



Recovery of high-value metals from geothermal sites by biosorption and bioaccumulation



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HIGHLIGHTS

- Biosorption methods used for metal recovery from geothermal fluids are reviewed.
- The type of metals present in geothermal site from different locations is shown.
- The use of different biosorbents for the high-value metals recovery is summarized.
- Key aspects associated with metal recovery from geothermal fluids are discussed.

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ABSTRACT

Generation of geothermal energy is associated with a significant amount of geothermal fluids, which may be abundant in high-value metals, such as lithium, cesium, rubidium, and other precious and rare earth metals. The recovery of high-value metals from geothermal fluids would thus have both economic and environmental benefits. The conventional technologies applied to achieve this are mostly physicochemical, which may be energy intensive, pose the risk of secondary pollution whilst being inefficient in recovering metals from dilute solutions. Biological methods, based on biosorption or bioaccumulation, have recently emerged as alternative approaches, as they are more environmentally friendly, cost effective, and suitable for treating wastewater with dilute metal contents. This article provides a comprehensive review of the related biological technologies used to recover the high-value metals present in geothermal fluids as well as critical discussion on the key issues that are often used to evaluate the effectiveness of those methods.

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1. Introduction

Geothermal energy, the heat energy generated and accumulated deep within the Earth, is now used in many different ways. The most common form of direct utilization is the use of hydrothermal fluids for heating spaces, raising plants in greenhouses, agricultural drying, water heating at fish farms, melting snow, and some industrial heating processes (e.g., pasteurizing milk). The high temperature water heated by the natural heat flow below the Earth's surface or by volcanoes, can also be used to generate electricity (Bourcier et al., 2005). This form of geothermal energy

represents a clean and renewable energy resource. The International Geothermal Association (IGA) reported that, in 2010, there was a total installed capacity of 10,715 monitoring wells for geothermal power in 24 countries, capable of generating ca. 67,246 GWh of electricity. Similarly, the Geothermal Energy Association (GEA) noted that in 2010 geothermal electricity generation plants were in operation in 24 countries, with the direct utilization of geothermal energy occurring in about 70 countries. Several research groups have engaged in geothermal exploration and development activities for a number of years.

Geothermal fluids are water that is heated by the natural heat flow from the depths of the Earth. These fluids are potentially significant sources of valuable minerals and metals (Bourcier et al., 2005), some of which can be recovered for profit (Brown and Simmons, 2007). However, industrial utilizations of

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geothermal fluids seldom focus on the recovery of minerals/metals via cost-effective technologies. Among the various metals found in geothermal fluids, lithium (Li) is often used for the production of ceramics, glass and aluminum, and is also a vital component in rechargeable lithium batteries. Cesium (Cs) and rubidium (Ru) are used interchangeably in applications in thermionics, as oxygen getters in vacuum tubes, and alloys in photocells (Bourcier et al., 2005). Gold (Au), platinum (Pt), palladium (Pd) and silver are precious metals, widely used as catalysts in various industries, agriculture and medicine due to their specific physical and chemical characteristics (Ramesh et al., 2008). Rare-earth metals are used in lighting and optical applications, such as light-emitting diodes (LEDs), lasers, and electronic video displays, enabling color and light adjustment, miniaturization of microelectronics parts, and compliance with environmental and energy-efficient standards (Song et al., 2013).

Some efforts have been made to develop recovery technologies for these metals from geothermal fluids (Bourcier et al., 2005), including physical, chemical and biological approaches. Although various treatments such as chemical precipitation, chemical coagulation, electrochemical technologies, ion exchange, and membrane technologies can be employed to recover high-value metals from liquid solution, they have their inherent advantages and limitations in application. For example, chemical precipitation is widely used for metal recovery from inorganic liquid solutions. The metals can be easily precipitate by the addition of precipitant agents or by pH adjustment, but this process requires a large amount of chemicals, thereby producing large amounts of sludge. Using electrochemical technologies, ion exchange and membrane technologies can obtain high efficiency in metal recovery with high metal selectivity, lower chemical consumption, but the costs for the operation and facilities maintenance are higher. On the other hand, biological approaches (such as biosorption) may not be as efficient as some of the physicochemical methods, but they are more environmentally friendly, less polluted, and may have excellent performance when recovering metal ions from very dilute solutions (Das, 2010), which is usually the case for geothermal fluids. Therefore, this review will focus on eco-friendly technology related to recovering high-value metals from geothermal sites, with the emphasis on biological approaches.

2. Types and concentrations of the high-value metals present in geothermal fluids from different sites

Geothermal fluids are heated as they flow through hot rock bodies, interacting with the host rock and becoming increasingly saturated with various minerals. The chemical composition of geothermal fluids is thus determined by their origin, the hot rocks they

have interacted with, and the temperature and pH of the fluids. The literature shows that geothermal fluids contain significant concentrations of potentially valuable metals, including lithium (Li), cesium (Cs), rubidium (Rb), precious metals such as gold (Au), platinum (Pt), palladium (Pd), silver (Ag), and rare earth metals such as scandium (Sc), yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu) (Harrar and Raber, 1984; Hedenquist and Lowenstern, 1994; Bourcier et al., 2005; Brown and Simmons, 2003; Brown and Simmons, 2007; Michard, 1989). As shown in Table 1A, the concentration of three major metals found in the geothermal sites (namely, Li, Cs, and Rb) varies significantly depending on the geographical location. Several countries (e.g., New Zealand, Mexico, California, Italy, Costa Rica, Iceland, and Turkmenistan) regularly monitor the concentration of Li, Cs, and Ru. There is a wide range in the concentrations of Li, Cs, and Ru, which are 0.3–219 mg/l, 0.02–39 mg/l, and 0.04–170 mg/l, respectively. For example, in the Salton Sea, California, the total concentrations of Li, Cs, and Ru are 194, 20, and 170 mg/l, respectively, which are markedly higher than those found in other locations in the world (Table 1A). This shows the potential use of developing recovery technology for the considerable amount of valuable metals present at some geothermal sites.

Precious metals (e.g., Au, Pt, Pd and Ag) can usually be extracted from geothermal fluids, which are related to the process of subduction zone magmatism in modern and ancient volcanic arcs (Hedenquist and Lowenstern, 1994; Bourcier et al., 2005). As shown in Table 1B, the concentration of precious metals in the geothermal fluids at different locations varies due to the geological characteristics of these sites. At sites in New Zealand, the USA (California), and Iceland, the concentrations of gold (Au), platinum (Pt), palladium (Pd) and silver (Ag) were in the range of 0.1–80 µg/l, 0.26–20 µg/l, and 2–20 µg/l, and 0.4–2400 µg/l respectively. In particular, the Taupo Volcanic Zone in New Zealand has been found to have higher total concentrations of Au, Pt, Pd and Ag than other areas (Table 1B). More specifically, as Brown and Simmons (2003) noted, the concentrations of Au and Ag in the Taupo Volcanic Zone are in the ranges of 0.1–23 µg/l and 3–2400 µg/l, respectively (Table 1B).

While many rare earth metals (i.e., Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) are also found in geothermal sites, there is a lack of quantitative data on these, although Table 1C gives some figures for Ce, Nd, Sm, Eu, Gd, Dy, Er, and Yb (Michard, 1989). Unfortunately, only three regions have published data on this issue, namely California, New Mexico, and Italy. Table 1C shows that the Salton Sea in California has higher concentrations of rare earth metals than the other sites, with the levels for

Table 1A
Lithium (Li), cesium (Cs) and rubidium (Rb) concentrations present in different geothermal sites.

Country (location)	Lithium (Li) conc. (mg/l)	Cesium (Cs) conc. (mg/l)	Rubidium (Rb) conc. (mg/l)	References
New Zealand (Wairakei)	13.2	2.5	2.9	Ellis and Mahon (1977)
New Zealand (Broadlands)	11.7	1.7	2.2	
Iceland (Hvergerdi)	0.3	0.02	0.04	
Costa Rica (Miravalles)	11.7	1.7	2.2	Vaca et al. (1989)
Mexico (Cerro Prieto)	27	39	11	Mercado and Hurtado (1992)
Italy (Mote Amiata)	21.9	0.7	2.1	Vitolo and Cialdella (1995)
USA (Salton Sea, California)	194	20	170	McKibben and Hardie (1997)
New Zealand (North Island)	2.0–21.1	0.1–3.5	0.3–3.5	Hirner et al. (1998)
Indonesia (Salak)	17	4.5	5	Gallup (1998)
Mexico (Los Azudres)	0.1–65	0–18	0–10	González-Partida et al. (2005)
Mexico (Los Azudres)	0–6.9	0–1.5	0.05–3.0	
USA (Brawley, California)	219	19	67	Klein and Gaines (2012)
Turkmenistan (Cheleken Peninsula)	215	14	NA	

NA: not available.

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