Removal of arsenic from aqueous solution by adsorption on Leonardite

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HIGHLIGHTS

- Leonardite, a waste product in coal mines was converted to low-cost adsorbent.
- Leonardite char was prepared for use to remove arsenic from aqueous solution.
- The Leonardite char at 450 °C was successfully used for the removal of arsenic ions.
- There is no leaching of toxic metals to water after the adsorption.

ARTICLE INFO

ABSTRACT

The present investigation deals with the uptake of As(III) and As(V) ions from aqueous solution at 25 °C by a new prepared Leonardite char carbonized at 450 °C. Arsenic adsorption experiments were carried out in batch systems to determine the amount of As(III) or As(V) adsorbed as a function of particle sizes of adsorbent, contact time and solution pH per fixed As concentration. In this study, the 75 μm size of the Leonardite char was chosen since it had the maximum removal of As(III), whereas the removal of As(V) was close to 100%. The optimum equilibrium contact time and pH used for adsorption of both As(III) and As(V) were 3 h and pH 7. The adsorption data showed good fit to both Langmuir and Freundlich isotherm models. The Langmuir monolayer capacities for As(III) and As(V) were estimated to be 4.46 and 8.40 mg per gram of Leonardite char, respectively. The effect of SO_4^{2-}, NO_3^- and Cl^- as competing anions on As(III) and As(V) removal was also investigated at pH 7. The removal of arsenic due to these anions decreased in the following order: $SO_4^{2-} > NO_3^- > Cl^-$. Finally, the Leonardite char was applied successfully for arsenic removal from ground water samples.

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1. Introduction

Arsenic contamination in drinking ground water caused by industrial effluents and some agricultural activities is a worldwide problem. Arsenic is potentially toxic to humans as chronic effects for a long times intake food and drinking water with arsenic contamination. The chronic effects include skin diseases, cancer, neurological and so on [1]. Although, arsenic is known to be essential for life in small amounts, it becomes toxics for humans when ingested in large amounts (lethal dose 50–340 mg). Arsenic is a contaminant which represents a potential risk for human being since it can enter the food chain through plants or water. Arsenic pollution from natural sources was reported in China, Taiwan, India, Bangla-

desh, USA, Thailand, etc. [2–4]. In 1958 the world health organization (WHO) recommended a maximum allowable concentration of 0.2 mg/L for arsenic in drinking water. This value was lowered to 0.05 mg/L in the first edition of the *Guidelines for Drinking-water Quality* published in 1984. A provisional guideline value for arsenic was set in the 1993 Guidelines at the practical quantification limit of 0.01 mg/L, based on concern regarding its carcinogenicity in humans [5].

In surface water, arsenic is mostly present in two forms: arsenate (As(V)) and arsenite (As(III)). The stable form which dominates in surface water is arsenate while arsenite exists in anaerobic underground water [6]. The toxicity of arsenic depends on its oxidation and its various forms, i.e. the As(III) is more toxic than As(V), and the organic arsenic is less toxic than inorganic forms [7]. One of the arsenic contamination problems in Thailand lately was from metal and coal mining operation that exposed waste sulfide minerals and found to be highly acidic and contained

arsenic in mine drainage. The major arsenic problems in Thailand involve arsenic contamination of soil surface water and ground water at Ron Phibun District, Nakhon Sri Thammarat Province due to tin ore dressing plants are set to remove arsenic contents in ore during the last century. The typically large amounts of arsenic are released and dumped as waste [8]. In the mines, arsenic is a widely constituents of many types of sulfide minerals, realgar (AsS), arsenopyrite (FaAsS), orpiment (As$_2$O$_3$), etc., which arsenopyrite is the most common arsenic mineral. However, these minerals are relatively rare in the natural environment. The oxidation of arsenopyrite (FeAsS) in mine wastes is the common mechanism that distributes arsenic into the environment. In the metal mines, the greatest concentrations of these arsenic minerals occur in mineralized areas and are found in close association with the transition metals as well as Cd, Pb, Ag, Au, Sb, P, W and Mo. The discharge of mining drainage water containing arsenic contributes to its dispersion in the environment [9]. The resulting contamination of surface waters, groundwater and sediments is a matter of great public concern due to the deleterious effects of arsenic on human health. These contamination waters require neutralization and arsenic removal before being released to the environmental.

A range of different methods can be used for the removal of arsenic from surface water and patents protect a number of these technologies [10]. The most commonly used technologies for removing arsenic from aqueous solution are ion exchange resin, adsorption on activated alumina, co-precipitation with iron or alum, reverse osmosis, membrane filtration, modified coagulation/filtration, and enhanced lime softening.

Anion exchange units operate using the same principle as a water softener. In this case the arsenic is exchanged for chloride. There are several varieties of adsorptive media available including activated alumina (AA) and other types of media including some with proprietary ingredients. Activated alumina and most of the other adsorptive media will either not remove As(III) or are not very efficient at the removal of As(III) [11]. Pre-oxidation of As(III) to As(V) is always preferred to the removal efficiency. The efficiency of removal is dependent on the pH of the water. Reverse osmosis (RO) is generally installed as a point-of-use treatment system and usually requires pre-filtration to remove sand and grit that might foul the RO membrane. However, cost effective, straightforward methods are necessary for the people in developing countries, particularly technologies utilizing materials that are widely available [12–15].

Consequently attempts have been made in order to find new simple efficient techniques. For dilute concentrations, adsorption is one of the suitable methods for removal of arsenic. Then, adsorption is considered to be a relatively simple, efficient and low-cost arsenic removal technique, especially convenient for application in rural areas and has the potential for regeneration [16]. A better knowledge of arsenic immobilization mechanism in experiment systems is necessary to develop remediation processes. Due to the difference in sorption efficiency, and in toxicity between As(III) and As(V) remediation processes often suggest immobilizing arsenic in its highest oxidation [17]. The influence of pH upon sorption depends upon the adsorbent material and chemical from of arsenic with maxima exhibited in the pH range of 3–9. The naturally occurring ores (bituminous, coal, lignite, illite, kaolinite, etc.) as adsorbent for arsenic removal have been used by some researchers as extensively as precipitant in adsorption technique [18–20]. The retention of arsenic on clay is dependent on the quantity and type of clay. In general soil with higher clay content retains more arsenic than soils with lower clay content. The order for the sorption of arsenic on clay type is kaolinite > vermiculite > montmorillonite [21]. However most of these adsorbents entail several problems in term of efficiency and cost. Several investigators have reported adsorption methods for the removal of arsenic from water

samples, however, there is still a need to develop effective field deployable adsorbents and delivery systems.

Leonardite is a special low rank coal. It derives either from lignite that has undergone oxidation during surface exposure or it represents sediments enriched in humic substance [22]. Leonardite contains large amounts of humic substances which has a complex in properties from carboxylic and hydroxylic sites of functional groups in humic substances and various inorganic minerals. The inorganic minerals, approximate present shale group (illite, muscovite, montmorillonite), the kaolin group (kaolonite–aluminium silicate), etc. [23,24]. The ash content major is clay varied from mine but is usually 15–70% on dry basis [25,26]. It derives from lignite that has under oxidation during surface expose, or represents sediment enrichment of humic acids which were leached from overlain lignite [27]. In generally, natural Leonardite has a wide range of compositions. For example, the humic substance can range from 20% to 70% or more. It occurs in conjunction with deposited of lignite and usually obtained as byproduct of the mining [28,29]. Kalaitzidis et al. [22] investigated the details of the minerals in Greek Leonardites and showed that dominant phases are clay minerals in the form of illite and mixed clay-layers of illite–montmorillonite. Suarez-Ruiz et al. [23] found that the main clay in Portuguese Leonardite identified was kaolinite, followed by illite, montmorillonite and illite–montmorillonite. In Knudson [31] study, Leonardite char adsorbents could be used to adsorb mercury vapour, sulfur dioxide and nitric oxide gases. Because, in particular, Leonardite has a very high oxygen (carboxylic group) content in comparison with other lignite type materials, then, in carbonization process, carboxylic acid group in Leonardite earlier liberated carbon dioxide. The deliberation of carbon dioxide provides a more porous structure and also opens channels for remaining mineral material (clays).

From previous studies, the sorption activity of clays encompasses at least three parameters, namely, surface areas, pore distribution, and surface acidity/basicity. The presence of minerals matter in Leonardite can affect activation and subsequent sorption and desorption processes. Many researchers studied Leonardite or Leonardite char as low cost adsorbents for removal cations in water or gas [32–34]. Lignite mines in Lampang province which is in the northern region of Thailand, is mined in open pits and used for power generation of electricity. This Leonardite is in the benches outcrop at the lignite open pits. In the mine, a low grade Leonardite was dumped on-site storage in lignite mine and made problem to the surrounding area and have a negative impact on aquatic and terrestrial systems through runoff. This low grade Leonardite was identified to contain lower than 15% of humic acid and high mineral matter. The aim of this present work concentrates on investigating Leonardite char as a potential adsorbent from coal mine waste for removing arsenic which is low-cost, easy to operate household system and without any chemical pretreatment from contaminated surface water at a relatively low level. The adsorption parameters namely, activation temperature, effect of particle sizes, shaking time, adsorption isotherm and effect of some anions have been studied of both As(III) and As(V) in spiked deionizer water. In this work, the details of raw materials before and after activated were studied for removal of arsenic in water. Finally arsenic in-spiked tap water and contaminated surface waters without any pretreatment was examined. Therefore, this research will be opened for potentially economic environmental protection and their advanced application.

2. Materials and methods

2.1. Reagents

All chemicals used were of analytical reagent grade and deionized water was used for preparation of all solutions. A 1000 mg/L