RED MUD AS MULTIFUNCTIONAL MATERIAL FOR POLLUTANTS CAPTURING FROM WASTEWATER

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Red mud is a waste of alumina manufacturing from bauxite using the Bayer process, containing a mixture of minerals with ion exchange properties. Previous experiments have demonstrated the ability of red mud, raw or processed, to capture and retain chromium ions from wastewater and sludges. The present study highlights the ability of chemically modified red mud to capture other organic and inorganic substances, such as those found in effluents of hide processing. Laboratory analysis of the residual solutions, before and after treatment with the mineral complex of red mud, by potentiometric, gravimetric, photocolorimetric, and spectrophotometric methods, has shown that: the phosphate and sulphate content can be reduced by 80-99%, depending on their pH, silicon content can be reduced by 93%, the content of metal-complex dyes can be reduced to 100 % for blue dyes range, the chemical oxygen demand can be reduced by approximately 85%. The mineral complex of red mud is a multifunctional material for wastewater treatment, by simple, effective, and reproducible processes, which can be embedded in the composition of building materials and design of roads.

Keywords: mineral matrix, multifunctional, wastewater.

INTRODUCTION

Tannery wastewater is difficult to treat due to its high content of low biodegradability chemicals (Banuraman *et al.*, 2013).

For tannery wastewater treatment, various treatment options (Sivaprakasam *et al.*, 2008; Imran *et al.*, 2012; Kanagasabi *et al.*, 2013) were studied. Despite these efforts, most treatment plants for such tannery wastewater operate based on the principle of chemical coagulation of pollutants in water cumulated from natural leather processing operations. Following the global chemical treatment in wastewater treatment plants, most of inorganic and organic content of wastewaters from natural leather processing is transferred into residual sludge, whose traceability is not always very clear and which must be subsequently managed in accordance with environmental protection regulations.

Depending on the particularities of each tannery, various procedures can be adopted in order to reduce wastewater treatment costs, which are generally significant. The pre-treatment of individual wastewaters may be a solution for both reducing the amount of residual mud resulted in wastewater treatment and for an expansion of mud recovery possibilities.

A special category of wastewaters from tanneries is that of wastewater resulting from preliminary operations designed to prepare the dermis for tanning: washing, soaking, liming, deliming, pickling. In addition to a high load of organic substances, these wastewaters also contain many inorganic compounds.

Due to their high organic matter content, these wastewaters have a particularity, given their very high chemical oxygen demand. In previous studies (Niculescu, 2013) it was shown that, for this type of industrial effluents, chemically modified red mud has the ability to reduce chemical oxygen demand by approximately 85%.

In this study we considered the possibility of treating industrial effluents for controlled capture of various inorganic substances using a mineral complex made by chemical modification of red mud (Niculescu *et al.*, 2009), a waste of manufacturing alumina from bauxite using the Bayer process.

Red mud, raw or processed, has a great ability to capture and retain a wide range of pollutants, such as dyes, anions, heavy metals (Fu *et al.*, 2011; Huang *et al.*, 2008; Vaclavikova *et al.*, 2006). Chemical modification of red mud to develop its ability to capture a specific compound (such as chromium, for example) and physical conditioning (Niculescu *et al.*, 2009; Niculescu *et al.*, 2010) do not cancel the affinity of this material for other chemical species. Recent results (Wendling *et al.*, 2012) have set apart the mineral complex from red mud waste as a tool for managing the aquatic ecosystem due to its sorption capacity for dissolved organic carbon, phosphorus, and for all nitrogen species found in water.

In this work we studied the possibility of reducing phosphates which, although they are not specific to hide processing, can be found in larger or smaller amounts in wastewaters from all operations preceding tanning, as well as the sulphates found in significant amounts in waters resulting from pickling operation, discharged at a rate of approximately 50% before leather tanning using basic chromium salts. Simultaneously, the mobility of iron and silicon in the mineral complex composition was tested, due to their instability at pH variations in experimental conditions.

EXPERIMENTAL

Experimental Techniques

Experiments were conducted to transfer phosphates and sulphates from wastewaters into the chemically modified and conditioned red mud.

The mineral complex (chemically modified red mud) was dispersed in wastewater samples, in a solid/liquid ratio of 1/10. The adsorption process was carried out at room temperature (approximately 20°C), under stirring for 4 h. After stirring time lapse, each dispersion was vacuum filtered. After stirring program completion, dispersions were vacuum filtered, and filtrates were analysed to determine colour changes and sulphate, silicon and phosphate content.

Methods of Analysis

Residual solutions from preliminary operations of natural leather tanning, before and after treatment with the mineral complex, were analysed using: potentiometric methods to determine pH, according to STAS 8619/3-1990, gravimetric methods to determine sulphate content, according to STAS 8601-1970 and photocolorimetric methods to determine phosphate and silicon content, using a HANNA Multi-Parameter Ion Specific Meter C209.

RESULTS AND DISCUSSIONS

Waste waters from operations preceding tanning (washing, soaking, liming, deliming, pickling) were analysed both before and after treatment with the mineral complex based on chemically modified red mud.

Wastewaters from the following operations before treatment: washing (pH 6.80, phosphate content 85 mg/l); soaking (pH 6.80, phosphate content 130 mg/l, silicon content 10.55 mg/l); liming (pH 12.11, phosphate content 255 mg/l); deliming (pH 8.70, phosphate content 10.3 mg/l, silicon content 1.06 mg/l); pickling (pH 2.55, phosphate content 30.2mg/l, sulphate content 34000 mg/l, silicon content 1.24 mg/l).

Table 1 presents codes assigned to studied wastewaters.

Table 1. Origin of studied wastewaters

Sample code	Sample W	Sample S	Sample L	Sample D	Sample P
Technological operation	Washing	Soaking	Liming	Deliming	Pickling

Analytical results, illustrated in figure 1, demonstrate that values of phosphate ion content decrease significantly after treatment of wastewaters with chemically modified red mud. The capture and retention rate of phosphate ions by chemically modified red mud may be influenced to a certain extent by the amount and nature of the other compounds found in wastewaters (particularly organic substances), which compete for the adsorption centres of red mud particles, but the significant influence is that of pH value at which the adsorption process starts.

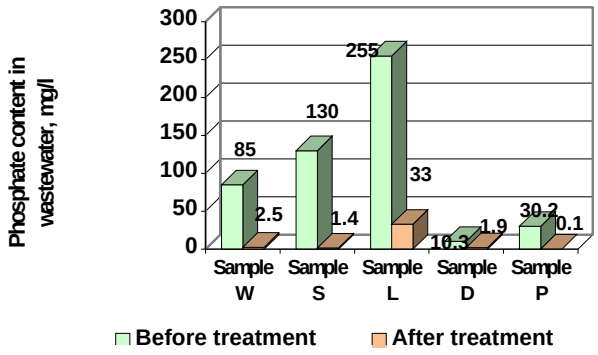

Figure 1. Reduction of phosphate content

Table 2 presents initial pH values of wastewaters, an important parameter in relation to the point of zero charge of the mineral complex.

Table 2. Initial pH value of wastewater

Sample	Sample W	Sample S	Sample L	Sample D	Sample P
Initial pH	6.80	6.80	12.11	8.70	2.55

The proportion in which phosphate ions can be removed from wastewaters using chemically modified red mud is given in figure 2.

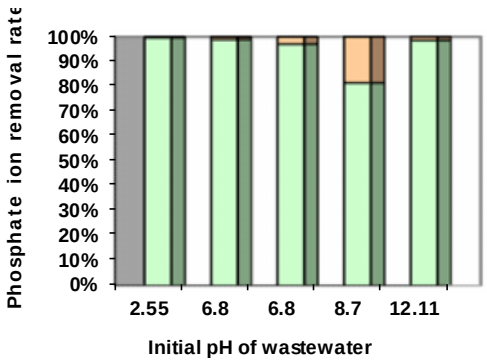

Figure 2. Influence of pH on the phosphate ion removal rate

It should be noted that the higher the difference between the initial pH of the solutions and the pH of the aqueous extract of chemically modified red mud used as adsorbent, the more effective the removal of phosphate ions.

Results of the experiment to capture phosphate ions from wastewaters of leather processing are in accordance with recent results of experiments to remove phosphorus from water, using either raw red mud, or improved by thermal processing or combined with photocatalysis, in which case phosphorus removal may exceed 94% (Qin *et al.*, 2012; Tie *et al.*, 2013; Zhang *et al.*, 2013).

In the case of wastewater from the pickling operation, an 85% reduction in sulphate content is also noticed, figure 3, as well as a significant increase in pH value, from 2.55 to 7.54, until it falls into the range regulated for discharge into sewers and natural receptors (6.5-8.5), in accordance with national (NTPA-001/2002 and NTPA-002/2002 with subsequent amendments) and European standards.

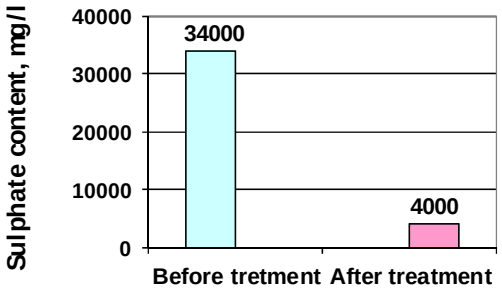

Figure 3. Reduction of sulphate content

This is an important aspect, because in most of the technologies applied in chromium tanning, half the residual float from pickling process is discharged, and sulphate content of over 30,000 mg/l and pH < 3 is a significant burden for wastewater treatment plants.

Because the pH values of wastewaters from tannery have a very wide range, and chemically modified red mud has a complex mineral matrix, random tests were carried out by photocolorimetry on iron and silicon content. The results of these tests confirmed that the iron is not solubilized in the mineral matrix, being undetectable after wastewater treatment, while in the case of silicon, both content decreases in wastewater after treatment with chemically modified red mud, and content increases in wastewater after treatment with chemically modified red mud were recorded, figure 4.

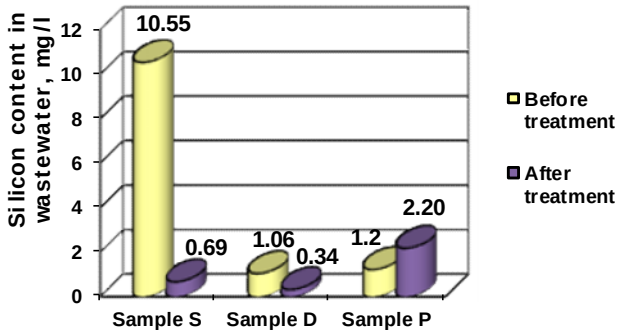

Figure 4. Evolution of silicon content in wastewaters

This behaviour is the consequence if significant differences in pH of the tested wastewaters. Experimental results prove the ability of the material to retain silicon from wastewaters with alkaline or slightly acid pH, and transfer the silicon from the mineral matrix into the wastewaters at highly acid pH.

This study was focused on the composition of the liquid phase, to establish the effectiveness of removing some anions, but for practical applications, it is important to establish also the composition of solid phases, as well as their properties, given that previous papers (Niculescu *et al.*, 2011) have demonstrated the importance of the presence of phosphate ions in the inertisation process of chromium captured by red mud from wastewaters of leather tanning. In this regard, it is noteworthy that an individual treatment of wastewaters from leather processing, carried out in cascade, using the same charge of mineral complex based on red mud, could set the premises both for recirculating wastewaters and for enriching the mineral complex with various compounds to enhance its chemical stability, until reaching the point where it could be directed to applications not yet studied.

CONCLUSIONS

The material made of chemically modified red mud, designed to capture chromium and render it inert, is able to retain phosphates from wastewaters. The mineral complex based on red mud can reduce the phosphate ion content by over 80% from tannery wastewaters. By treating wastewaters from preliminary operations of leather tanning, using the mineral, the higher the difference between the initial pH of the solutions and the pH of the aqueous extract of chemically modified red mud used as adsorbent, the more effective the removal of phosphate ions.

In the acid pH range, the mineral complex is able to reduce sulphate content by over 85%.

In wastewater with slightly acid or alkaline pH, the mineral complex can reduce silicon content by 30% to 80%.

The mineral complex made by chemical modification of the alkaline red mud waste is a multifunctional material.

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