A STUDY ON ACTIVATION PROCESS OF RED MUD TO USE AS AN ARSENIC ADSORBENT

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Abstract

Red mud, an industrial waste from the alumina-producing Bayer process, releases a huge amount quantity in the world and becomes an important pollution resource. The aim of this study is to evaluate the effect of activation conditions on the properties of the treated red mud to use as an Arsenic adsorbent. Five parameters of the activation process including calcination temperature, calcination time, acid concentration, reaction temperature, and reaction time were studied using Response Surface Methodology. The optimum conditions were obtained at calcination temperature of 274.42°C in 3.04 hours and activating concentration of H_2SO_4 is 1.18M at 87.88°C in 3.93 hours. The As^{5+} adsorption ability from simulated solutions was conducted to test effect of activating parameters.

Keywords*:* Activation, Adsorption, Arsenic, Red mud

Introduction

Vietnam is one of the large bauxite reserve countries in the world, ranking third after Guinea and Australia. Total reserves of bauxite ore have been estimated to be about 5.5 billion ton, of which about 91 million tons are located in the North and about 5.4 billion tons in the South [1], concentrated in the Central Highlands. Bauxite has been identified as an important resource for the economic and social development, contributing to the stabilization of political and security situation in Highlands region. However, the process of exploiting and processing bauxite ores entails the disposal of a large quantity of red mud (about 90% of raw ore).

The mud contains an excessive amount of iron oxide and hydroxide ions, which can cause serious environmental problems if they are not treated. The red mud affects the water environment not only locally but spreading over to the surrounding area as rain water seeps through old red mud ponds. The rain can carry soluble, caustic chemicals further, polluting other surface water sources such as lake and rivers Even though some measures have been taken to prevent these water leaks (such as lining the impoundments with extra polymeric membrane), the sheer volume of this waste means large areas of land are being turned into landfill [2][3].Because of the environmental impact of red mud and its enormous volume, the treatment of red mud is an extremely urgent issue. One of the promising solutions for this issue is to convert the harmful red mud to useful products such as adsorbents [4].

Another environmental problem in Vietnam is arsenic pollution of ground water. According to statistics, about 21.5% of the Vietnamese population (approximately 17.2 million persons) are directly using the ground water source from the wells for needs of daily life such as eating, drinking and others. In some provinces of North area of Viet Nam such as Ha Nam, Vinh Phuc, Ha Tay, Ha Noi, Hai Duong, etc. it has been found that the ground water contained arsenic at a high concentration, which is causes plenty of diseases. As reported in the “Clean Water Program” of UNICEF, water samples from 517 among 900 wells in Quynh Loi – Ha Noi had been tested following the international standard. It was found that about 70% of the well water sample contain the arsenic over the permitted

standard; in these, there were some samples which exceed the standard by up to 50 -60 times. However, there is still no effective solution to separate the arsenic up to now [5-7].

Therefore, research on conversion of red mud into an effective adsorbent for arsenic adsorption is necessary and important to solve the two environmental issues simultaneously. In this study the application of modeling software to design and optimize the activation factors of the treatment process for red mud was investigated and the optimization of the arsenic adsorption was also carried out.

Material and Methodology

The red mud material was collected after Bayer process, supplied by Tan Binh Alumina factory, Ho Chi Minh city, Vietnam. The composition of the red mud is shown in Table 1 which was supplied by the factory. The simulated As(V) solution at concentration 2.0 mg/l was prepared with the analytical grade of $Na_2HAsO_4.7H_2O$ which purchased from Merck Co.

Table 1: Chemical Components of Red mud

Component	Al_2O_3	Fe_2O_3	SiO_2	TiO_2
Content (%)	18 – 25	40 – 50	2 – 4	2,5

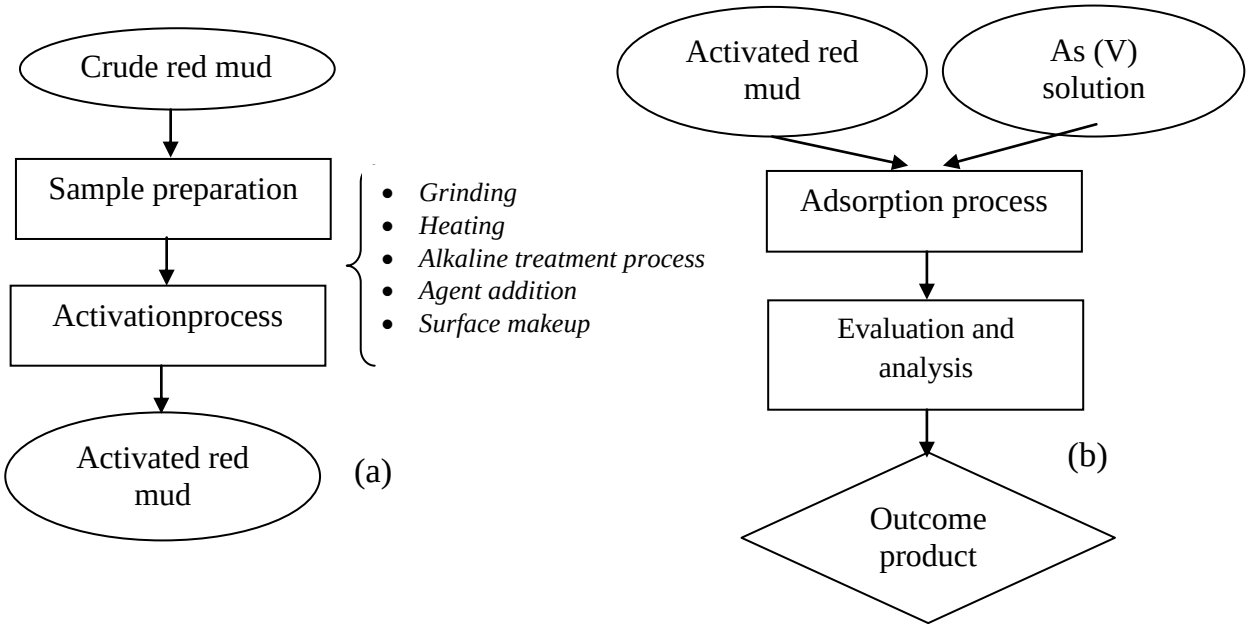

Figure 1. Flow chart of activating process (a) and adsorption process (b)

The sample preparation including the alkaline treatment process, drying and grinding were applied on the raw material to get the homogeneous material for further experiments. The overall flow charts of the experimental process are shown in Figure 1. The activation process comprised two steps: calcinations and acid treatment. Five parameters of the activation process were selected: calcination temperature; calcination time; concentration of H2SO4 solution; reaction temperature; and reaction time. Study ranges of the influence factors were shown in Table 2 below. The product of the activation process was used as the adsorption material for arsenic adsorption process.

Adsorption experiments were carried out batch-wise. A desired amount of activated red mud powder was added to glass flasks containing 100 ml of arsenic solution of defined concentration 2.0 mg/l As(V) at room temperature. After obtaining equilibrium, the solutions were filtered and the amount of As(V) in the solution was determined by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) method and the amount of As(V) adsorbed was calculated from the difference between the initial and final concentration. Moreover, the specific surface areas of crude and activated red mud were evaluated by the Brunauer-Emmett-Teller (BET) method.

In the preliminary study,the variable alternating method was manipulated in to determine the study ranges of influent factors. The preliminary investigated ranges of heating temperature, heating time, acid (H_2SO_4) concentration, activating temperature and activating time were 300 – 900˚C, 2 – 5hrs, 0.4M– 1.3M, 60 – 90 ˚C, 1 – 9hrs, respectively.

For experimental design, regression analysis of the data was carried out by statistical design software (Design – Expert). Second-order experimental design withcentral composite design model was used to study the effect of theoperating parameters. The results were used to obtain the functional equation, which shows the effect of influent factors to the response surface and calculate the optimization conditions.The data on independent variable were rescaled for convenience as shown in Table 2.

Table 2: Studied Range of Influence Factors and Response Functions

Influence Factors	Symbol	Level		
		Upper +1	Basic 0	Lower -1
Heating temperature (˚C)	Z_1	400	300	200
Heating time (hr)	Z_2	5	4	3
Acid concentration (M)	Z_3	1,2	1	0,8
Activating temperature (˚C)	Z_4	90	80	70
Activating time (hr)	Z_5	4	3	2
Response Function	**Symbol**		**Unit**	
The As (V) adsorption capacity	Y		mg/g	

Results and Discussion

Result of the Preliminary Study

The effect of heating time on As (V) adsorption capacity is shown in Figure 2. The red mud powder was heated from 300˚C to 900˚C to study the effect of heating time on adsorption capacity. The results showed that increasing the temperature will lead to an increase in the capacity of the adsorbent until 305 ˚C. Adsorption capacity reached a critical value around 350˚C and after that it declined. The internal and external surface area of red mud powder increases when the temperature is increased. However, after reaching the critical value, higher temperatures may break down certain substances in the mineral structure of red mud and the sintering process occurs, which will decrease adsorption capacity. Therefore, the heating temperature's investigation range is from 200 to 400˚C.

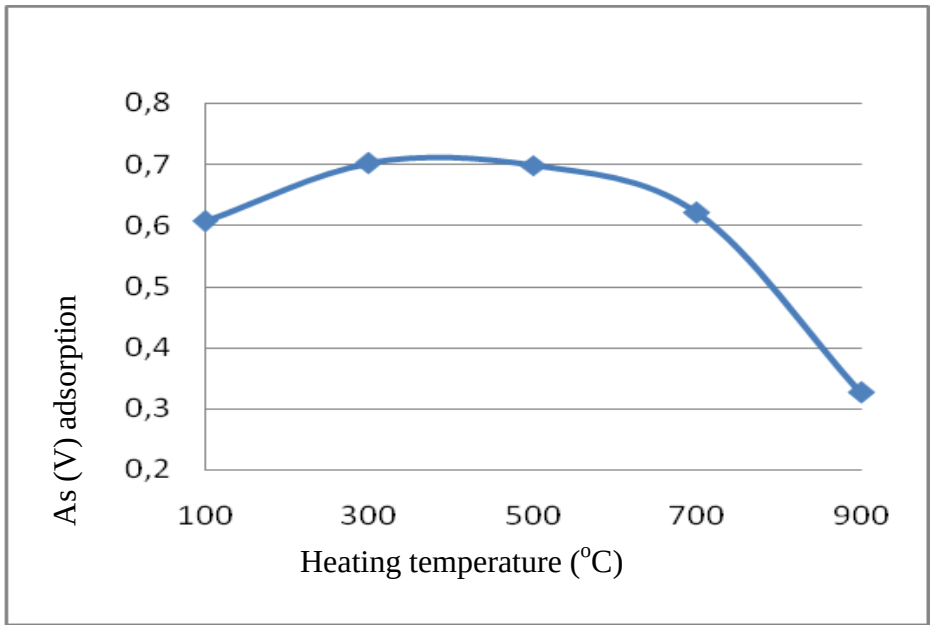

Figure 2. Effect of heating temperature on As (V) adsorption capacity

Figure 3 presents the influence of heating time on As (V) adsorption capacity. The heating times have no considerable influence in range of 2 to 5 hours. At 4 hours adsorption capacity reach the highest value. Therefore, the investigation heating temperature's investigated range is from 200 to 400°C.

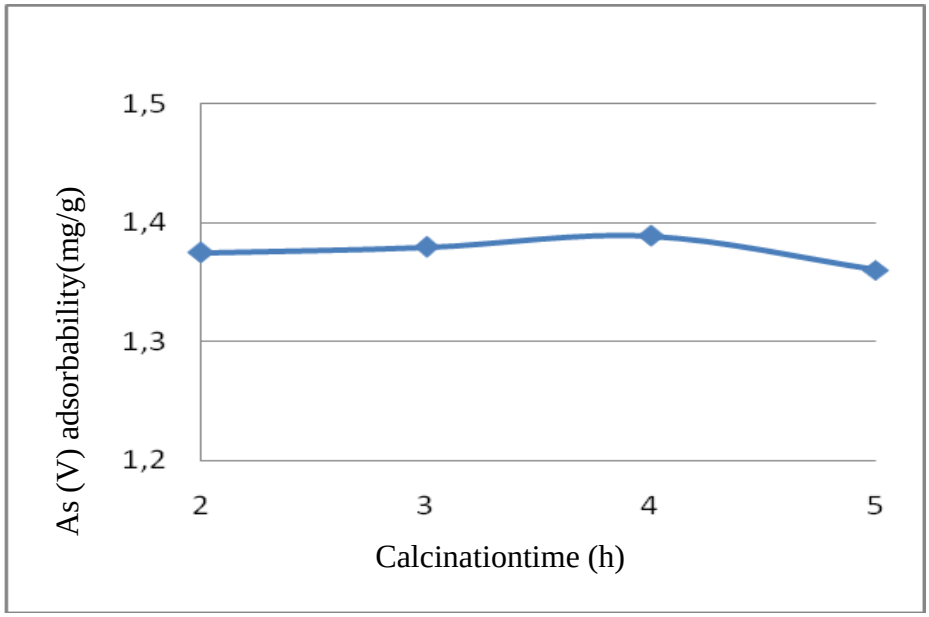

Figure 3. Effect of heating time on adsorption capacity

The effect of acid concentration on As (V) adsorption ability is shown in Figure 4. The adsorption capacity reached the highest value at 1M of acid concentration and then it decreased. Because when increasing acid concentration, large amount of aluminum, iron were dissolved by H_2SO_4 and removed from the structure of red mud and specific surface area was increased. But further increasing the value of acid concentration will lead to the decrease of adsorption capacity due to the dissolution of Goethite(α-$Fe_2O_3.nH_2O$) which adsorbs arsenic well. The value of acid concentration's study range is 0.8M – 1.2M.

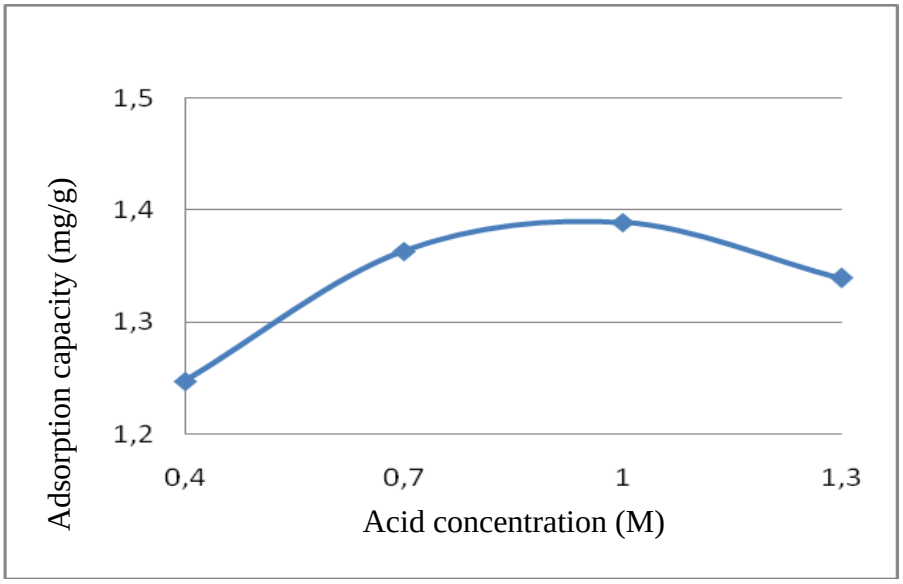

Figure 4. Effect of acid concentration on adsorption capacity

Figure 5 and Figure 6 show the effect of acidactivation temperature and acid activation time. The adsorption capacity reached the highest value at 80˚C and then declined. The rate of dissolution of minerals in red mudoccurred faster since the increasing of the activating temperature, leads to theincreasing of specific surface area. The activating temperature's investigated range is from 70 to 90˚C. On the other hand, increasing the activating time initially led to rise in adsorption capacity but the highest value of adsorption capacity reached at 3 hours then it went down and remained flat. Reason can be explained as most of the ions in red mud reacted with acid and were dissolved, therefore the specific surface area and internal space were increased.

According to the above results, the following set of conditions was chosen to be the center points for the experimental design in this study: heating at 400˚C temperature in 4 hours, then it was activated with H_2SO_4 1M in 3 hours at 80˚C.

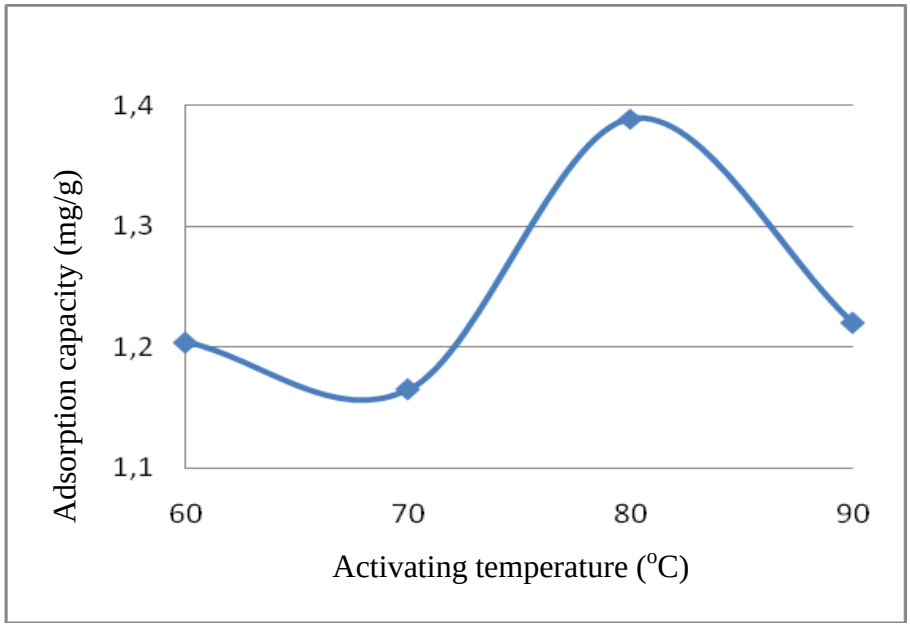

Figure 5. Effect of activating temperature on adsorption capacity

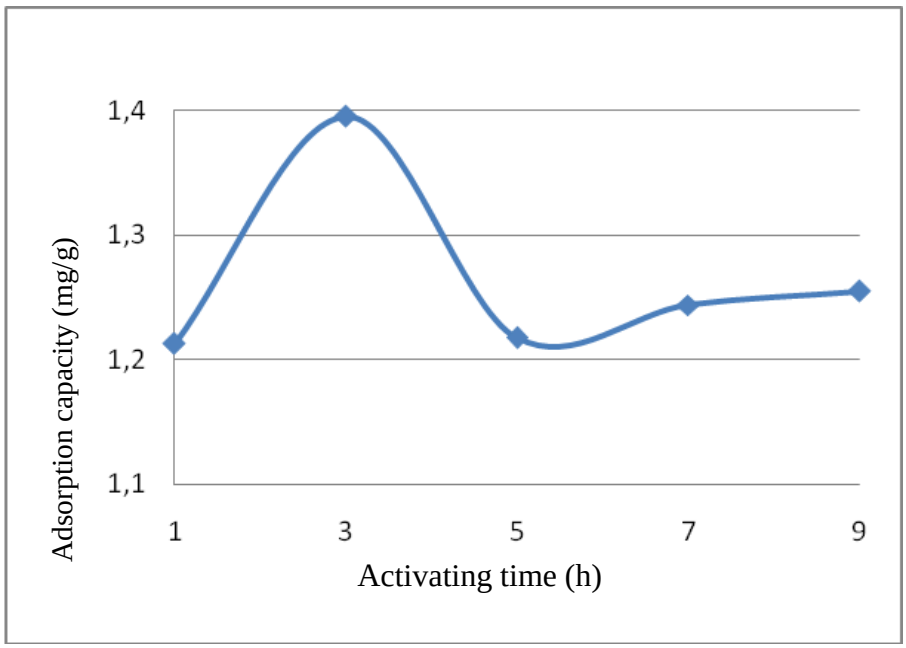

Figure 6. Effect of activating time on adsorption capacity

Result of Response Surface by the Design-Expert

The data obtained above is then used to calculate and construct the responsemodel by Design Expert software, which was also tested for its compatibility. The response model obtained from the software is:

$Y = -15{,}03 + 9{,}16Z_1 + 3{,}22Z_1Z_4 - 2{,}1Z_2Z_3 - 0{,}62Z_2Z_5 - 4{,}47.10^{-5}\ Z_1^2 - 0{,}106Z_2^2 - 3{,}23Z_3^2 - 0{,}22Z_5^2$.

Using this model, Design-Expert software was employed to find the optimal condition of activation process. Further calculation demonstrated that activated red mud reached its highest adsorption level at 3.135 mg As/g with heating temperatureof 274.42˚C in 3.04 hours, and it was activated by 1.18M H_2SO_4 solution at 87.88˚C in 3.93 hours. Some typical surface response graphs are reported in the Figure 7.

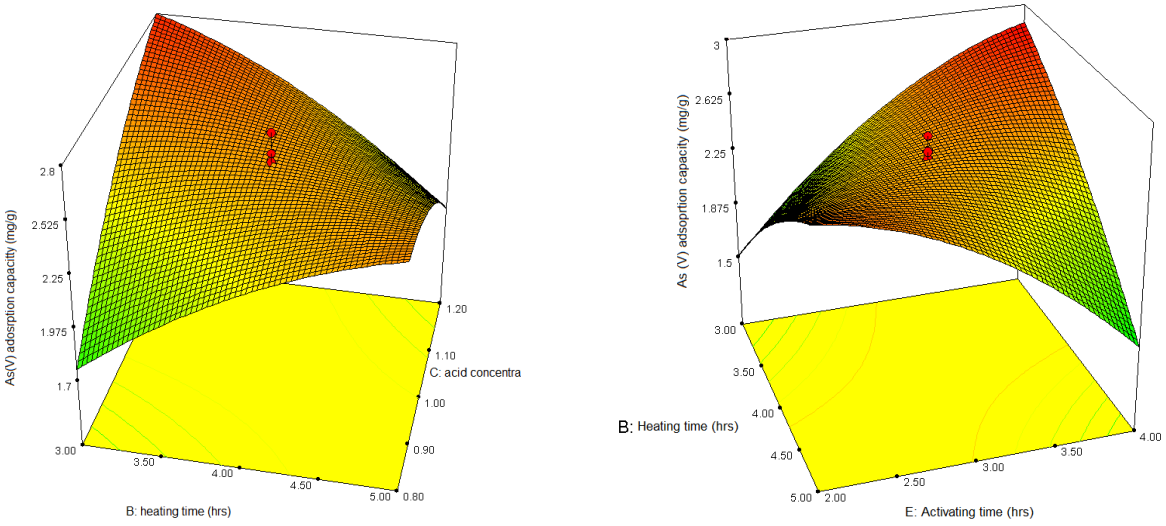

Figure 7. Typical graphs illustrate effect of two parameters on As(V) adsorption capacity

Results of Specific Surface Area

Table 3. Comparison of Specific Surface

Area Sample	Specific Surface Area (m^2/g)
Crude red mud	67,81
Activated red mud	241,879

Activated red mud has higher specific surface area than that of the crude one, this result is one of the reasons that lead to the increase of activated red mud's adsorption capacity. Aluminum ions, iron ions and other metallic ions reacted with H_2SO_4 acid in activation process. Moreover, the diameter of activated red mud's internal pores may have increased after activating process. These can be considered as the main reasons which lead to the increasing of specific surface area of activated red mud.

Conclusions

The investigation of five parameters of the red mud activation process has been studied. They are calcination temperature, calcination time, acid concentration, acid activation temperature, acid activation time. An experimental model describing the effects of the 5 influencefactors was established based on Design-Expert software with the As (V) adsorption capacity as a response function. Basing on this model, the highest As (V) adsorption capability of activated red mud was predicted to be 3.135mg As/g with preparing conditions ofheating temperature at 274.42°C in 3.04 hours, acid concentration is 1.18 Mat 87.88°C and activating time in 3.93 hours.

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