**CHEMICAL ENGINEERING TRANSACTIONS** Volume 24, 2011
Editor Sauro Pierucci

 ISBN 978-88-95608-15-0 ISSN 1974-9791
DOI: 10.3303/CET1124205

# Removal of Benzene From Aqueous Solution Using Raw Red Mud

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Adsorption techniques are widely used to remove certain pollutants from groundwater. Benzene, which is one of the organic compounds of gasoline, is one of the problematic species by its toxicity and carcinogenic. Although many natural adsorbents may be used in the removal of benzene, their use is restricted due to cost and availability. In this sense, the red mud, that is a waste from aluminum industry generated in large quantities in Brazil, can be used as low cost adsorbent, especially if used in its raw form. This paper evaluated the benzene kinetics adsorption in thermostatic bath. The benzene adsorption process took 1 h to attain equilibrium and followed the pseudo-second-order model. The results were obtained by liquid chromatography. The maximum amount of benzene removal was 98%. Based on the results, it was possible to conclude that red mud has a good potential to remove benzene in groundwater.

## 1. Introduction

The pollution of groundwater by chemicals is a worldwide problem and become more frequent due to population growth and consequently the expansion of industrial activity. Benzene, which is one of the organic compounds of gasoline, is well-known as pollutant of groundwater.

With the concern of preserve the environment and public health, many processes have been studied. Conventional methods for removal of organics include oxidation, reduction, ion exchange, biofiltration and membrane technologies (Qu et al, 2009). However, the use of these technologies can be expensive and most times do not work well at low concentration of the pollutants (Okoronkwo and Anwasi, 2008). Among these processes, the adsorption can be used in order to remove aromatic compounds dissolved in water to recover their qualities, potability and release levels according to that established by legislation (in Brazil it is: 5μg $L^{-1}$ for benzene). With the current trend of using methods that minimize losses and that are adequately effective, researches have been evaluating the use of waste or by-products, especially those generated by industrial processes.

Please cite this article as: Souza R.S., El Didi H.S. and Gurgel Carlos Da Silva M., 2011, Removal of benzene from aqueous solution using raw red mud, Chemical Engineering Transactions, 24, 1225-1230
DOI: 10.3303/CET1124205

Among the various wastes generated by mining, one type of solid waste, called red mud (RM), is largely produced from the alumina industry. This material is formed as a by-product of the caustic leaching of bauxite to produce alumina ($Al_2O_3$); it has reddish-brown color and a superfine particle size distribution. Its major constituents are $Fe_2O_3$, $Al_2O_3$, $Na_2O$, $SiO_2$, $TiO_2$ and CaO, which are responsible for its high surface reactivity (Chvedov, 2001). In Brazil were produced approximately 16 million tons of red mud in 2009 (ABAL, 2009). The largest production was in Pará`s State, located in north of the country.

The aim of this paper was to study the adsorption removal percentage of benzene dissolved in water, evaluating the kinetics and equilibrium adsorption in thermostatic bath. This work intends to evaluate the potential use of this material as an alternative adsorbent, due to its low cost and availability.

## 2. Materials and Methods

### 2.1 Red mud

The alkaline red mud used in this study has been obtained from Alunorte S.A. plant (Pará-Brazil). Freshly samples had pH 11.0 and the microanalysis revealed its principal chemical components as $Fe_2O_3$ (45.8%), $Al_2O_3$ (19.8%), $Na_2O$ (10.8%), $SiO_2$ (29.28%), $TiO_2$ (5.9%) and traces of CaO. The BET method indicated that the specific surface area of RM sample was about 8.17 $m^2\ g^{-1}$ and $pH_{zpc}$ determined a point of zero charge at pH 8.3 (determined by potenciometric titration).

RM was sieved and the particle size used in this paper was 0.855mm, then it was dried at 105°C for 12 h to remove moisture and any organic impurities.

### 2.2 Analytical method

The benzene concentration determination was carried out using Liquid chromatographic analysis at a Shimadzu LC 10A fitted with a manual injector and UV detector (λ = 254nm). Separations were conducted using a ODS Hypersil Column (Thermo Scientific), particle size 5µm, id with 4.6mm and length 250mm. The mobile phase was methanol and water (80:20), flow rate of 1mL $min^{-1}$ and 20µL volume injected.

### 2.3 Batch adsorption kinetics

All chemicals were analytical grade and, therefore, no further purification was necessary. All experiments were conducted in duplicate and the mean values were considered. Adsorption studies were carried out by shaking 100mL of benzene solution at 200 rpm with 1 g of RM in the bottles for 5 h at room temperature (23±1 ◦C). After reaching equilibrium, the solutions were filtrated and then it was analyzed benzene in the HPLC. Benzene adsorbed was calculated as equation 1

$$q(t) = \frac{V}{m}\left(C_0 - C(t)\right) \tag{1}$$

Where $q$ is the concentration of the benzene adsorbed (mmol $g^{-1}$); $C_0$ and $C_t$ are the initial and final concentrations of the benzene in solution (mmol $L^{-1}$), respectively; $V$ is the solution volume (L) and $m$ is the mass of RM (g).

The removal percentage (% Rem) was also calculated through the expression:

$$\%\,\mathrm{Rem} = \left(\frac{C_0 - C_e}{C_0}\right) \cdot 100 \tag{2}$$

Where $C_e$ is the benzene`s concentration in equilibrium time.

**2.4 Kinetic study**

A kinetic investigation was conducted in order to further expose the adsorption mechanism of benzene onto red mud and rate-controlling steps. Kinetics of adsorption is one of the important characteristics defining the adsorption`s efficiency.

Sorption kinetics are controlled by different steps including solute transfer to the sorbent particle surface, transfer from the sorbent particle surface to the intra particle active sites and retention on these sites via sorption, complexation and intraparticle precipitation phenomena (Itodo et al., 2010).

In literature there are many mathematical models to determine what are the mechanism and the rate-determining of in each adsorption process (Vasques, 2008). In this work, it will be analyzed the pseudo-first-order, pseudo-second-order and Intraparticle diffusion models, which are expressed, respectively, as:

$$\frac{\partial q}{\partial t} = k_1(q_e - q) \tag{3}$$

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{4}$$

$$q = k_i t^{0,5} \tag{5}$$

Where $k_1$, $k_2$ and $k_i$ are the kinetics models constants; $q$ is the amount of benzene adsorbed per unit mass of adsorbent at t (min) and $q_e$ (mmol $g^{-1}$) is the amount of benzene adsorbed per unit mass of adsorbent at equilibrium.

## 3. Results and Discussion

**3.1 Batch adsorption kinetics**

Experiments were conducted to evaluate the kinetic removal of benzene with 1.28 mmol. $g^{-1}$ concentration. The benzene removal kinetics by the red mud is observed in Figure 1.

It can be verified that it was needed at least 60 minutes of contact time for the system reaching equilibrium in the benzene removal. Furthermore, this study showed that about 98% of benzene was removed from the fluid phase. There was no significant change in concentration after 300 minutes.

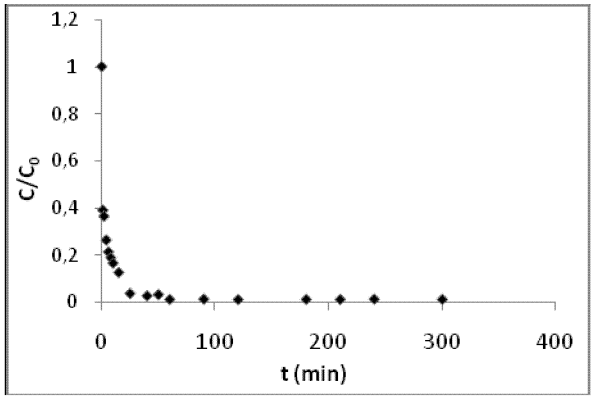


*Figure 1: Dimensionless decrease of benzene concentration in the fluid phase*

Figure 2 represents the fraction of benzene removed from the solution as a function of time, the results indicated that removal of benzene occurred in fast way. The removal kinetics curves were fitted to pseudo-first and pseudo-second order models, as showed in the Figure.

Table 1 shows the values of constants of the removal rates. As well as the correlation coefficients ($R^2$) obtained by the least squares method.

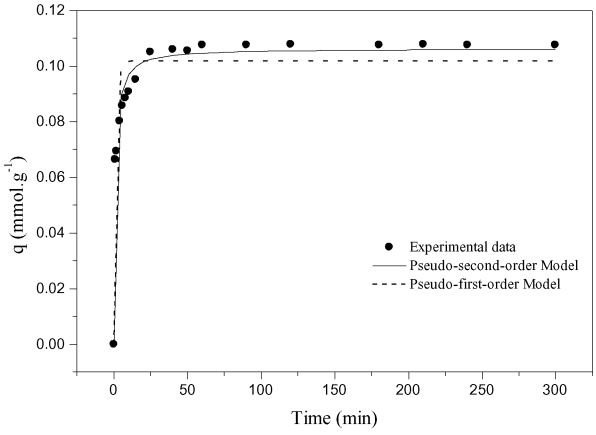


*Figure 2: Benzene removal kinetics and fitting data to models pseudo-first-order and pseudo-second-order.*

*Table 1: Parameters and correlation coefficient for the models pseudo-first-order, pseudo-second-order*

| Pseudo-second-order | | | Pseudo-First-order | | |
|---|---|---|---|---|---|
| qe (mmol $g^{-1}$) | $k_2$ (g $mmol^{-1}$) | $R^2$ | qe (mmol $g^{-1}$) | $k_1$ ($min^{-1}$) | $R^2$ |
| 0.103 | 9.67 | 0.969 | 0.10179 | 0.65338 | 0.889 |

It is observed from Figure 2 and Table 1 that the model of pseudo-second-order was better represented the kinetics of benzene in red mud, the study of kinetic experiments were made by the intraparticle diffusion model to experimental data and it was possible to identify the stage that controls the adsorption process.

**3.2 Intraparticle diffusion**

According to this model, if the plot of q versus t1/2 gives a straight line, the adsorption process will be controlled by intra-particle diffusion, while, if the data exhibit non linear plots, two or more steps will influence the adsorption process (Yao et al., 2010). At the first, sharper portion may be considered as an external surface adsorption or faster adsorption stage. The second portion describes the gradual adsorption stage, where the intra-particle diffusion is rate-controlled. The third portion is attributed to the final equilibrium stage, where intra-particle diffusion starts to slow down due to the extremely low adsorbate concentrations in the solution (Koyuncu, 2008). In the intermediate stage where the adsorption is gradual, the process may be controlled by intra-particle diffusion.

Although three different stages exist for the kinetic behavior of aqueous phase adsorption, all three stages are not necessarily involved. It was shown that the existence of either the second or the third stage was limited by several factors, such as characteristics of adsorbent and concentrations of adsorbate (Choi et al., 2007).

The kinetics experimental intraparticle diffusion data shows that the adsorption occurs in three stages, as presented in Figure 3.

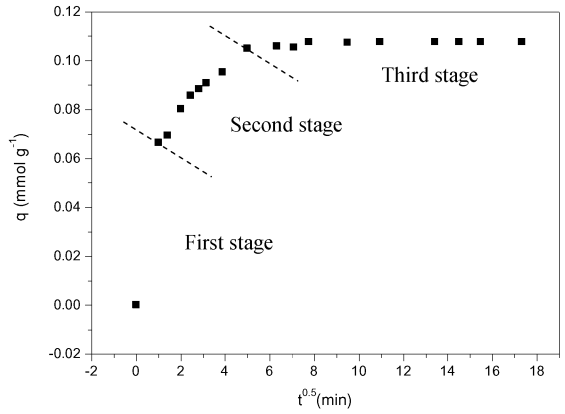


*Figure 3: Intraparticle diffusion kinetics of benzene adsorption.*

In Figure 3, we can see that the first stage in the adsorption was completed in about 1 min. The second stage demonstrate a linear relationship, thus the process may be controlled by intra-particle diffusion. This indicates that intra-particle diffusion was involved in the benzene adsorption onto red mud, but it was not the sole rate-controlling-step (Yao et al., 2010).
In the determination of the ki values, the calculation taked into account of only the range of 1 to 5 min of the adsorption process. The ki value is 0.097 mmol $g^{-1}$ $min^{-0.5}$ and a satisfactory linear regression coefficient ( $R^2$=0.97) was obtained, this confirm that the intraparticle diffusion controlled the process.

## 4. Conclusion

The adsorption equilibrium was attained within 60 min contact time. The experimental adsorption kinetics could be fairly fitted by the pseudo- second-order kinetics model. The benzene removal was 98%. The processes were mainly intraparticle-diffusion-controlled through the analysis of external mass transfer coefficient and effective particle diffusion coefficients.
From the research results in this paper, it can be concluded that the raw red mud exhibited a high capability to adsorb benzene from aqueous solutions. Furthermore, the use of a waste material without any treatment makes it a viable alternative to its use as adsorbent.

## Acknowledgements

The authors would like to thank FAPESP and CAPES for the financial support in this study.

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