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Environmental uses of zeolites in Ethiopia

Isabel Díaz

Instituto de Catálisis y Petroleoquímica, CSIC, c/Marie Curie 2, 28049 Madrid, Spain

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ABSTRACT

In the past six years we have been intensively collaborating with the Chemistry Department of Addis Ababa University as well as Haramaya University to bust scientific knowledge related to zeolites and zeolite applications. Initially, we teamed up with geologists and government actors in the mining sectors; as a result we got access to natural zeolites from the north of the country, as well as other industrial minerals such as kaolin. In parallel we developed research activities in the use of zeolites as adsorbents and in catalytic processes related to environmental applications of necessity in Ethiopia. In the first part of this paper I will describe two examples of adsorption processes using mineral resources: one is a natural stilbite used to develop an adsorbent to remove fluoride from drinking waters; and the second one uses virgin kaolin to prepare a synthetic zeolite 4A that we used to remove chromium from tannery wastewaters. Finally, two catalytic examples will be described: in the first one we tackled the photocatalytic degradation of dyes from textile industries using Ti-modified natural and synthetic zeolites, and in the second one we used modified mordenites, both natural and synthetic, for the conversion of glucose into 5-HMF.

1. Introduction

Despite scattered findings of zeolites deposits around Ethiopia, no efforts have been made in exploring deeply the presence and potential industrial interest of zeolites in this country. Research and development of scientific knowledge related to zeolites coupled with capacity building may contribute to gain the interest of stakeholders. With this aim, in the past six years we have been intensively collaborating with the Chemistry Department of Addis Ababa University as well as Haramaya University to bridge this gap. In the same line, the Research and Development Directorate of the Ministry of Mines was interested in exploring new applications of industrial interest involving other Industrial Minerals already under exploitation along the country, such as bentonite and kaolinite. When we surveyed the accessible Ethiopian industries, we learnt that the main demand of zeolites was as adsorbents or ion exchangers in water and wastewater treatments.

Zeolites are crystalline microporous aluminosilicates with a defined three-dimensional structure composed by Silicon and Aluminium tetrahedra which share oxygen vertices. These tetrahedral units may connect in different fashion giving yield to a wide variety of topologies and thus forming a wide range of porous structures. Zeolites are found in nature, in volcanic areas all over the world, but they can also be synthesized in the laboratory. In the case of natural zeolites, the inorganic network is composed of silicon and aluminium in such a way that the final network charge is negative, and thus generating the necesity of extra framework cations that compensate the charge. This counter cations are located in the pores or cavities of the zeolites. These counter ions are known as extra framework cations, since they are not directly bonded to the inorganic network, but are retained by steric effects and electrostatic interactions. This type of interactions allows for an exceptional mobility characteristic of the main applications of zeolites in industry as cation exchangers in the sectors of water purification and detergents. Application of natural zeolites for water and wastewater treatment by adsorption is still a promising technology in environmental cleaning processes. Adsorption properties of natural zeolites in comparison with other chemical and biological processes have the advantage of removing impurities also at relatively low concentrations and allow conservation of water chemistry.

According to the report of 2010, the global market for natural zeolites grew from 3.98 million to 5.5 million tons and in the same time period, the usage of synthetic zeolites was projected to reach 1.86 million tones [1]. While 90% of natural zeolites are mainly applied in the construction industry, the remaining 10% find uses in processes such as waste water treatment, animal feeding, horticulture, odor control and other miscellaneous applications. However, due to the large presence of impurities, natural zeolites have lim-

E-mail address: idiaz@icp.csic.es

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ited applications for industrial processes where synthetic zeolites are preferred.

In Ethiopia the incredible economic growth of the past ten years is mainly due to the development of new manufacturing plants including textile and tanning factories. However, the environmental protection and WASH (Water, Sanitation and Hygiene) Programs are not running as fast as the increasing industrial development. More potentially polluted water will eventually become accessible as drinking water points. In addition to this, there are already geogenic contaminants such as Fluoride and Arsenic which are already polluting drinking waters all over the world. Fluoride contamination of groundwater is a spontaneous process occurring in volcanic areas where the groundwater passes through F-containing volcanic rocks such as fluorite (CaF_2), fluoroapatite ($Ca_5(PO_4)_3F$) and cryolite (Na_3AlF_6). In small concentrations, it is beneficial for children in strengthening bones and preventing tooth decay [2]. However, an excessive intake of fluoride leads to dental or skeletal fluorosis and its continuous intake in time may lead to cancer, osteosclerosis or even liver and kidney damages in human beings [3]. In Ethiopia more than 8 million people in rural areas of the Rift Valley, are at high risk due to a regular exposure to fluoride contaminated groundwater, the largest source of water for human consumption [4].

The leather and textile industries are becoming one of the major industrial sectors in Ethiopia that contributes substantially towards the national economy. According to the Ethiopian leather evaluation final report by UNIDO (2012) there were 26 tanneries in Ethiopia and almost all of them employ chrome tanning [5]. The wastewater of tanning process is usually discharged, without proper treatment, into the sewerage system leading to a health and environmental problem [6]. The Ethiopian Environmental Pollution Control Proclamation No. 300/2002 has limited the total chromium and Cr(VI) from tannery wastewater to the environment to 2 mg/L and 0.1 mg/L, respectively.

In the case of Ethiopian Textile Industry, the Development Institute (ETIDI), has reported that more than 14,250,406 kg of various types of dyes and chemicals have been used by their factories in 2011. The Ethiopian Environmental Protection Authority (EPA) as an environmental regulatory and monitoring body is setting the laws on environmental pollution control which is generating an urgent demand for treatment of textile wastewater. A wastewater with high concentrations in chromium salts and dyes may be pro-carcinogenic and exhibit high level of toxicity [7].

In our work, we have emphasized the use of natural or synthetic zeolites for environmental remediation in the lines described above. In this manuscript, a forth section is included devoted to the use of zeolites in green chemistry (the conversion of glucose into of 5-HMF) in an attempt to provide other contribution to the sustainable industrial development in which zeolites may play a role. The information included in this manuscript is a small review of the work done in these years related to these uses already mentioned. Four Phd Thesis were developed in the course of the research exposed in this manuscript. Six more Phd Thesis are currently in progress and directly or indirectly related to the use of Zeolites in the Chemistry Departments of Haramaya and Addis Ababa Universities in Ethiopia.

2. Results and discussions

Zeolites are a vast natural resource in Ethiopia that remains unexploited due to lack of scientific knowledge and available manpower with a geology background and means to initiate the systematic exploitation of this resource. Previous studies showed abundant resources of mordenite and clinoptilolite near Nazret [8] and philipsite and also clinoptilolite in the Awassa area [9]. In our attempt to thrive the exploitation and further involvement of zeolites in the chemical industry of Ethiopia, we have been engaged for the past six years in academic activities with the Inorganic Stream of the Chemistry Department at Addis Ababa University aiming to fill up the gap developing capacities in the scientific knowledge related to zeolites. From research point of view, we devoted extra efforts in developing new research lines using local knowledge in electrochemistry [10], synthesis of coordination compounds [11–13] and green chemistry [14–17]. At the same time, we have collaborated with the Earth Science Department of Addis Ababa University as well as with the Directorate of Research and Development of the Ministry of Mines of Ethiopia in order to survey the potential deposits of natural zeolites in the country. One of the collaborative projects developed in the north region of the country, yielded several zeolitic phases and at least one highly-pure large deposit of stilbite could be identified [18]. Besides, we have devoted large efforts in adding value to other Industrial Minerals, such as Bentonite [19–21] and Kaolinite [22,23], with known deposits at early stages of exploitation. On our side, we analyzed the samples and evaluated potential applications that could justify their commercial exploitation. The initial identification of the zeolitic phases was carried out by XRD and ICP. Depending on the type of zeolite, purity and chemical composition, the natural zeolites were tested in two groups of applications: adsorption or catalysis. Adsorption processes involved defluoridation of drinking waters, and removal of chromium from tannery wastewater. Catalytic processes involved photodegradation of dyes from textile wastewaters and the conversion of glucose to 5-HMF.

2.1. Zeolitic phases devoted to adsorption

Two cases are presented in the following paragraphs of natural resources employed in adsorption processes devoted to environmental remediation.

2.1.1. Defluoridation of drinking water

It has been reported that the consumption of fluorinated water remains above the recommended healthy limit of 1.0 mg/L in the majority of rural areas in developing countries. Thus, more than 260 million people all over the world are exposed to dental or skeletal fluorosis, becoming an endemic health problem in at least 25 countries: fourteen in Africa including Ethiopia, eight in Asia, and six in America [24]. In countries or places where the infrastructure allows for other sources of clean water, fluorosis could be easily mitigated by simply avoiding the consumption of fluorinated water. However, there are millions of inhabitants in rural areas that can only access to polluted water where defluoridation of water is the only measure to prevent health problems related to fluoride. Over the years, a large number of materials and methods have been proposed at least to minimize the effect of the fluoride problem. Commonly used technologies of defluoridation involve the use of adsorbents either aluminium or calcium phosphate based. As anion exchangers, hydrotalcites (also called layered double hydroxides or LDH) are also potential high capacity materials [25,26]. We investigated the fluoride uptake by layered double hydroxide (LDH) and calcined layered double hydroxide (CLDH). Furthermore, practical use of these synthetic minerals was studied in continuous mini-column experiments using groundwater from the Ethiopian Rift Valley. CLDH have shown maximum removal capacity of 222 mg F^-/g from synthetic aqueous solution, which is higher than the expected value of 144 mg F^-/g, and maximum fluoride removal capacity of 2.2 mg/g with groundwater from the Ethiopian Rift Valley. The main disadvantage of this type of materials is that they dissolved under the real conditions of groundwater, leading to high levels of dissolved aluminium to the drinking water as well as a notable increase of the final pH. In the case of Ethiopia,

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