Study on Chemically Modified Red Mud for Pollutants Capturing from Industrial Effluents

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This study demonstrates the ability of mineral complexes, resulting from chemical modification of red mud waste, of capturing various substances found in wastewaters from the preliminary operations of natural leather tanning process. Red mud is a waste of alumina manufacturing from bauxite using the Bayer process, containing a mixture of minerals with ion exchange properties. Experiments have revealed that, besides its intrinsic ability to capture ionic chromium from wastewater and sludge, the mineral complex of chemically modified and conditioned red mud has an affinity for other compounds found in effluents resulting from leather processing. The current study has shown that, by treating individual wastewaters from preliminary operations of leather tanning, using a mineral complex based on red mud, the phosphate content of washing, soaking, liming, and pickling wastewater can be reduced by 80-99%, depending on their pH, and sulphate content in the pickling float by 88%. Simultaneously, the possibility of reducing silicon content, which may be found in washing and soaking wastewaters, by 93%, while the presence of silicon in other wastewaters is insignificant. The transfer of these substances into the mineral complex is simple, effective, and reproducible.

Keywords: wastewaters, mineral complex, multifunctional, red mud

Hide processing in order to obtain semi-processed leather for footwear, garment, furniture upholstery, technical or decorative articles, etc., occurs through an alternation of chemical physical and mechanical operations, with high water consumption, which generates a large amount of solid waste and wastewaters [1]. Tannery wastewater is difficult to treat due to its high content of low biodegradability chemicals [2].

For tannery wastewater treatment, various treatment options [3-6] 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. One solution is water pretreatment using pollutant-specific adsorbent materials, which involves using an array of materials that often generate costs and labor whose quantification leads to a rather low economic efficiency. From this perspective, a pre-treatment of individual wastewaters may be a solution for both reducing the amount of residual mud 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. Wastewater resulting from the washing operation contain large amounts of salt and organic residues. Wastewater from the soaking operation contain salt, sodium carbonate and emulsifiers, in addition to soluble proteins, blood serum and solid organic impurities. Wastewater from the liming operation contain large amounts of proteins, in particular keratin, and large amounts of hydrated lime, sodium sulphide, sodium hydrosulphide. Deliming wastewaters contain: ammonium salts, inorganic acids, organic acids. Pickling wastewater mainly contain sodium chloride, calcium salts, inorganic acids.

Due to their high organic matter content, these wastewaters have a particularity, given their very high chemical oxygen demand. In previous studies [7] 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, a waste of manufacturing alumina from bauxite using the Bayer process.

Chemical modification of the red mud was achieved, according the principle presented in [8], by treating raw red mud, having a *p*H about 13, with magnesium chloride solution 1M concentration, added in small doses under continuous stirring and checking the *p*H value, to stabilize 9 ± 0.02. The dispersion obtained was filtered under vacuum and the sediment was gradually dried at 50°C, 60°C and 70°C to achieve constant mass. Conditioning was carried out by heating at 110°C and was maintained at this temperature for 3 h [9].

Red mud, raw or processed, has a great ability to capture and retain a wide range of pollutants, such as dyes, anions, heavy metals [10-15].

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Chemical modification of red mud to develop its ability to capture a specific compound (such as chromium, for example) and physical conditioning [9, 16] do not cancel the affinity of this material for other chemical species.

Recent results [17] 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 *p*H variations in experimental conditions.

Experimental part

Materials and methods

Mineral complex based on chemically modified red mud, according to the process presented in [15], with the following characteristics [10]: appearance: solid, pulverous, hematite red coloured material; texture and morphology of particle surface: large, mostly flat aggregates, with wide spaces in-between, highlighted by Scanning Electron Microscopy (SEM); composition: Na_2O 5.00%; MgO 3.00%; Al_2O_3 20.00%; SiO_2 9.00%; P_2O_5 1.50%; SO_3 1.50%; Cl 2.50%; CaO 3.44%; TiO_2 7.84%; V_2O_5 0.33%; Cr_2O_3 0.20%; MnO 0.10%; Fe_2O_3 47.10%, determined by X-ray fluorescence spectroscopy; *p*H of aqueous extract: 9.0±0.2; point of zero charge (PZC): in acid range, at *p*H=6.21, determined by potentiometric titration; BET specific surface: 48.0673 m^2/g, determined using an ASAP device (Accelerated Surface Area and Porosimetry) 2020 System, using nitrogen as analytical adsorbent; particle size, determined by dynamic scattering (DLS) on a Zetasizer Nano device is submicronic, of 83.4 nm diameter in 13.23% of the volume, while the remaining 86.77% is filled with particles of 669.0 nm diameter.

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

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.

Experiments were conducted to transfer phosphates from wastewaters from: I – washing, II – soaking, III – liming, IV – deliming, V – pickling, as well as sulphates from float V – pickling, into the chemically modified and conditioned red mud. Experiments were carried out as shown in the process flowchart in figure 1.

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.

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.

Table 1 presents codes assigned to studied wastewaters.

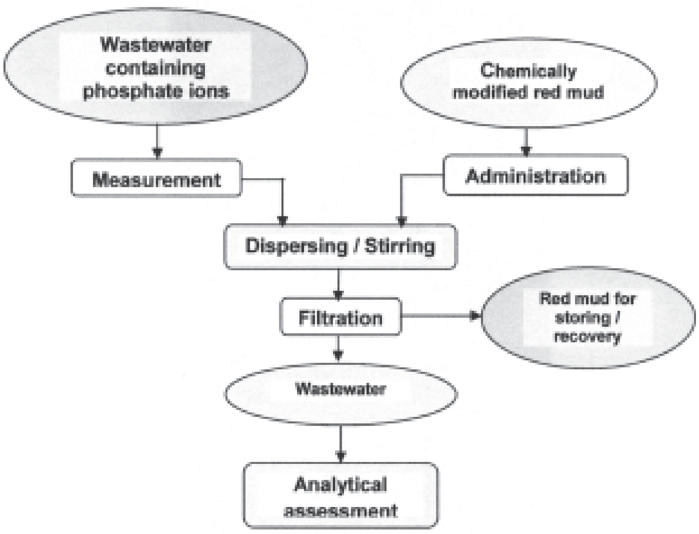

Fig. 1. Process flowchart of experiments conducted to reduce phosphate ion content in wastewater

Table 1
ORIGIN OF STUDIED WASTEWATERS

Sample code	Sample I	Sample II	Sample III	Sample IV	Sample V
Origin of sample (technological operation)	Washing	Soaking	Liming	Deliming	Pickling

Sample	Sample I	Sample II	Sample III	Sample IV	Sample V
Initial pH	6.80	6.80	12.11	8.70	2.55

Table 2
INITIAL *p*H VALUE OF WASTEWATER

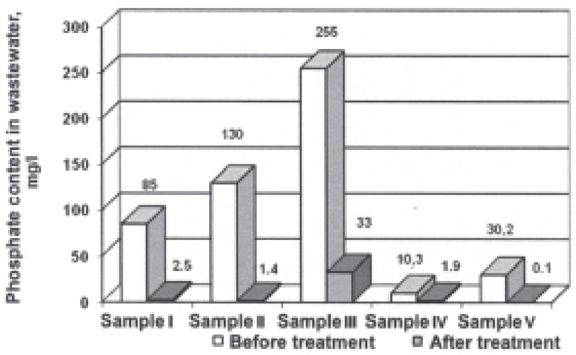

Fig. 2. Reduction of phosphate content

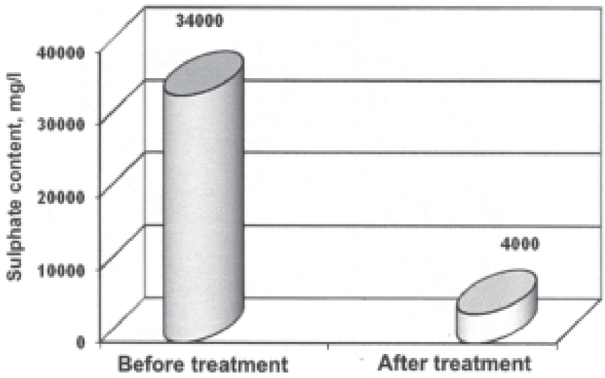

Fig. 4. Reduction of sulphate content

Analytical results, illustrated in figure 2, 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 centers of red mud particles, but the significant influence is that of *p*H value at which the adsorption process starts. Table 2 presents initial *p*H values of wastewaters, an important parameter in relation to the point of zero charge of the mineral complex.

The proportion in which phosphate ions can be removed from wastewaters using chemically modified red mud is given in figure 3.

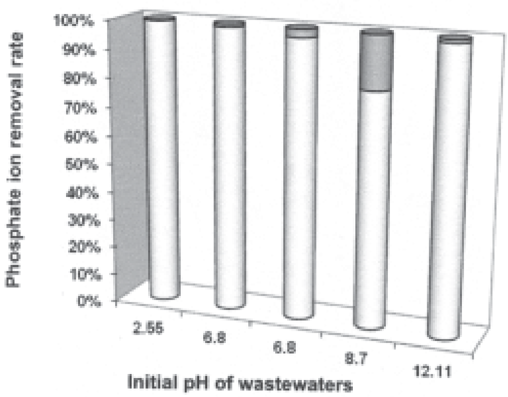

Fig. 3. Influence of *p*H on the phosphate ion removal rate

It should be noted that the higher the difference between the initial *p*H of the solutions and the *p*H 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% [18-20].

In the case of wastewater from the pickling operation, an 85% reduction in sulphate content is also noticed, figure 4, as well as a significant increase in *p*H 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.

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 *p*H < 3 is a significant burden for wastewater treatment plants.

Given that chemically modified red mud has a complex mineral matrix and tested wastewaters have a very wide range of *p*H values, random tests were carried out by photo colorimetric methods 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 5.

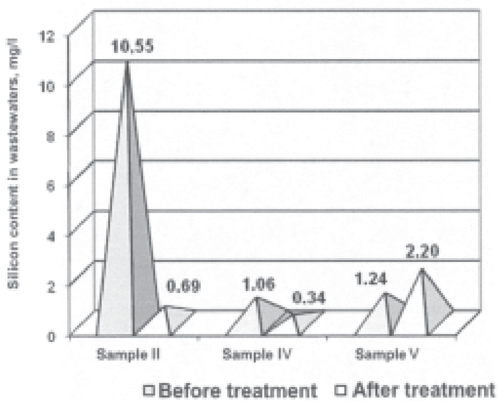

Fig. 5. Evolution of silicon content in wastewaters

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

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 [21] have demonstrated the importance of the presence of phosphate ions in the inertization 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 specific material designed to capture chromium and render it inert, made of chemically modified red mud is able to retain phosphates from wastewaters. By treating wastewaters from preliminary operations of leather tanning, using the mineral complex based on red mud, phosphate ion content can be reduced by over 80%. The higher the difference between the initial *p*H of the solutions and the *p*H of the aqueous extract of chemically modified red mud used as adsorbent, the more effective the removal of phosphate ions.

In the acid *p*H range, the mineral complex is able to reduce sulfate content by over 85%.

In wastewater with slightly acid or alkaline *p*H, 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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