is highly variable (Table 1). Sanchez and Ayuso [93] stated that removal equilibrium was attained after 6 h, while Aziz et al. [90], Wu et al. [45] and Aziz et al. [29] found that a much shorter contact time of 60 min was adequate for effective removal of metals. Regarding pH, Rouff et al. [24] reported that a pH change from 7.3 to 8.2 increased the removal amount of lead from 14% to 45%. Increasing limestone concentration in the test solution improved removal efficiency in all studies. Sdiri et al. [4] found a substantial improvement in removal of metals when the limestone concentration increased from 1 to 5 g·L^{-1}; cadmium removal jumped from 8% to 70% and copper removal also rose, although less dramatically, from 25% to 30%. The study data showed that removal efficiency was dependent upon the physicochemical characteristics of the individual limestone samples. The greatest improvement in removal occurred for zinc where the percent removal more than doubled between 1 and 3 g·L^{-1}. All these results indicated a much higher removal efficiency for the Tunisian limestones than was shown by Wu et al. [45], who studied the effects of pure limestone concentration and temperature on the removal of cadmium, copper and zinc. They concluded that increasing the amount of limestone from 5 to 20 g·L^{-1} enhanced the removal of cadmium, copper and zinc from 15.3% to

Table 1 Removal efficiency studies with limestone in batch systems [4]

Location of limestone	Ion	Initial concentration /(mg·L^{-1})	pH	Amount of limestone /(g·L^{-1})	Temperature /°C	Removal /%	Source
Penang, Malaysia	Cu	5	7	14, 28, 56	25	90	[90]
Huangshi, china	Cd	9	–	5, 10, 20	20, 50	22–70	[45]
	Cu	2	–	5, 10, 20	20, 50	49.5–100	[45]
	Zn	10	–	5, 10, 20	20, 50	24–60	[45]
Oviedo, Spain	Cd	56	6.5	20	25	87.8	[110]
Chihuahua, Mexico	Pb	100	4.85	10	25	90	[28]
New York, US	Pb	0.2	7.3, 8.2, 9.4	0.5	22	14–45	[24]
Ipoh, Malaysia	Cd	2	7	14, 28, 56	25	94–97	[29]
	Cu	2	7	14, 28, 56	25	96–98	[29]
	Zn	2	7	14, 28, 56	25	85–90	[29]
Gafsa, Tunisia	Cd	10	3–6	1, 3, 5	25, 30, 35	9.8–73.8	[4]
	Cu	10	3–6	1, 3, 5	25, 30, 35	48.6–84.1	[4]
	Zn	10	3–6	1, 3, 5	25, 30, 35	30.7–88.2	[4]
Gabes, Tunisia	Cd	10	3–6	1, 3, 5	25, 30, 35	2.5–55.3	[4]
	Cu	10	3–6	1, 3, 5	25, 30, 35	21.4–70.4	[4]
	Zn	10	3–6	1, 3, 5	25, 30, 35	25.3–88.6	[4]
Bizerte, Tunisia	Cd	10	3–6	1, 3, 5	25, 30, 35	25.9–99.0	[4]
	Cu	10	3–6	1, 3, 5	25, 30, 35	62.4–94.3	[4]
	Zn	10	3–6	1, 3, 5	25, 30, 35	63.0–86.8	[4]

50.5%, 49.5% to 90% and 20% to 45%, respectively. These efficiencies are lower than those measured by Sdiri et al. [4]. Wu et al. [45] also found that a change in the temperature from 20 to 50 °C led to an average removal increase of 19.9%, 10.3% and 10.4% for Cu^{2+}, Cd^{2+} and Zn^{2+}, respectively. The effect of increasing temperature on removal efficiency found by Sdiri et al. [4] was more substantial than was reported by Wu et al. [45].

4.4 Comparison to other treatment methods

Comparative study has been undertaken to find out the advantages of the most commonly used methods for heavy metals removal. This review was limited to passive treatment technologies that commonly used limestones as low cost media for heavy metal remediation. Only few documents reviewing remediation technologies for heavy metal contaminated waters are available [11,111,112]. Therefore, this review may add some points to previous studies in relation to this matter [30,112]. Fu and Wang [11] succinctly reviewed the removal of heavy metal ions from wastewaters. Hashim et al. [112] reviewed the existing technologies commonly adopted for heavy metals removal from water bodies and soil. They divided the treatment technologies into different classes, including chemical, biological/biochemical/biosorptive and physico-chemical treatment technologies. According to those

authors, numerous advantages can be observed such as the (i) complete or substantial destruction/degradation of the pollutants, (ii) extraction and treatment or/and disposal of pollutants, (iii) stabilization in less mobile or toxic forms and (iv) separation of non-contaminated materials and their recycling from polluted materials. In this review, special attention has been paid to passive treatment technologies. Those technologies used natural limestones as low cost remediation materials; they are undergoing further labora-tory tests to ascertain their efficiency for heavy metal removal. The noticeable advantage of the passive treatment technologies is their high sorption capacity [4,30,112]. However, the adsorption capacity depended on the sorbed metal and its affinity to limestone surface. It was clearly observed that metal with high binding strength (e.g., Pb, Cu) showed higher affinity to limestone. Those techniques generally involved physical processes such as civil construction of barriers, physical adsorption or absorption, mass transfer as well as harnessed chemical or biochemical processes. Most of the times, two or more processes are coupled together to deal with the contamination problem.

Schematic diagram of the most widely used treatment technologies and their relative processes is presented in Fig. 5. Though *in-situ* treatment may include chemical treatments (e.g., reduction, soil washing), this review focused on passive treatment technologies as it involve limestone as reactive medium. It is well known that various
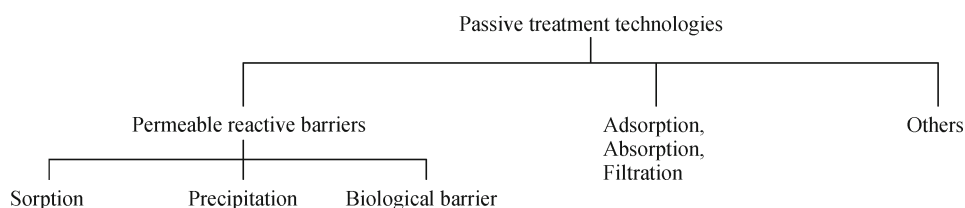
Fig. 5 Schematic diagram of passive treatment by limestone and the involved removal mechanisms [112]

materials including red mud, blast furnace slag and other industrial byproducts are considered efficient materials to chemically stabilize heavy metal ions in wastewater. Our previous works confirmed that limestone was much more efficient than the above mentioned materials for heavy metal removal in aqueous systems [4,83]. It was also demonstrated that sorption and precipitation were the main reactive mechanisms. Those conclusions are in agreement with the review of Fu and Wang [11], and Hashim et al. [112].

5   Discussion

Passive treatment technologies that involve physico-chemical treatment processes, along with their advantages and limits are summarized in Table 2. Mostly, two or more processes are coupled together to deal with the contamination problem. Generally, the reactive media (e.g., lime, red mud) is placed in sub-surface across the pathway of heavy metal contaminated wastewater which move downward under its own gravity to create a passive treatment system. Various type of mechanisms can take place when the contaminated water come to contact with the reactive media. Among these mechanisms, transformation, sorption and precipitation of the desirable contaminant are the most active processes. For instance, heavy metal contaminant

can be passively sorbed to the reactive material either through ion exchange or surface process (i.e., complexation, precipitation) [93,24]. The benefits of using natural limestone as reactive medium lie in its low cost, largely available material coupled with its high efficiency in heavy metal immobilization through various remedial processes (such as precipitation and sorption). Moreover, the effects of impurities in natural limestone were found to be very important in removing heavy metals in aqueous systems. Detailed description of the possibly involved mechanisms in heavy metal removal by impure limestone can be found in our previous work [4]. The objectives of the present study re-evaluate the efficiencies of natural geological materials (i.e., limestones) in removing toxic metals from aqueous solutions and discuss the feasibility of using natural carbonates in wastewater treatment.

Sdiri et al. [83] undertook the removal experiments using a batch system, they indicated that natural limestones were highly efficient in the removal of heavy metals (Pb (II), Cd(II), Cu(II) and Zn(II)) from an aqueous solution. Chemisorption and precipitation were the main processes that influenced removal rates, especially for the purest limestone. Limestone with higher concentration of impurities such as silica, iron and aluminum oxides, showed much better removal efficiency than the pure one. It is therefore recommended as an efficient medium for the removal of selected heavy metals from wastewaters.

Table 2   Passive treatment technologies for wastewaters (modification after Gazea et al. [111])

Technology/process	Metal ions	Advantages	Disadvantages	References
Sorption process in permeable reactive barriers (PRBs)	Pb, Cd, Zn, Cu and other heavy metals	Cheap geomaterials and high sorption capacity	Depends on pH and metal ion to be removed. Field scale studies is needed	[4,11,29,89,90,111]
Precipitation in PRBs		*In-situ* application in synergy with electrokinetic treatment	Clogging by metal hydroxides and carbonates	[4,11,111]
Biological barriers	Fe, Ni, Zn, Al, Mn, Cu, As, Cr	Remove both divalent and trivalent metal ions	–	[7,25,113]
Absorption by inorganic surfactants	As, Pb, Cd, Ni, Zn	Surfactants are available highly complexing agents	pH-dependent process	[112]
Membrane technology	Pb, Cd, Zn, Cu and other heavy metals	High removal efficiency	Filter clogging	[112]
Adsorption	As, Pb, Cr, Cd, Ni, Zn	Wide range of heavy metals can be removed	Frequent regeneration activated carbon, if used. Field applications of minerals and derived materials is not yet performed	[112]

Different mechanisms, including precipitation, coprecipitation and sorption would be involved in the removal of heavy metals by natural limestones (Fig. 6). Chemisorption and precipitation are the main processes that influenced removal rates. Pure limestone samples retain metal cations via chemical reactions. Lower purity limestone may involve other physico-chemical processes like chemisorptions and adsorption to the edge groups (i.e., silanol groups) in addition to chemical phenomenon, so it showed higher removal rate than the purest samples. Despite the fact that it was not possible to quantitatively evaluate the contribution of each mechanism, the use of adsorption models such as intra-particle diffusion and pseudo-second-order models could be useful tools in term of qualitative interpretation. It is well known that limestones can remove lead well by the process of precipitation at low pH. Furthermore, physico-chemical properties of metal cations are determining factors in the removal of each metal. For instance, metal cation with higher electronegativity and relative binding strength can be more readily adsorbed to the natural adsorbent. The presence of different kind of edge groups (i.e., aluminol, silanol and siloxane) sustains the retention via chemisorption and physisorption.

The idea of generating alkalinity with anaerobic limestone treatment systems has recently gained attention by the mining community [111]. Those passive systems designed for mine water pretreatment have become known as anoxic limestone drains and buffering capacity is introduced, in the form of alkalinity, into the acid drainage. The effluent of the anoxic drains could be transferred through a constructed wetland for the subsequent removal of the contained metals; pH changes are contingent upon the buffering effect of high alkalinity that is usually caused by limestone addition [111].

6 Future prospect and conclusions

Several passive and active treatment systems currently exist for *in-situ* treatment of heavy metal contaminated water. This review focused on passive treatment technologies and the relative reactive processes that will determine further clarify the action mechanism of each reactive medium used for the immobilization of heavy metals. According to Hengen et al. [115], passive treatment generally had lower overall environmental impacts than active treatment technologies. The minimization of transport distance and using recycled materials or materials
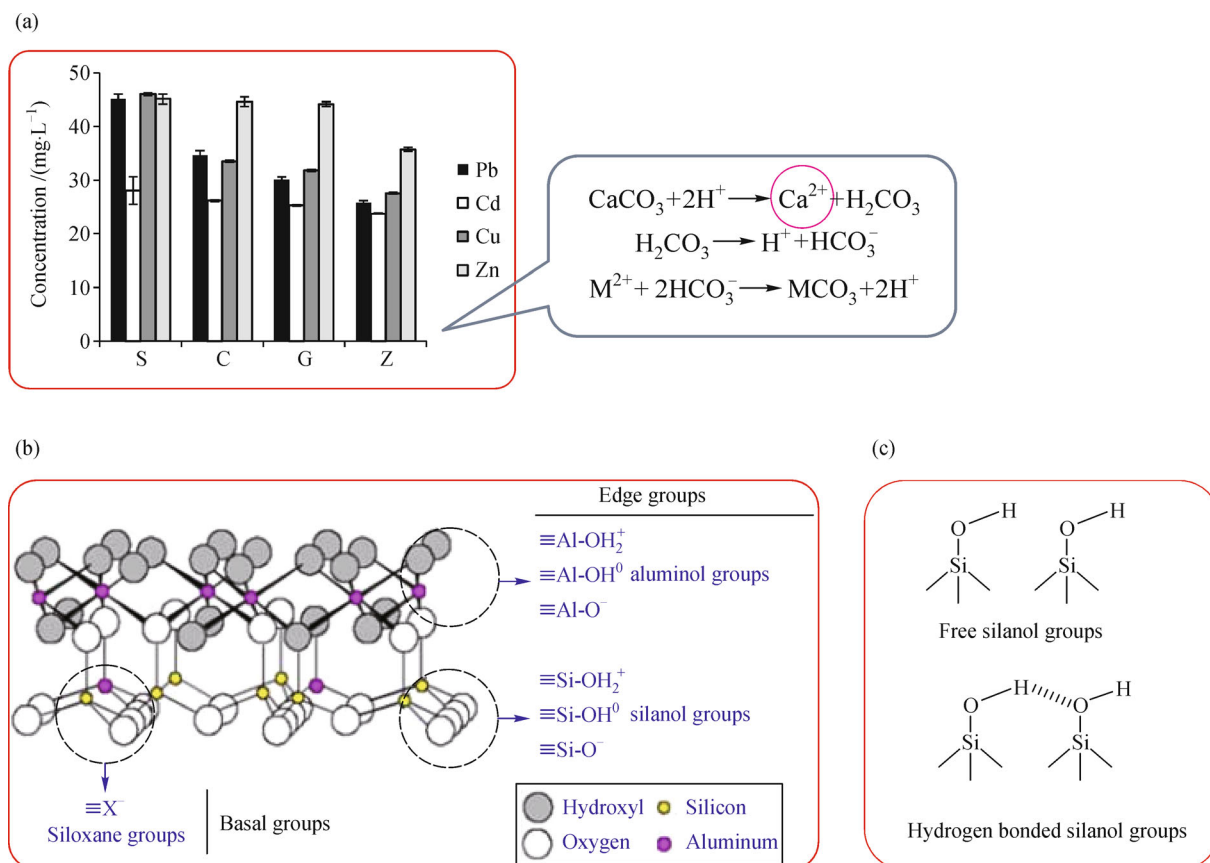

$$CaCO_3 + 2H^+ \longrightarrow Ca^{2+} + H_2CO_3$$
$$H_2CO_3 \longrightarrow H^+ + HCO_3^-$$
$$M^{2+} + 2HCO_3^- \longrightarrow MCO_3 + 2H^+$$

Fig. 6 Summary of the main removal mechanisms: (a) precipitation, (b) sorption and (c) chemisorption (modification after Gu and Evans [114]). S, C, G. and Z are limestone samples from Bizerte, Gafsa, Gabes and Gafsa suburbs locations, respectively. Bars represents the dissolved Ca concentration released in water solution.

requiring a lesser degree of processing provided enhanced environmental benefits. It is unlikely that large-scale mining operations would rely solely on passive treatment. Carbonate minerals are beneficial in the removal of heavy metals from water. Thus, limestone offers the potential for low cost effective media for treatment of heavy metals from waters. Adsorption and precipitation as metals oxide and probably as metals carbonate were two of the mechanisms that contributed to the removal of metals from their solution [29]. However, one should consider combination of different treatment methods to meet the optimal operational conditions for heavy metal removal from wastewater. The environmental impact of those treatment technologies needs to be considered. Like other natural minerals such as quartz, clays and clinoptilolite, natural limestone (i.e., calcite) is useful for various environmental applications as sorbents. Before their reuse, those minerals have to be purified. Therefore it is necessary to develop a new methodology to desorb the immobilized metal from natural geological materials (especially limestone), used as reactive medium in passive treatment technologies. Several parameters can be considered when looking for optimal conditions that will allow highly efficient the desorption process. Those parameters may include (1) extraction solution, (2) the ratio of the sample mass to the volume of the extracting solution and (3) pH of the suspension, among others. In addition, design considerations for effective heavy metal treatment is of primary importance. In-situ passive treatment technologies may involve cost-effective local materials (e.g., limestone).

This review have summarized most studies on the removal of heavy metals by a geological and naturally abundant material (i.e., limestone). Data from the current study showed that natural limestones were highly efficient in the removal of heavy metals (Pb, Cd, Cu, Co, Hg and Zn) from aqueous solutions. Chemisorption and precipitation were the main processes that influenced the removal rates. Limestone with high contents of impurities showed better removal efficiency. Kinetic data generally showed a high degree of fitness to the pseudo-second order models because of the interactive behavior of both metals and limestone samples during the reaction. The comparative studies suggest that natural limestone are promising geological materials that can be effectively used to remove toxic heavy metals from wastewater. An in-depth study of field treatment strategies is needed for sustainable *in-situ* treatment of heavy metal contaminated wastewater.

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