Hexavalent Chromium Adsorption Using Red Mud As Adsorbent

Maroš Soldán
Faculty of Materials Science and Technology
Slovak University of Technology
Trnava, Slovakia
maros.soldan@stuba.sk

Jozef Fiala
Faculty of Materials Science and Technology
Slovak University of Technology
Trnava, Slovakia
jozef.fiala@stuba.sk

***Abstract*—Hexavalent chromium is usually produced by an industrial process. Cr(VI) is known to cause cancer. Cr(VI) compounds may be used as pigments in dyes, paints, inks, and plastics. It also may be used as an anticorrosive agent added to paints, primers, and other surface coatings. Adsorption is economically feasible alternative of chromium removal. We have used spectrophotometric method for monitoring of hexavalent chromium adsorption from aqueous solution with the use of red mud as adsorbent. We have monitored the influence of temperature and surface treatment on the adsorption process.**

Keywords— red mud; adsorption; chromium

I. INTRODUCTION

Red mud is a highly alkaline solid waste residue formed after the caustic digestion of bauxite ores during the production of alumina with pH 10–12.5. It contains a mixture of many metal oxides, 30–60 % of which constitutes Fe_2O_3; in addition, other constituents like TiO_2, Al_2O_3, and SiO2. Due to the alkaline nature and the chemical and mineralogical species present in red mud, this solid waste causes a significant impact on the environment and proper disposal of waste red mud presents a huge challenge where alumina industries are installed. [1]. Because of the alkaline nature and the chemical and mineralogical species present in red mud, this solid waste causes a significant impact on the environment, and proper disposal of waste red mud presents a huge challenge where alumina industries are installed [2-3]. The amount of the residue generated, per tonne of alumina produced, varies greatly depending on the type of bauxite used, from 0.3 tonnes for high grade bauxite to 2.5 tonnes for very low grade. Yearly production of red mud in Slovakia was about 70 000 kg and supplies are estimated at 8 million tons. [4]

As red mud has a strong alkalinity, which will cause some potential risks to its reuse, pre-treatment to change the alkalinity will produce beneficial effects. In the past years, several methods have been proposed such as acid neutralization, seawater wash treatment, heat treatment and the combination of above three treatments. Acid neutralization is widely used for red mud treatment and this method can remove alkali metals and other inorganic impurities as well as some organics. It is generally found that acid neutralization can increase the surface area and pore volume, favoring adsorption. Heat treatment can decompose unstable compounds and organics; however, it can also cause particle aggregation or sintering. Utilization of red mud will produce significant benefits in terms of environment and economics by reducing landfill volume, contamination of soil and ground water, and release of land for alternative uses. Moreover, it can be used to produce valued materials for other applications and thus saving natural resources. [5]

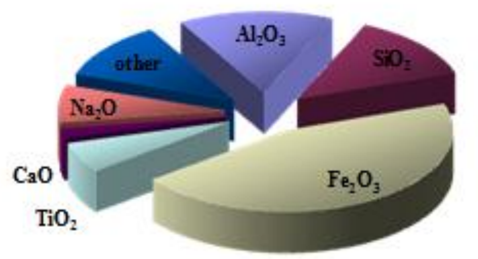

Fig. 1. *Chemical composition of red mud*

Heavy metal pollution affects the quality of the environment and human life. Hexavalent chromium, Cr(VI), is a highly harmful ion that is suspected to cause cancer in mammals and is toxic to aquatic life at low concentrations. The hexavalent form is 10–100 times more toxic that the trivalent form when both are introduced by oral ingestion. In aqueous solution, Cr(VI) forms several species depending on both pH and total concentration. Hexavalent and/or trivalent chromium ions are commonly found in industrial waste, mainly from the electroplating, leather tanning, metal finishing, and textile industries. The effluent from these industries can contain hexavalent chromium at concentrations ranging from tenths to hundreds of mg L^{-1}. [6]

Adsorption is the procedure of choice, which being the widely used physicochemical method for heavy metal removal because adsorption does not need a high operation temperature and several materials can be removed simultaneously. Recently, a variety of adsorbents have received much more attention for the removal of metal ions. The use of more metal adsorbent is the granular activated carbon, active diatomaceous earth and resins. Activated carbon adsorption method is a method applied earlier, and this method is very effective for the removal of heavy metal. However, it is more difficult to regenerate, and the processing cost is higher, so the application is narrow. [7–8].

II. Experimental

Red mud was pretreated by chemical or non-chemical ways:

- Activated: 190 ml of distilled water and 18 ml 31 % HCl were added to 10 g of mud. Suspension was 20 minutes heated by 100°C and filled up with distilled water up to 800 ml. pH = 8 was reached by addition of 22 % NH_3. This suspension was 10 minutes heated at 50°C, filtered and three times decanted with distilled water. The slurry was dried at 110°C and annealed at 550°C for 2 hours.

- Non-activated: 10 g of mud were filled up to 100 ml with distilled water. Suspension was mixed and filtered. Then slurry was dried at 110°C and annealed at 550°C for 2 hours. [9]

Morphology of samples was documented by scanning electron microscope TESLA BS 500 and JEOL JSM 7600F.

The adsorption experiments were carried out at different times (0, 1, 2, 3, 24 hours) and temperatures (25, 30, 40, 50 °C) with occasional stirring on a shaker. Subsequently, the sample was filtered, the first part of the filtrate was not used to determine of the concentration due to saturation of the filter paper. The concentration of chromium was determined spectrophotometrically using diphenylcarbazide method at 540 nm.

Adsorption efficiency at the appropriate time was established using (1):

$$\eta_t = \frac{c_0 - c_t}{c_0} \cdot 100\% \qquad (1)$$

ηt – adsorption efficiency at certain time,

c_0 – Cr(VI) concentration of the sample before adsorption,

ct – Cr(VI) concentration of the sample after adsorption.

III. Results And Discussion

Figure 2 shows the surface of non-activated red mud, which is relatively rough morphology with a set mostly consisting of micro-aggregates. Particle size ranges from 0.5 to 1 μm. Activation leads to the lees incurred particle surface morphology and smooth surface while creating a wrinkled (porous) structure (Fig. 3), which increased the size of its specific surface. This is mainly due to dissolution of salts present on the surface by used HCl.

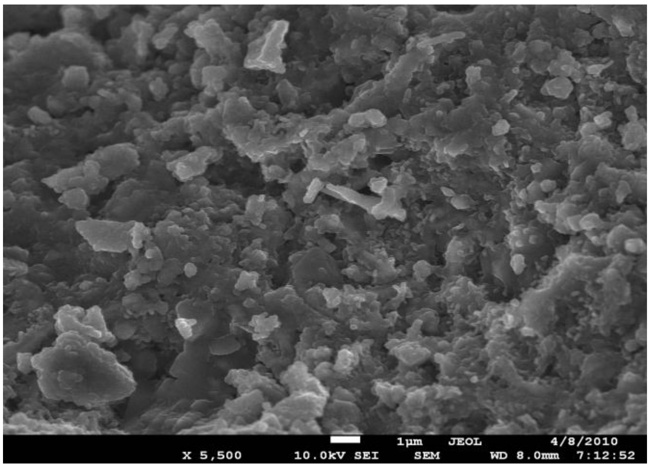

Fig. 2. *The surface of non-activated red mud*

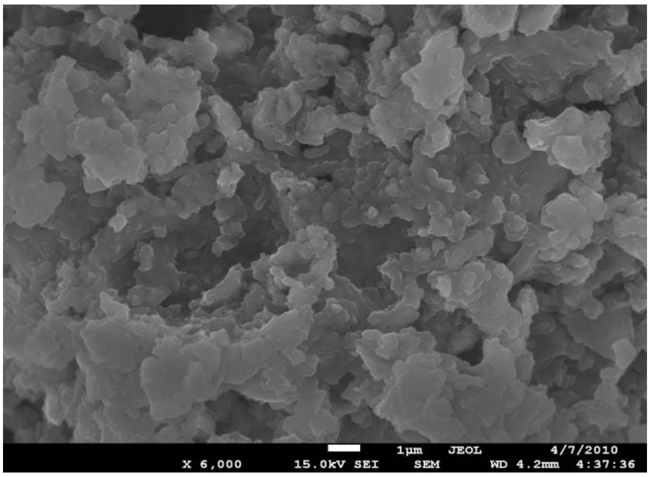

Fig. 3. *The surface of activated red mud*

Cr(VI) adsorption experiments (Fig. 4,5) have shown significant difference between activated and non-activated red mud. The treatment of adsorbent (activation) has a positive effect on adsorption. This process has increased the number of active centers on the surface of the adsorbent, resulting in a significant reduction in the concentration of chromium in the solution. It can therefore be said that the adsorption of chromium using activated adsorbent is more efficient, because the activation of the surface increases sufficient number of active centers for the process of adsorption. Active centers on the surface of the adsorbent are distributed homogeneous and adsorption takes place until saturation of its surface in monolayers.

Adsorption efficiency using activated red mud at 25°C for 24 hours was 64.52 %, while using non-activated form adsorption efficiency at the same temperature and the same time was 7.73 %. It can be concluded that with the use of chemically modified - activated adsorbent about eight to ten times higher adsorption efficiency is reached. Activating the surface of adsorbents increases the number of pores which also leads to an increase in the specific surface area.

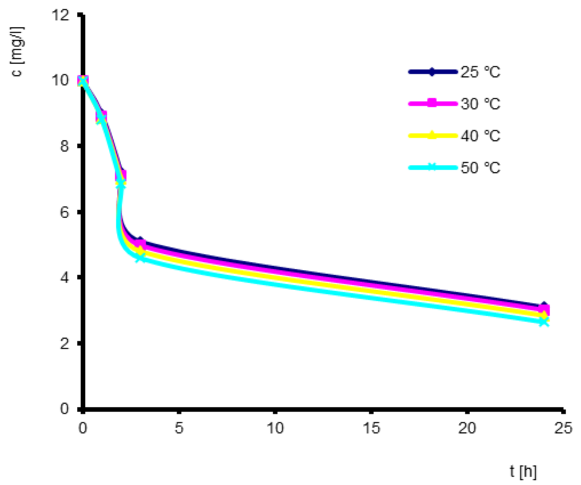

Fig. 4. *Adsorption of Cr(VI) using activated red mud at different temperatures*

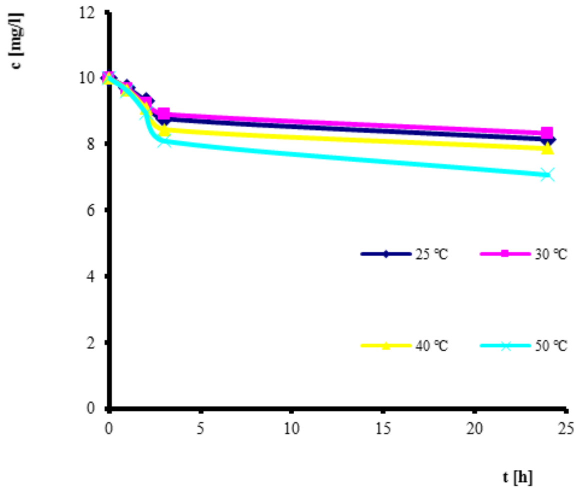

Fig. 5. *Adsorption of Cr(VI) using non-activated red mud at different temperatures*

Fig. 6, 7 shows the impact of different temperatures on the adsorption efficiency of adsorbents examined at intervals studied. The temperature has two main effects on the adsorption process:

- increasing the temperature increases the rate of diffusion of adsorbate molecules in the phase interface and the internal pores of the adsorbent particles, which is due to the reduction in viscosity of the solution,

- change in temperature affects the equilibrium capacity of the adsorbate.

The homogeneity of the surface of the adsorbent increased at higher temperatures with an increased attractiveness of active centers and adsorbed ions. Greater adsorption due to higher temperatures may be due to increased rate of particle diffusion inside of the adsorbate, which supports the claim that the adsorption process is endothermic in nature.

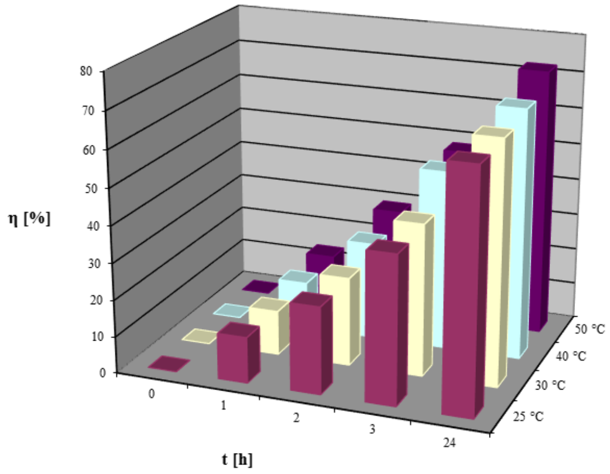

Fig. 6. *Influence of temperature on adsorption of Cr(VI) using activated red mud as adsorbent*

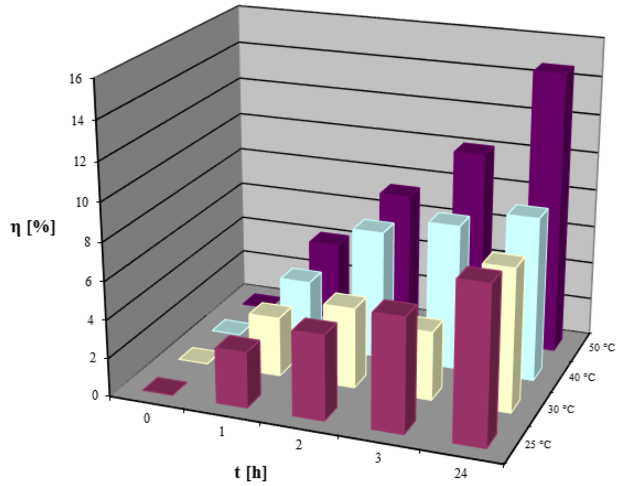

Fig. 7. *Influence of temperature on adsorption of Cr(VI) using non-activated red mud as adsorbent*

For better illustration the effectiveness of removal of chromium at different temperatures is shown in the Table 1. Increased temperature caused a slight increase (about 15 %) in adsorption efficiency.

TABLE I. COMPARISON OF ADSORPTION EFFICIENCIES AFTER 24 HOURS OF ADSORPTION

Red mud	**η [%] at 25°C**	**η [%] at 30°C**	**η [%] at 40°C**	**η [%] at 50°C**
Activated	64.52	65.23	68.77	73.59
Non-activated	7.73	6.96	8.61	14.57

IV. CONCLUSIONS

The applicability of red mud, which is considered as dangerous industrial waste, as an alternative adsorbent was investigated in activated and non-activated forms. The aim of red mud activation was to increase the size of the specific surface area, which could lead to a positive influence of adsorption. Activation of the surface of red mud changes the surface properties of adsorbent mainly electrostatic, hydrophobic and hydrophilic. We can conclude that activation has a positive impact on the adsorption efficiency. The increasing temperature had positively influenced the adsorption of chromium, but not as high as the treatment of the surface.

Acknowledgment

This contribution was created with the support of the project: Studying the use of advance oxidative processes for metalworking fluids lifetime extension and for their following acceleration of biological disposal at the end of the life cycle“ (VEGA 1/0640/14).

References

[1] A. Bhatnagar, V. J. P. Vilar, C. M. S. Botelho, and R. A. R. Boaventura, “A review of the use of red mud as adsorbent for the removal of toxic pollutants from water and wastewater”, Environmental Technology, vol 32(3), pp. 231–249, 2011

[2] A. López, I. Marco, B. M. Caballero, M. F. Laresgoiti, A. Adrados, and A. Aranzabal, “Catalytic pyrolysis of plastic wastes with two different types of catalysts: ZSM-5 zeolite and red mud“, Applied Catalysis B: Environmental, vol 104(3-4), pp. 211–219, 2011

[3] Y Zhao, J. Wang, Z. K. Luan, X. J. Peng, Z., and L. Liang, “Removal of phosphate from aqueous solution by red mud using a factorial design“, Journal of Hazardous Materials, vol. 165(1-3), 1193–1199, 2009

[4] M. Soldán, Ľ. Čaplovič, B. Galbičková, and K. Gerulová,”Evaluation of the structure of industrial wastes“, Advanced Materials Research., vol. 664, pp. 185-190, 2013

[5] W. Shaobin, H. M. Ang, and M.O. Tadé, “Novel applications of red mud as coagulant, adsorbent and catalyst for environmentally benign processes“, Chemosphere, vol. 72(11), pp. 1621-1635, 2008

[6] A. Maleki, B. Hayati, M. Naghizadeh, and S. W. Joo, Adsorption of hexavalent chromium by metal organic frameworks from aqueous solution”, Journal of Industrial and Engineering Chemistry, vol. 28, pp. 211-216, 2015

[7] J. Pradhan, S. N. Das, and R. S. Thakur, “Adsorption of hexavalent chromium from aqueous solution by using activated red mud”, Journal of Colloid and Interface Science, vol 217 (1), pp. 137-141, 1999

[8] L. Chang-jun, L. Yan-zhong, L. Zhao-kun, Ch. Zhao-yang, Z. Zhong-guo, and J. Zhi-ping, “Adsorption removal of phosphate from aqueous solution by active red mud”, Journal of Environmental Sciences, vol. 19(10), pp. 1166-1170, 2007

[9] K. C. Pratt, and V. Christoverson, “Hydrogenation of a model hydrogen-donor system using activated red mud” Fuel, vol. 61(5), pp. 460-462, 1982