Synthesis of zeolites from carbon by-products for the retention of Cr from the tannery industry effluents

Abstract

Cr effluents are a widespread environmental problem associated with tannery wastewaters. The present study aimed at evaluating the potential use of low-cost sorbents such as zeolites-based carbon by-products in the retention of Cr from the tannery industry effluents, which is crucial for environmental protection and economic reasons.

Introduction

Although the synthesis of zeolitic materials from fly ash generated from the combustion of coal in thermoelectric plants has been extensively researched from conventional methods and more sophisticated treatments, there are few studies on the use of mining waste from the coal on a global scale. Rios and Williams' carried out for the first time the synthesis of zeolitic materials from natural clinker as starting material. The natural clinker is part of the sterile material obtained as a result of the exploitation of coal and the coal geologists define it as a pyrometamorphic rock generated as a consequence of the thermal alteration of the sedimentary protolith from the natural combustion of carbon mantles. Rios et al. report the synthesis of different types of zeolites ( sodalite, cancrinite, filipsite and faujasite) from natural clinker. The great compositional similarity of the natural clinker with the volcanic material from which the natural zeolites originate by post-magmatic hydrothermal activity, could justify the development of future research in the field of the synthesis of new materials of great industrial application. Its potential application could consume only a small part of the natural clinker generated by the combustion of coal, the final products (zeolites) obtained could reach a value added much higher than that presented in the applications that currently the natural clinker has in the industry carboniferous of our country. The zeolitic materials synthesized by Rios et al. show suitable adsorbent properties for their application in the treatment of contaminated effluents. The contamination of water by heavy metals is an aspect of great economic and environmental importance in many parts of the world. Pollution by chromium (Cr), due to its high toxicity, is considered among the most aggressive for the ecosystem and the health of the population. This is a pollutant in surface and groundwater as a result of numerous industrial activities such as the preservation of wood, textile staining, leather tanning, electroplating and metallic finishes. Cr exists mainly as valence states Cr(III) and Cr(VI), although Cr(0), Cr(II) and Cr(V) can also occur. The anions of Cr(III), chromate (CrO$_4^{2-}$) and dichromate (Cr$_2$O$_7^{2-}$), are strongly oxidizing, with chromate being a known carcinogen and an alleged mutagenic and teratogenic agent.

On the other hand, the toxicity of Cr(III) is negligible, since it often forms insoluble hydroxides under conditions of almost neutral pH. US EPA it requires 0.05 and 0.1 mg/L of Cr(VI) in drinking water and inland surface waters, respectively. Consequently, the Cr containing sewage should be treated to reduce the Cr(VI) to the permissible limits before discharge into the environment. The conventional methods used to eliminate Cr(VI) from industrial wastewater include the reduction followed by chemical precipitation, adsorption by activated carbon, electrochemical precipitation, ion exchange, solvent extraction or reverse osmosis, highlighting the retention by adsorption or by ion exchange. However, these processes have some disadvantages, such as incomplete metal extraction, large amount of reagents and energy consumption, generation of toxic sludge and other waste products and usually very high costs. Therefore, it is necessary to resort to the use of less expensive alternative technologies for the treatment of contaminated effluents. The waste management of the coal industry should raise three possible and simultaneous alternatives, reduction, reuse and recycling. The waste treatment strategy should consider that these represent a potential resource which could be exploited and not simply a problem to solve. The technological innovation contemplates the recycling of waste associated to the coal industry (by the exploitation of coal or by the combustion of this in thermoelectric plants) in order to carry out the synthesis of zeolites with application in the retention of Cr from effluents of the tannery industry taking advantage of its ion exchange capacity. In the case of the retention of Cr, there are references on the exchange of this element in some natural zeolites and on its use in the wastewater treatment of the leather industry. In some works it is mentioned that the retention of Cr decreases sharply with the increase in the concentration of this ion in the wastewater; in others it is indicated that this ion breaks the zeolitic structure by removing Al and entering the structure. Santiago et al. report that the unmodified zeolite is ineffective for the retention of Cr(VI), so this should be modified with the use of organic cations or bacteria. On the other hand, it is important to perform a comparative study of the speed and relative capacity of retention of Cr(VI) in FAU type zeolites synthesized from natural clinker and fly ash, although it might be necessary to modify it with some bacteria that promotes the reduction of Cr(VI) to Cr(III), the latter being retained in the zeolite by ion exchange. In case of using the biosorption process, the modified zeolite could be used as a competitive and selective catalyst in catalytic oxidation of volatile organic compounds.

Materials and methods

Cr effluents should be collected from the tannery industry, taking into account on-site analyses of the pH and electrical conductivity. For the treatment of Cr effluents, low-cost sorbents such as zeolites-based carbon by-products can be used as sorbents. Characterization
of sorbents should include X-ray diffraction and scanning electron microscopy. The sorption of Cr onto zeolites-based carbon by-products can be studied in laboratory batch experiments, which should be carried out at room temperature to investigate the efficiency of the sorbents for removing Cr from the tannery industry effluents.

**Conclusion**

Preliminary results reveal that the use of low-cost sorbents such as zeolites-based carbon by-products can be effective in reducing the Cr concentration, and, therefore, these sorbents can be applied in wastewater management scenarios, particularly in the treatment of Cr effluents. However, it will be necessary to design and execute detailed experiments to explore further application.

**Acknowledgments**

The author thanks to Dr. Craig Williams for introducing him to the science of zeolites and to the Universidad Industrial de Santander and the University of Wolverhampton for providing research facilities for the study of zeolites.

**Conflicts of interest**

The author declares that there are no conflicts of interest.

**References**