CHARACTERIZATION OF A NEW MATERIAL FOR COLLECTION AND
INERTISATION OF RESIDUAL CHROMIUM

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Chemical modification and thermal conditioning of red mud waste, a by-product resulting from
extraction of alumina from bauxite, have led to a mineral matrix with properties of collecting
chromium from waste water and sludge. This paper highlights the relationship between structure,
properties and processing by physical-chemical analyses, performed before and after processing
red mud. Its characterization consisted in: determining the composition by X-ray fluorescence,
determining specific BET surface, determining particle size and distribution by dynamic light
scattering (DLS), establishing texture and morphology of particle surfaces by scanning electron
microscopy (SEM), measuring their points of zero charge (PZC), determining the ability of
collecting chromium by static adsorption tests. Analytical investigations reflect the fact that
processing raw red mud leads to: a slight change in composition; extension of specific surface of
particles by over 30% and modification of particle sizes and distribution from 35 nm to average of
669.0 nm for 86.77% of the volume and 83.4 nm for 13.23% of the volume; the change of texture
as a result of new solid phases with a different crystallization system; the modification of the
points of zero charge and reaching a chromium collecting capacity of 60 mg/g, superior to other
unconventional adsorbent materials.

Key words: mineral matrix, specific surface, residual chromium.

INTRODUCTION

Turning hides into tanned leather involves circulation of significant amounts of
water and many chemical and mechanical processing operations, generating large
amounts of waste in the form of leather fragments, sludge and wastewaters.

Currently, most of the world leather production is processed by tanning with basic
chromium salts, and therefore, a large amount of generated wastes contain chromium.
The main ways to reduce the impact of chromium circulated in tanneries consist in
approaching best practice, which prevents the appearance of hexavalent chromium in
manufacturing flow and provides good management of chrome leather waste and
unexhausted chrome floats.

In this regard, research focused on creating an effective material for residual
chromium capturing and inertisation from tanneries was initiated. In support of this
material, the mineral matrix of red mud waste was chosen, originating from the
extraction of alumina from bauxite, whose properties of capturing heavy metals have
been demonstrated. Red mud has very high alkalinity and its main constituents are:
crystalline hematite (Fe₂O₃), titanium dioxide (TiO₂) in polymorphic forms anatas and
rutile, boehmite (gamma-AlOOH), quartz (SiO₂), sodalite (Na₄Al₃Si₃O₁₂Cl) and gypsum
(CaSO₄·2H₂O), with the presence of calcite (CaCO₃) in small amounts, whewellite
(CaC₂O₄·H₂O), gibbsite Al(OH)$_₃$ and other minor or major components depending on
processed bauxite and on the operating parameters of industrial plant. Typical values for
chemical composition of red mud are 30-60% Fe₂O₃, 10-20% Al₂O₃, 3-50% SiO₂,
2-10% Na$_2$O, 2-8% CaO and 0-25% TiO$_2$ (Hind et al., 1999). Based on these data, previous research was aimed at initiating new solid phases in the mineral matrix of red mud, capable of seizing captured chromium, very important in order to obtain a material that meets the requirements for storage as inert material. Technology of creating the adsorbent material for capturing and seizing chromium from wastewaters and muds from leather processing is easy to make, does not involve hazardous materials, produces no waste and ends with zero noxious emissions.

This paper focused on the characterization of adsorbent material, which involves approaching modern and high accuracy instrumental analytical techniques to provide additional information. Physical-structural analysis methods of materials are basic elements in determining the relationship between structure-property-processing for any field of material science. The methods through which various characteristics of red mud can be highlighted are those specific to mineral materials and are based on modern instrumental techniques.

**EXPERIMENTAL**

**Materials**

Red mud waste used in experimental research comes from storage landfill S.C. Alum S.A. Tulcea (characterized by very high pH and high alkalinity); red mud treated and conditioned according to a procedure developed in other works (Niculescu et al., 2008; Özgünay et al., 2008); 0.1 N hydrochloric acid solution, from SC SILAL TRADING SRL Bucharest; sodium chloride solution (SC CHIMOPAR SA Bucharest) of 0.5 M concentration, prepared in the laboratory; basic chromium sulphate solutions (BASF Germany), with different concentrations of chromium, prepared in the laboratory.

**Methods**

X-ray fluorescence to determine the mineralogical composition, using a Philips PW2400 spectrometer; drawing BET isotherms with ASAP (Accelerated Surface Area and Porosimetry) 2020 System to determine specific areas of material particles; dynamic light scattering DLS on a 270 Nicomp type device to determine size particle and distribution; scanning electron microscopy (SEM) with a JSM-SA (Surface Analysis) type microscope to highlight the changes occurring as a result of physical and chemical processes in the texture and morphology of particle surface; potentiometric titration with a Consort C833 device to determine the point of zero charge (PZC) of particles (Atun and Hisarli, 2000; Ghiga et al. 2007); the specific surface of the material is determined by the BET isotherm; static adsorption to determine the capacity of collecting chromium in treated and conditioned red mud. To determine chromium collection capacity in the material obtained treating and conditioning red mud basic chromium sulfate solutions were prepared, with chromium concentrations ranging from 320 mg/l and 3200 mg/l, which were put in contact with the material resulting from red mud treatment with magnesium chloride at pH 9, in liquid/solid ratio of 10/1, 20/1, 40/1 and 80/1, at room temperature (approximately 25°C) for four hours. Dispersions were filtered under vacuum and the residual solutions were analyzed by atomic absorption spectroscopy for the determination of chromium using AAanalyst 800 (PerkinElmer) spectrometer.
RESULTS AND DISCUSSIONS

Semi-Quantitative Analysis

From data analysis of X-ray fluorescence the energy and intensity of characteristic photons emitted by the sample can be found. These features allow identification of chemical elements contained in a sample of material, and determining the mass or concentration in which these are available. Mineralogical content of raw red mud is as follows: Na₂O 5.00%; MgO 2.00%; Al₂O₃ 18.00%; SiO₂ 7.20%; P₂O₅ 0.79%; SO₃ 0.81%; Cl 1.30%; CaO 3.53%; TiO₂ 8.90%; V₂O₅ 0.36%; Cr₂O₃ 0.31%; MnO 0.16%; Fe₂O₃ 51.90%. Mineralogical content of trated red mud is as follows: Na₂O 5.00%; MgO 3.00%; Al₂O₃ 20.00%; SiO₂ 9.00%; P₂O₅ 1.50%; SO₃ 1.50%; Cl 2.50%; CaO 3.44%; TiO₂ 7.84%; V₂O₅ 0.33%; Cr₂O₃ 0.20%; MnO 0.10%; Fe₂O₃ 47.10%.

It is clear that, unlike raw red mud composition, in the material obtained by treatment with magnesium salts and conditioning by a certain thermal treatment, significant changes occur, due to formation of new solid phases including chlorine and magnesium ions, according to anticipations.

Determining BET Specific Surface

Dry raw red mud is a fine granular material, in which 90% of particles are smaller than 75 μm. In previous experimental studies (Ghiga et al. 2007; Niculescu (Ghiga) et al. 2008) BET specific surface of particles was determined, located at the value of 36.5797 m²/g. For treated and conditioned red mud, the analytical results reveal a specific area of 48.0673 m²/g, which represents a specific area extension of over 30% compared to the specific surface of raw red mud (36.5797 m²/g), which was expected, as a consequence of changes induced by formation of new solid phases.

Determining Particle Size and Distribution

DLS measures Brownian motion and correlates it with particle size. The relationship between size and velocity of a particle due to Brownian motion is given by Stokes-Einstein equation. Zetasizer Nano device measures the fluctuations of scattered light intensity and uses them to calculate the size of particles in the sample. Figures 1 and 2 present the results of DLS analysis of raw red mud compared to red mud treated with magnesium chloride resulting from processing.

![Figure 1. Distribution of raw red mud particles](image)

There is a clear change of particle size and distribution as a result of the formation of new solid phases. While particle distribution is very dense in the raw red mud, due to their very small size, of about 35 nm, in the red mud treated with magnesium chloride, larger particles and aggregates are abundant, ranging from 432 to 949 nm with an average of 669.0 nm, which takes up 86.77% of the volume, while smaller particles, 56-105 nm in size, with an average of 83.4 nm, represent 13.23% of the volume.
It should be noted that the dimensional range of the raw red mud is no longer found in the treated red mud, which is a consequence of crystal growth and formation of new solid phases, but also of the aggregation of particles.

**Establishing Texture and Morphology of Particle Surface**

Scanning electron microscopy (SEM) can reveal changes and differences occurring as a result of physical-chemical processes, in the texture and morphology of particle surface, providing information that can help, for example, to determine the correlations between technological parameters and particle surface properties, in order to improve techniques of creating a particular material. Figures 3 and 4 present SEM images of raw red mud compared to red mud treated with magnesium chloride resulting from processing.

In Figure 3, the uniformly distributed small granules correspond to iron and titanium, and large flat particles correspond mainly to aluminum. Overall, raw red mud particles have a dense distribution, which cannot be said about the red mud treated with magnesium chloride, whose SEM image is shown in Figure 4. It is clear that very small particles are no longer found in the processed material, the latter having a totally different texture, with much larger and mostly flat aggregates, with wide spaces between them, which proves that the material has a much higher porosity. These changes are the result of formation of new solid phases of carbonate hydrotalcite, $\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}\cdot4\text{H}_2\text{O}$, with hexagonal structure, forming platelike, flat crystals.
Determining Point of Zero Charge (PZC)

In terms of electricity, red mud particle surface has a significant negative charge due to adsorbed ionized hydroxyl groups, aspect also proven by the point of zero charge value. PZC experimentally determined in previous studies is situated in the acid range at pH values of 6.25 to 6.50 for wet raw red mud and from 6.28 to 6.69 for dry raw red mud (Ghiga et al. 2007; Niculescu et al. 2008).

Changes induced by formation of new solid phases as a result of chemical and thermal treatments undergone by red mud waste, affect properties of superficial charge of particles, a feature of these being the point of zero charge (PZC), parameter which is generally sensitive to mineralogical composition of red mud.

PZC of the treated red mud is at a pH value of 6.21, in acid range, favorable for capturing positive charge ions, which corresponds to theoretical predictions which was the basis for developing technology capable to ensure the induction of new solid phases with properties of capturing chromium.

Determining the Capacity of Collecting Chromium

The chromium concentration in exhausted solutions is at reasonable values (allowed in industrial effluents) up to a certain amount of chromium charge in red mud, value associated with the adsorption efficiency of over 99. Figure 5 graphically represents the variation of the chromium amount collected by red mud in relation to the amount of chromium found in solution, at neutral final pH.

The left side line stands for the adsorption stages up to saturation with chromium ions and the right side line stands for the supersaturation by random adsorption beyond adsorption capacity. The intersection of the straight lines represents the adsorption capacity of the material. It may be noted that this point is close to the value of 60 mg/g of neutralized red mud.

The literature in recent years (Wu et al., 2008) presents attempts to capture the trivalent chromium in different conventional or unconventional adsorbent materials whose maximum adsorption capacity (mg/g) was in the range of 4 ... 40 mg/g.

Figure 5. Variation of chromium quantity retained in red mud treated with MgCl₂

From this perspective, the obtained adsorbent material has a capacity of chromium capture of about 50% higher than the capacity of other conventional and unconventional materials; therefore it can be considered an advanced material.
CONCLUSIONS

Methodology for characterizing material for capture and sequestration of chromium, made of mineral waste, namely red mud, requires approaching modern high accuracy instrumental analytical techniques to provide additional information.

X-ray fluorescence spectra allowed to establish the difference in composition between raw red mud and treated and conditioned red mud. BET isotherms showed an extension of the specific surface of red mud as a result of processing, by approximately 30%. Dynamic light scattering (DLS) revealed the modification and distribution of particle sizes from 35 nm to averages of 669.0 nm for 86.77% of the volume and of 83.4 nm for 13.23% of the volume.

By means of scanning electron microscopy (SEM) it was highlighted that raw red mud particles have a dense distribution and a homogenous texture, while the treated red mud particles have a totally different texture, with much larger and mostly flat aggregates with wide spaces between them, which proves that the material has a much higher porosity.

Using data from potentiometric titration of red mud particles points of zero charge (PZC) before and after treatment and conditioning were determined and it was found that, in both cases, they are located in the acid range, at pH values between 6.00 and 6.50, favourable for capturing positive charge ions, such as chromium ions, from wastewaters and sludge resulting from leather processing.

Tests of adsorption of chromium in chemically treated and conditioned red mud, performed in static condition, have led to a chromium capturing capacity of 60 mg/g, superior to other unconventional adsorbent materials, a result which justifies further research in this direction.

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