

## Conference Paper

# Obtaining of Maghemite Containing Red Mud for Effective As(V) Adsorption

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## Abstract

This paper describes the studies of the use of red muds as adsorbents for cleaning solutions from As(V). The red mud is a waste that contains a large amount of iron oxides and hydroxides, which are excellent adsorbents of arsenic, especially those possessing magnetic properties and large specific surface area. The purpose of the experiment was to study the possibility of obtaining an effective adsorbent by direct extraction of alumina from bauxite using the caustic alkali fusion method and optimization of the process. The main iron-containing phase of the red muds obtained by fusing bauxite with caustic alkali was maghemite, which has a large specific surface area. Arsenic adsorption experiments were carried out using red muds obtained through bauxite alkali fusing at different temperatures and time of fusion, as well as the mass ratio of caustic alkali to bauxite. The red muds obtained by fusing bauxite with caustic alkali at 400° C and NaOH to bauxite mass ration 1.5 within 70 minutes have the highest effectiveness removing arsenic. Their As(V) uptake capacity was over than 37 mg/g.

**Keywords:** red mud, maghemite, nanoparticles, As(V) adsorption, optimization

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Published: 31 December 2020

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Selection and Peer-review under the responsibility of the TECHNOGEN-2019 Conference Committee.

## 1. Introduction

To date, red mud (sludge from alumina industry) represent non-recyclable waste generated after processing of bauxite [1] occupying large areas of land, at the same time the red mud contains a big amount of valuable components. The most interesting of them are rare earth metals, aluminum, iron and titanium [2, 3].

One of the useful properties of red mud is the ability to adsorb harmful impurities from gases and liquids: sulfur oxides [4], heavy non-ferrous metals [5–7] and ions of weak acids, the most harmful of which are arsenic and antimony compounds [8]. Arsenic is one of the most dangerous elements found in a large number of natural compounds [9, 10]. In many countries, most notably Asia, its content in groundwater exceeds threshold values [11–13]. The most polluted arsenic regions are Bangladesh and its neighboring Indian state, where more than 100 million people are potentially poisoned by arsenic through water wells; experts say more than 21% of deaths in this region are caused

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by arsenic poisoning [14]. Large amounts of arsenic in groundwater can be found in Greece, Czech Republic, US and Canada [15].

Mines and sulfide mineralization sites are the main sources of arsenic, with large amounts released by enterprises that store waste in dams without proper pre-treatment. In the Ural region of Russia, the main source of arsenic is the copper industry that processes arsenic-containing concentrates [16]. Their pyro- and hydrometallurgical processes generate effluent containing up to 1 g/L of arsenic, which wants proper treatment [17].

Arsenic causes a whole bunch of dangerous diseases in people such as diabetes, digestive, cardiovascular and neurological conditions, and increases the risk of cancer [18, 19]. Therefore, in order to reduce the effect of arsenic on large populations of people, it is necessary to develop cheap and effective methods for purifying drinking water, constantly monitoring the level of pollution and observing the form of arsenic in the water and its sources.

Many countries have already adopted rules limiting the arsenic content in drinking water to 0.01 mg/L, as recommended by WHO and ESEPA [20, 21]. A large number of arsenic water treatment methods have been proposed such as oxidation and precipitation [22], coagulation [23], co-precipitation [24], the use of membranes and reverse osmosis [25], electrolysis [26] and ion exchange resins [27].

However, these methods are rather complicated, expensive or waste generating, and are less effective at very low concentrations. Adsorption thus remains the most common and economical method [28]. Effective adsorption requires materials with the smallest particle size and a large specific surface area, with high porosity and a large number of active centers, e.g., coal – but its preparation is expensive. Therefore, new highly efficient and cheap sorbents from widely available raw materials must be developed to scale up the adsorption process and make it usable by the poorer populations.

Previously was shown [2] that in the processing of bauxite by alkali fusion, one can obtain the red mud with high iron content. Besides, the iron in the red mud are presented in the form of nanoparticles of maghemite [29], which, according to the literature [28], are an effective sorbent for cleaning solution from arsenic. It is also shown [29] that due to the special physical and chemical properties of the red mud obtained by alkali fusion, arsenic capacity increases tenfold: 0.4 mg/g for convenient Bayer red mud against 32 mg/g for red mud obtained by fusing bauxite with alkali.

In this paper, a study was carried out to find the optimal parameters for the synthesis of high-performance sorbents by fusing bauxite with caustic alkali at different initial parameters using an orthogonal plan of the second-order experiment. The variable

parameters were: temperature and duration of fusion, as well as the mass ratio of caustic alkali to bauxite.

## 2. Experimental

The study used analytical grade chemical agents; the water was distilled in a GFL distiller. NaOH had been supplied by ZAO Soda (Sterlitamak, Russia). Bauxites and commercial samples of red mud had been obtained from an alumina plant in Kamensk–Uralsky (Sverdlovsk Region, Russia). The original solution produced by dissolving  $As_2O_3$  with As(V) concentration of 10 g/L had been obtained from the Ural Mining and Metallurgical Company (Verkhnyaya Pyshma, Russia).

The activated red mud was obtained from bauxite by fusing it with caustic alkali. A 20 g bauxite sample was crushed to 80% of particles less than 74 microns and thoroughly mixed with 20 g caustic alkali; then 10 mL water was added to the mixture. The produced pulp was placed in a 100 mL ceramic crucible and mixed well into a homogeneous mixture. The crucible was then placed in a muffle furnace (Tulyachka–10P), and heated up from room temperature to the desired temperature and then left in the furnace for 1.5 hours. The obtained sinter was studied for phase composition and subsequent leaching.

The sinter was crushed by hand using an agate pestle to pass 100% of the particles through a 150  $\mu\text{m}$  sieve and was then leached. For that purpose, the crushed sinter was placed in a 200 mL beaker containing 100 mL water and leached for 30 minutes at 80° C. The resulting pulp was filtered, and the solid residue (red mud) was repeatedly washed with hot water to reach the neutral pH. The washed red mud was dried at 80° C overnight to prevent phase transformations of iron oxides and hydroxides. The red mud thus obtained was analyzed by various physicochemical methods and tested for effectiveness as a sorbent of arsenic.

The study of the phase composition of bauxite, sinter and red mud was performed through powder X-ray diffraction spectrometry (XRD) with an XRD–1800 diffractometer using a Cu–K radiator ( $\lambda = 1.541841 \text{ \AA}$ ) and a graphite monochromator. The chemical composition of bauxite and red mud was determined using powder X–ray fluorescence spectrometry (XRF) with an XRF–2000 detector. Scanning electron microscopy (SEM) images were taken to determine the morphology of red muds (JEOL JSM-6390, Tokyo, Japan).

Arsenic adsorption experiments were performed by mixing a certain amount of red mud (10 g/L) with As (V) solution of a known concentration in a plastic Erlenmeyer vessel. The Erlenmeyer vessels were agitated at 100 rpm with an Ecros laboratory shaker at

room temperature of  $25 \pm 2^\circ \text{C}$  until pseudo-equilibrium was reached [28]. Arsenic adsorption by different types of red mud was tested with an initial concentration of As (V) of 150 mg/L for 24 hours. Upon reaching the adsorption equilibrium, the red mud was separated by centrifuge; the solution was then collected to determine the final As (V) content using inductively coupled plasma optical spectrometry (ICP-MS). All the tests were performed twice; the mean values are presented here.

The sorbent capacity was determined by the mass balance formula Eq. (1):

$$q_e = (C_i - C_f) * V / m, \quad (1)$$

where  $q_e$  is the sorbent capacity in mg/g,  $C_i$  and  $C_f$  is the initial and final concentration of arsenic in mg/L,  $V$  is the solution volume in L, and  $m$  is the sorbent mass in g.

### 3. Results and Discussion

The chemical composition of the used bauxite is presented in Table 1. Figure 1 shows the XRD pattern of the bauxite. As can be seen from the data in Table 1 and Figure 1, this bauxite mainly consists of boehmite and hematite, with a small amount of rutile, diaspor, quartz, and chamosite. This bauxite is characterized by a high iron content, which makes it a good object to study the possibility of obtaining an iron oxide-based adsorbent from red mud.

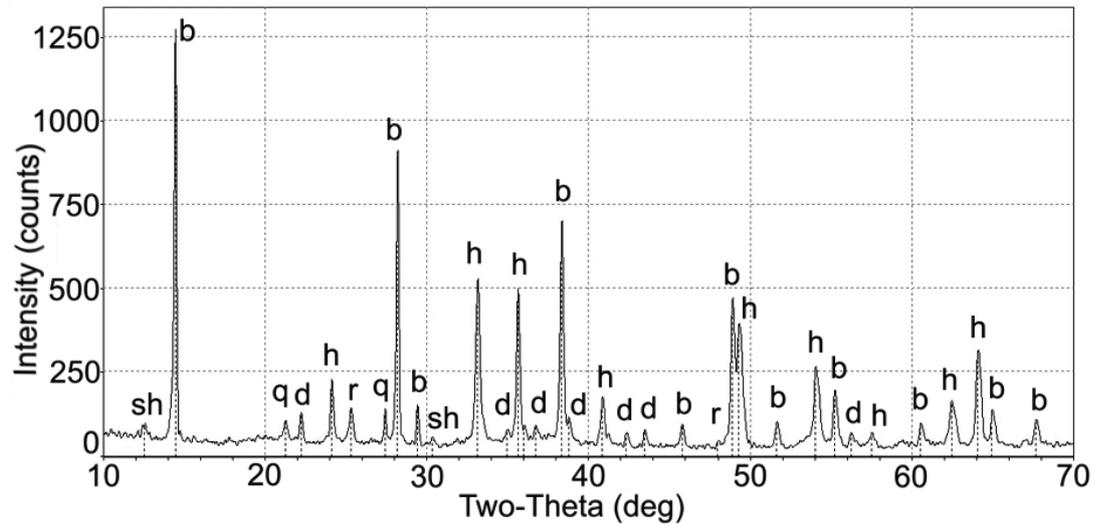
TABLE 1: The chemical composition of Middle–Timan bauxite.

$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{SiO}_2$	$\text{TiO}_2$	CaO	$\text{CO}_2$	MgO	LOI	$\mu\text{Si}^1$
51.00	28.00	4.44	2.84	0.62	0.60	0.33	11.15	11.49

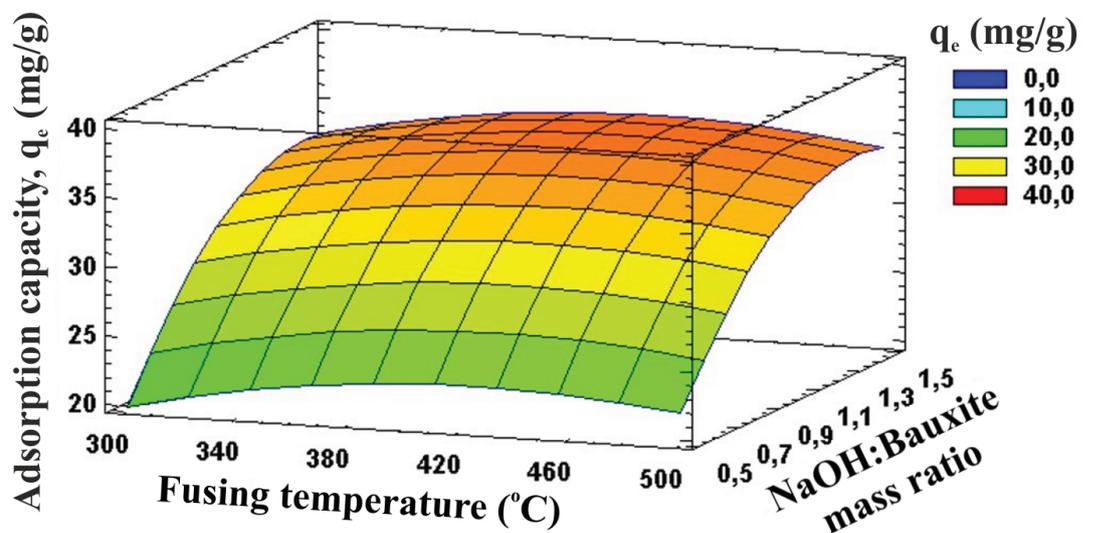
<sup>1</sup>  $\mu\text{Si}$  – a silica ratio equal to the mass ratio of alumina to silica in bauxite.

To study the effect of alkali fusing conditions on the red mud adsorption capacity a multifactorial experiment was carried out. The results of the experiments are shown in Figures 2 and 3. As can be seen from the data obtained, the mass ratio of NaOH to bauxite and the time of fusion have the greatest influence on the capacity of red mud, which is associated with a more complete interaction of caustic alkali with hematite in bauxite to form sodium ferrite. The temperature of the fusing process, in turn, has the least effect on the capacity of the red mud. Nevertheless, the maximum capacity is observed at a temperature of  $400^\circ \text{C}$ .

Thus, the optimal parameters of the sorbent synthesis obtained in this study are the temperature of  $400^\circ \text{C}$ , the mass ratio of NaOH to bauxite is 1.5 units, the duration of fusion is 70 minutes. With these parameters, it is possible to obtain a red mud with an arsenic adsorption capacity of 37 mg/g, which is comparable to artificially obtained adsorbents based on maghemite nanoparticles [2].



**Figure 1:** The XRD pattern of the Middle-Timan bauxite, where: b – boehmite; h – hematite; d – diaspore; q – quartz; r – rutile; sh – chamosite.



**Figure 2:** Estimated response surface of multifactor experiment at 90 minutes of fusing time.

When these parameters have been adopted the red mud with the following composition (Table 2) was obtained. According to the X-ray analysis the main iron-containing phase in the red mud was maghemite (Figure 4).

TABLE 2: The chemical compositions of the red mud obtained at optimal conditions.

Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>	CaO	LOI
2.27	5.67	67.28	3.97	6.82	1.48	9.53

In order to study the morphology of maghemite particles in the obtained red mud, micrographs were made using scanning electron microscopy (Figure 5). According to the photos, the red mud consists of particles smaller than 1 micron.

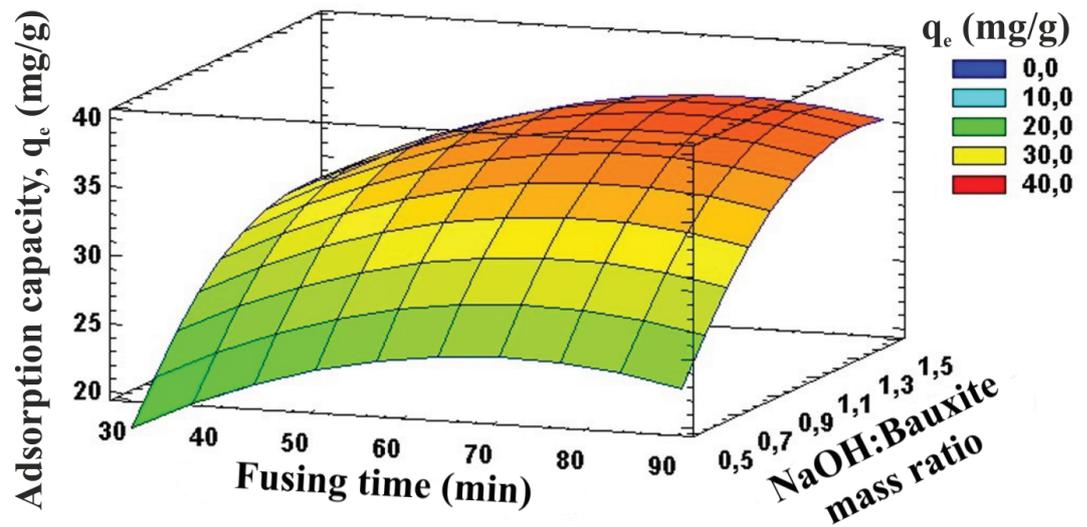


Figure 3: Estimated response surface of multifactor experiment at 400 °C.

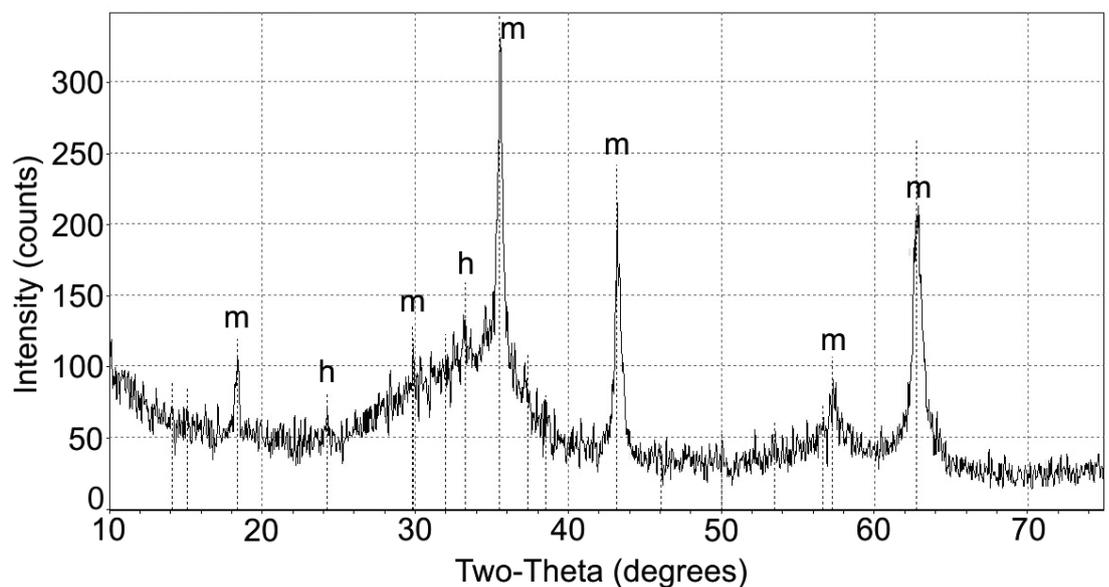
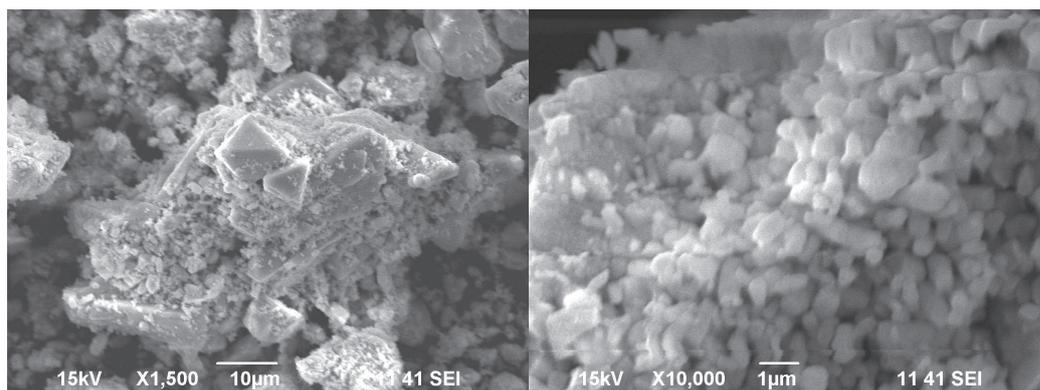


Figure 4: XRD–pattern of the red mud obtained at optimal conditions (m, maghemite; h, hematite).

## 4. Conclusions

Alkali fusing–leaching method for preparing As(V) adsorbents while processing bauxite in the alumina production was explored. In the first step, bauxite was fused with alkali at different temperatures and time, as well as the mass ratio of NaOH to bauxite to the conversion of Al, Fe and Si in the soluble form. In the second stage obtained sinters was leached by water to recover Al and Si in solution, as well as obtain red mud with high iron content. The optimal parameters for the synthesis of high-performance adsorbents of As(V) by fusing bauxite with caustic alkali at different initial parameters of fusing were performed using an orthogonal plan of the second-order experiment.



**Figure 5:** Microphotographs of red mud obtained at optimal conditions.

The optimal As(V) adsorption efficiency more than 37 mg/g was obtained after fusing at 400 °C and NaOH to bauxite mass ratio 1.5 for 70 min. The iron oxide content in the red mud obtained under the optimum conditions was 67.28%, that is much higher than in conventional Bayer process red mud. Also, high As(V) adsorption efficiency can be related to the phase composition of the red mud. According to the X-ray analysis, the main iron-containing phase in the red mud was maghemite. It can be concluded from the experimental results that the proposed method is efficient and energy-saving. Moreover, it appears to be suitable for the comprehensive utilization of the red mud.

*The work was supported by Act 211 Government of the Russian Federation, contract N° 02.A03.21.0006.*

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