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Removal of arsenic from groundwater by adsorption onto an acidified laterite by-product

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HIGHLIGHTS

- Acidified Laterite by Sulphuric Acid (ALS) is an efficient and low cost As sorbent.
- As(V) adsorption capacity of ALS is 3 times higher than that of raw laterite.
- Sulphate chemical groups are the main contributors in improving As(V) adsorption.
- The by-product ALS loses his performances upon regeneration.

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ABSTRACT

A low cost by-product material namely Sulphuric acid Acidified Laterite (ALS), generated during the production of Ferric Aluminium Sulphate (FAS) by acid leaching treatment, was employed as an adsorbent for the removal of arsenic from aqueous solution. In addition raw laterite was used for comparison purposes in the arsenic adsorption experiments. The raw and Acidified Laterite were chemically and physically characterised (elemental analysis, surface chemistry, pore texture parameters, PZC, and SEM observation). Arsenic adsorption batch and kinetics experiments were undertaken, and process parameters such as; pH, dose, particle size, and initial arsenic concentration were investigated. Adsorption isotherm and kinetics data were modelled using the pseudo first and pseudo second order kinetic models. The maximum loading capacities of raw laterite for arsenite and arsenate ions were 127.8 $\mu g\ g^{-1}$ and 301.2 $\mu g\ g^{-1}$, respectively. By contrast, the maximum loading capacities of Acidified Laterite for arsenite and arsenate ions are 171.7 $\mu g\ g^{-1}$ and 923.6 $\mu g\ g^{-1}$, respectively. It was found that the higher surface area and presence of residual sulphate surface groups on the ALS explained the increase in the adsorption capacities. Overall the results indicated that the laterite adsorbents proved to be effective materials for the treatment of arsenic-bearing aqueous solutions.

1. Introduction

The contamination of groundwater by arsenic has been recognized as a severe health issue. Contaminated aquifers are present in many areas of the world but especially in Bangladesh and West Bengal, India; where many wells have been identified as unsafe for consumption [1]. Chronic exposition to arsenic contaminated water can cause serious diseases like dermal pigments, skin and lung cancer. The World Health Organization lowered the drinking guideline from 50 ppb to 10 ppb in 1993 to encourage public organizations to confront this mass contamination. Since then different countries have been using the guideline limit as national standard while others still use the previous limit of 50 ppb. In the coming years the arsenic groundwater consumption is estimated to directly cause over 6500 deaths a year and over 2.5 million people may develop arsenicosis in the next 50 years [2].

These public health consequences show the urgent need for efficient and low cost arsenic removal systems. The ideal system would also need to be low maintenance and avoid the use of electricity; as most of the communities affected by groundwater arsenic contamination are rural areas. A review by Jain and Singh [3] presents the main techniques employed in removing arsenic from groundwater and shows the predominance of adsorption processes.

Adsorption systems use the affinity of different materials to remove soluble pollutants from an aqueous phase to the surface of a solid phase. Advantages of adsorption processes over other techniques are: its low running cost, the absence of electrical supply and its low maintenance requirements. Combined with their

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capacity to remove arsenic to very low levels and their high removal capacity, adsorbent materials are reliable media in treating arsenic. The extended review of arsenic adsorbents by Mohan and Pittman, [4] shows the considerable interest within the scientific community to develop low cost, high capacity adsorbents for arsenic removal.

In the development of efficient arsenic adsorbents, a wide range of materials have been used by a number of researchers [4]. Al, Fe, Ti and in a smaller proportion Mn based materials have shown very high removal capacity toward arsenic. Activated alumina, granular ferric hydroxide and granular titanium oxides are existing commercial arsenic adsorbents based on these metal oxides or hydroxides. The combination of various metal oxides and hydroxides, the development of coated materials or even 3D structured materials have also been explored for arsenic removal [5–11].

In this study the effectiveness of a low cost arsenic adsorbent, a laterite by-product, is presented. This material is derived from the processing of Ferric Aluminium Sulphate (FAS); where sulphuric acid is used to leach out iron and aluminium in order to produce a coagulant for the wastewater industry. This material is abbreviated to ALS for Sulphuric acid Acidified Laterite. The performance of this material in removing arsenic from the aqueous phase is compared to un-acidified, raw laterite.

Laterite is a naturally occurring ore composed of iron, aluminium, silica and titanium oxides. Previous studies showed the effectiveness of this ore in removing phosphate when used in wetland systems [12]. Several studies have presented data on the use of laterite ores in removing arsenic [13–16]. It is worth noting that laterite ores are widely present around the globe and are available in countries facing arsenic groundwater contamination [13]. Laterite ores possess a large variability in their composition and physical properties; depending on the mining area, but also within the mine itself, where different layers can be found [17]. The raw laterite used in this study, contains ∼5% of titanium oxides by weight, which are not commonly found in laterite ores.

The laterite by-product, ALS, is currently regarded as waste from companies producing FAS. These industrial ore by-products have been generally regarded as good candidates for adsorbent media. Red mud, which is produced during the alkali treatment of bauxite in the aluminium production industry, has also been studied in the removal of arsenic [18] or phosphate [19,20]. The possibility to use ore, by-products or wastes generated in different industrial sectors is a general trend in developing low cost adsorbents for any pollutant of interest [21–23].

However, a few studies investigating the use of modified laterite ore as adsorbents have been reported in the literature. The work by Maiti et al. [24] presents the production of an Acidified Laterite, which is a material produced by a two-step process. During the synthesis, the material produced is the Acidified Laterite without any metal salts produced for the wastewater industry.

In the present study, the laterite by-product ALS is generated at a negligible price as it allows the production of FAS, a valuable coagulant. The possibility to use the ALS as an arsenic adsorbent relies in its adsorption capacity and its ability to produce water with a very low level of dissolved arsenic.

2. Materials and methods

2.1. Laterite samples

Two different samples were used in this study, a raw Laterite mined in Ballymena (NI) by Clinty Chemicals Ltd. and an Acidified Laterite by Sulphuric acid (ALS) processed by Stevenson Quarries Ltd in the same location. The laterite ore is used to compare the improvement of the adsorption capacities of ALS over the raw material. The ALS sample is a by-product generated during the production of Ferric Aluminium Sulphate (FAS). The laterite ore is treated with sulphuric acid at an elevated temperature. During the process the concentrated sulphuric acid is diluted with water; making the solution boil, i.e., an exothermic reaction. Extra heat is provided by an external source (steam) to keep the solution at 70 °C. The sulphuric acid solution is then put into contact with the laterite ore for a short period of time in a batchwise process. The FAS solution composition varies depending of the laterite ore used initially. Depending on the final product requirements extra iron or aluminium salts are added and pH is adjusted. The two samples were dried at 60 °C for 24 h, sieved and stored before being used in the adsorption studies. Three different particle size fractions were used in this study: 1000–1180 μm; 500–600 μm and powder with particle size lower than 75 μm.

2.2. Adsorbents characterization

2.2.1. XRF (X-ray fluorescence analysis)

The chemical composition of ALS and laterite samples was analysed by XRF analysis using an Axios Advanced analyser from PANalytical. The fusion beads method was used to prepare the samples. Samples and flux were cast into fused beads at 950 °C.

2.2.2. BET (Brunauer–Emmett–Teller)

BET surface area, porosity and average pore size were measured using a Nova 4200e surface area and pore size analyser from Quantachrome Instruments. Samples were degassed for 16 h at 60 °C under vacuum and analysed at 77 K under nitrogen with 31 adsorption points and 19 desorption points.

2.2.3. PZC (point of zero charge)

The point of zero charge of the samples was analysed using the mass titration method. The simplified method to measure mixed oxides PZC presented by Reymond and Kolenda [25] was followed. The ALS sample, treated with H_2SO_4, was also rinsed and its point of zero charge measured again. The following washing procedure was used: 50 g of ALS with particle size of 75–180 μm, was stirred in distilled water maintained at pH 7 with NaOH for 16 h, then rinsed with deionised water and dried at 60 °C.

2.2.4. SEM (Scanning Electron Microscope)

The surface structure topography of laterite samples was evaluated by an EOL JSM-6500F field emission Scanning Electron Microscope. Probe current was set at 2 A, external voltage between 2–3 kV and emission current at 71 μA.

2.2.5. FTIR (Fourier Transformation Infra-Red Spectrophotometry)

Samples were analysed by FTIR using the KBr tableting method. A PerkinElmer Spectrum One FT-IR spectrometer instrument was used. The ALS and laterite samples were analysed before arsenic adsorption experiments and after equilibrium. Samples having been in contact with solutions of 1 and 10 ppm of As(III) and As(V) at pH 7 for 72 h were selected. The ALS washed sample was also analysed by FTIR.

2.3. Arsenic removal experiments

2.3.1. Chemicals

Chemicals used were of reagent grade or higher and received from Sigma Aldrich. Deionised water obtained by an ELGA Maxima ultrapure water system and having a resistivity of 18.2 MΩ cm was used in all solutions. Arsenate and arsenite stock solutions of 100 ppm were produced by dissolving the appropriate amount of $AsHNa_2O_4{\cdot}7H_2O$ and $NaAsO_2$ respectively and used for further dilutions. To minimize the effect of pH changes onto adsorption,