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Research article

Stabilization of arsenic and fluoride bearing spent adsorbent in clay bricks: Preparation, characterization and leaching studies

Vineet Kumar Rathore, Prasenjit Mondal*

Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, 247667, India

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ABSTRACT

The presence of arsenic and fluoride in groundwater has been observed throughout the world. Many technologies have been developed by various research groups in order to tackle this problem. Adsorption has emerged as one of the best possible technique for the removal of arsenic, fluoride and many other pollutants from drinking water. Although a considerable amount of work has been published on the adsorptive removal of arsenic and fluoride, the area related to the management of spent adsorbent is not well explored. Present paper deals with the adsorptive removal of arsenic and fluoride from aqueous solution by three different types of adsorbents, namely, thermally treated laterite (TTL), acid-base treated laterite (ABTL) and aluminum oxide/hydroxide nanoparticles (AHNP). Under the experimental conditions in batch operation, the adsorption capacities of TTL, ABLT and AHNP for arsenic are found to be 6.43 μg/g, 9.25 μg/g and 48.5 μg/g respectively, whereas for fluoride, these values are found as 0.21 mg/g, 0.85 mg/g and 4.65 mg/g respectively. After adsorption, the spent adsorbents have been stabilized in the form of clay bricks. The effects of spent adsorbent concentration on the properties of bricks and their leaching properties are investigated. The bricks have been tested for various properties like density, percentage water absorption, shrinkage, compressive strength and efflorescence. The maximum values of density and shrinkage of the bricks formed are found as 2.3 g/cm^3 and 10.2%, whereas the percentage water absorption and compressive strength of the bricks are found between 11 and 14% and 35 to 150 kgf/cm^2 respectively. All the test results are in accordance with the criteria set by Indian Standards. The leaching test of arsenic and fluoride from the bricks reveals that their maximum values in leachate are 510 μg/L and 2.1 mg/L respectively, which are below the permissible limits of USEPA standards.

1. Introduction

Water is one of the most basic necessities for living beings. Natural surface water or groundwater are known to contain many dissolved minerals in minor quantities, but the presence of these minerals above certain level can be very harmful to human health and can result in many kinds of diseases, deformations and malfunctioning of human body. According to World Health Organization (WHO), approximately 748 million people globally are forced to consume unsafe/contaminated drinking water resulting in very high rates of morbidity and mortality (WHO, 2014).

Groundwater and surface water may be contaminated due to excess amount of organic substances, inorganic substances, radioactive materials or heavy metals. As far as inorganic materials are concerned, arsenic and fluoride are considered as two of the most harmful pollutants present in drinking water and affecting human health most severely (Thompson et al., 2007). Presence of arsenic in excess quantities in groundwater are posing lethal threats to millions of people around the globe especially in countries like India, China, Bangladesh, Vietnam, Pakistan, USA and many others. Further, Bangladesh and India have the large number of population living in the areas most severely affected by arsenic contamination. On the other hand, the problem of fluoride contaminated groundwater is also prevalent in countries like India, China, Mexico, Pakistan and Egypt. In many parts of the world both arsenic and fluoride are simultaneously available in groundwater (Jadhav et al., 2015). Recently it has been reported that the groundwater of a large area of Rajnandgaon District of Chhattisgarh, India, is contaminated with both arsenic and fluoride (Rathore et al., 2016). Various techniques like ion exchange, reverse osmosis, chemical reduction, electrodialysis, distillation, biological processes, adsorption (Jagtap et al., 2012; Choong et al., 2007) and other processes have been

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* Corresponding author.
E-mail addresses: vineetrathore@gmail.com (V.K. Rathore), mondal2001@gmail.com (P. Mondal).

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investigated by different researchers to remove arsenic and fluoride from water. Amongst these techniques, adsorption has gained more interest due to low initial cost, low energy requirement, simplicity of design and possibility of reusing the spent adsorbent via regeneration. Since the economic conditions of the common people of most of the suffering countries are poor, extensive research is going on to produce low cost adsorbents including different types of natural clay soils. However, one of the main disadvantages of adsorption process is the management of spent adsorbents.

A large number of work is available on the development of adsorbent/low cost adsorbents from different routes for the removal of arsenic and fluoride (Jagtap et al., 2012; Choong et al., 2007). Some literature are also available on the simultaneous removal of arsenic and fluoride (Tang et al., 2010; Zhang et al., 2010; Jing et al., 2012; Deng and Yu, 2012). However, in these work efforts are mainly concentrated on the treatment of arsenic and fluoride contaminated groundwater. It is also reported in many of the literature that the spent adsorbent can be reused several times by the help of regeneration process, however the limitation of the regeneration is that it subsequently decreases the adsorption capacity of the adsorbent with every cycle of usage and the adsorbent needs to be discarded after certain number of cycles. Further, regeneration also creates some pollutants. The regeneration step can be neglected in the case of low cost adsorbents as they are mostly made from such raw materials that have almost no commercial value and their regeneration can be even more costly that the actual cost of the production. Thus, the concerns related to the disposal of spent adsorbent through regeneration still remain unanswered. Apparently, it seems that the solidification of spent adsorbent derived from low cost material may be an attractive route for its management. In reality, spent adsorbent management issue is not well studied, which is very important for the applicability of the adsorbents. Frequently, it has been observed that the spent adsorbent/sludge is disposed on ground leading to possible contamination of surface water and groundwater sources through seepage (Rouf and Hossain, 2003). Very few literature are available on the solidification/stabilization (S/S) of arsenic bearing spent adsorbent like activated alumina, iron oxide coated cement, zeolite or perlite supported magnetite, MgO etc. (Singh and Pant, 2006; Kundu and Gupta, 2008; Verbinnen et al., 2015; Tresintsi et al., 2014), however, these reports do not provide any information about its applicability for fluoride bearing spent adsorbent. The use of clay as a S/S material has also been reported in some places for the disposal of spent adsorbent. Rouf and Hossain 2003 reported that spent adsorbent containing arsenic can be mixed with iron slag and can be used for brick manufacturing. Further, they also indicated that the firing temperature and proportion of arsenic bearing iron slag in clay are the two main parameters controlling the leaching back of arsenic and brick quality. The S/S technique for disposal of fluoride bearing waste is also very poorly studied. Ponsot et al., 2013 performed the stabilization of high fluorine containing industrial waste in the form of sintered glass. Ismail and AbdelKareem 2015 demonstrated the use of waste animal bones for the defluoridation of water followed by reusing of fluoride bearing bones in concrete. As per the knowledge of the authors, there is no exhaustive report available on the solidification/stabilization of spent adsorbent containing both arsenic and fluoride. Recently one article has been published where solidification has been tested under single set of conditions only for the management of laterite based spent adsorbent, it does not deals with AHNP (Rathore et al., 2016). The present paper focuses on the application of S/S technique for the disposal of both arsenic and fluoride bearing spent adsorbent. For this purpose three different types of spent adsorbents obtained from the adsorption process are blended in different proportion with clay and bricks are made of it. The effect of sintering temperature is also studied and physical properties of the bricks are tested in order to evaluate the suitability of the bricks as building material. Further, leaching tests are conducted to evaluate the environmental concerns related to the utilization of the spent adsorbents as fillers in the clay bricks.

2. Materials and methods

2.1. Chemicals and reagents

All the chemicals used were of analytical grade and were used as supplied without any further processing. Millipore water (resistivity = 18.2 MΩ cm at 25 °C) was used in the entire study for the preparation of reagents. Distilled water was used for manufacturing the bricks with clay and spent adsorbents. Raw laterite (RL) was procured from Burdwan district, West Bengal, India (GPS coordinates: 23.25° N, 87.85° E). For electrolysis, aluminum plates were purchased from local market (99% pure aluminum, manufactured by Hindalco industries limited, India), cleaned by soaking them in 0.1 M HNO_3 for 1 h and polished with sand paper to remove the galvanizing coating over it. Stock arsenic and fluoride solutions of 1000 mg/L concentration was made by adding 1.734 g of $NaAsO_2$ and 2.21 g of NaF in one liter of Millipore water respectively and appropriate dilutions were made to make solutions of desired concentration.

2.2. Preparation of adsorbents

Thermally treated laterite (TTL): Raw laterite soil was cleaned, crushed and washed so as to remove clay and other organic matters present in the soil. Now, it was sieved to obtain particles of 1–1.7 mm size and kept in hot air oven at 105 °C for 24 h so as to remove all the moisture present in it and finally used for adsorption.

Acid-base treated laterite (ABTL): For producing ABTL, TTL was subjected to acid treatment with 2 N HCl (approximately 4 times w/v) at 70 °C for 3 h to leach out Fe, Al and Si ions in the solution. Excess amount of HCl (approximately 70%) was distilled by heating it up to 110 °C followed by addition of distilled water (approximately 3 times the volume of HCl remaining). Now for base treatment, 4 N NaOH was added to it and the pH was adjusted between 6.5 and 8.5. Finally the mixture was kept undisturbed for 24 h so as to allow the hydrolyzed mass (containing oxy hydroxides of iron and aluminum) to settle over the laterite. Now the upper layer having clear liquid was decanted from the top and the mixture was again washed with distilled water till the water is free from chloride ions (Maiti et al., 2010). Residual chloride in wash water was determined by titrating it with $AgNO_3$ in presence of potassium chromate with phenolphthalein as indicator. This treatment was performed in order to obtain higher amount of iron and aluminum hydroxides over its surface which facilitates the adsorption of both arsenic and fluoride.

Aluminum oxide/hydroxide nanoparticles (AHNP): For preparing AHNP, electrolysis was carried out in distilled water with aluminum plates (size 10 cm × 10 cm x 0.1 cm) as anode and cathode and NaCl as electrolyte. DC current was supplied with a current density of 196 A/m^2 to this system to produce the precipitates of aluminum hydroxide collected at the bottom of the reactor. These precipitates were washed several times with deionized water to remove the traces of electrolyte added during the electrolysis process. The precipitates were dried at 105 °C for 24 h and crushed to obtain particles of desired size and used for adsorption. Finally the precipitates were subjected to calcination in electric furnace at 700 °C to partially convert them into alumina.