



Removal of natural organic matter for drinking water production by Al/Fe-PILC-catalyzed wet peroxide oxidation: Effect of the catalyst preparation from concentrated precursors

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ABSTRACT

Catalytic wet peroxide oxidation (CWPO) has been assessed at semi-batch lab scale for the removal of natural organic matter (NOM) from raw surface water currently employed as feedstock in a drinking water treatment's plant. The peroxide solution has been stepwise added and its catalytic activation carried out by Al/Fe-pillared clays prepared from concentrated or diluted both, metal precursor solutions and clay suspensions (aqueous or ethanolic). An improved hydrolysis ratio ($\text{OH}/([\text{Al} + \text{Fe}])$) of 1.6 was found by Ferron analyses for the preparation of the concentrated metal precursor ($[\text{Al} + \text{Fe}] = 0.628 \text{ mol/dm}^3$), without significant metal loss by precipitation. Increased concentration of the pillaring precursor solution led to: (i) slightly decreased and (ii) more broadly distributed XRD-basal spacings, but also (iii) higher cationic compensation on the starting clay. Ethanol as suspension medium enabled the oligomer intercalation to be less susceptible against the clay concentration. It was achieved up to 96% of chemical oxygen demand (COD) removal in 4 h and total color removal in less than 45 min of reaction for a selected catalyst, under very mild conditions of room temperature and atmospheric pressure. The clay catalysts displayed high chemical stability against iron leaching. In addition, the solid prepared from the concentrated metal precursor in a 25% (w/v) ethanolic suspension successfully performed in a high demanding catalytic test, which involved very high humic substrate-to-catalyst ratio, prolonged time of reaction (24 h) and close to neutral pH of reaction (7.5), identical to that featured by the raw surface water.

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1. Introduction

One of the environmental concerns lately more studied is the efficient and affordable recovery of water resources contaminated with toxic organic compounds. Although the vast majority of the studies dealing with wastewater treatment to remove organic matter have involved microbiological steps as the best cost/benefit approach [1], this kind of technological application for feedstock refinement must be avoided in the production of drinking water. Microbiological safety is of course mandatory for these effluents and this is why disinfection is one of the stages demanding more care in the production of drinking water.

Although the removal of natural organic matter (NOM) from water resources has been usually solved by applying conventional coagulation/flocculation processes [2], a considerable increase in the content of NOM in surface waters has been observed during the past 25 years [3], in some cases, very difficult to be removed by standard physicochemical techniques. NOM brings many problems in drinking water treatment processes, including: (i) negative effect on water quality by color, taste and odor problems, (ii) increased coagulant and disinfectant dose requirements, which in turn results in increased sludge and potential harmful formation of disinfection by-products (DBPs), (iii) promoted biological growth in distribution systems, and (iv) increased levels of complexed heavy metals and adsorbed organic pollutants [4]. Therefore, the application of advanced oxidation processes (AOPs) for the treatment of surface streams in the production of drinking water has recently attracted a great interest. The AOPs are a set of technologies addressed to afford a continuous generation of hydroxyl radicals (HO^\bullet) by catalytic, photolytic, photo-catalytic, etc. strategies of activation, which are

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able to deplete a wide range of organic substances otherwise difficult to biodegrade [5].

Several studies have been recently devoted to find out the potential role that AOPs may play in the removal of NOM from natural waters. Most of them have assessed techniques where activation is carried out by means of radiation or dissolved catalysts [4], for instance: UV-light based applications (UV/H₂O₂) [6]; ozone based applications (O₃/H₂O₂, O₃/UV, O₃/H₂O₂/UV and O₃/H₂O₂/TiO₂) [7,8]; heterogeneous photo-catalysis (TiO₂/UV) [9] and Fenton homogeneous processes [10]. Although activation by solid catalysts displays clear advantages in terms of active site reusability and easier separation from the final effluent, till now the ability of heterogeneous Fenton-like catalyzed processes for NOM removal, other than those employing also some kind of radiation, has been rather scarcely studied in this application.

Among the AOPs, strong efforts are being done to develop solid catalysts able to generate the reactive radicals under ambient conditions of temperature and pressure, often being referred to as catalytic wet peroxide oxidation (CWPO). The Al/Fe-pillared clays constitute one of the most promising groups of structured materials that have successfully accomplished such a task [11,12]. Pillaring of natural or synthetic clays consists in the intercalation of voluminous inorganic polycations driven by cationic exchange, wherein by far the system more studied has been the tri-decameric Keggin polycation (Al₁₃)⁷⁺ [13,14]. Thus, the structural sheets of the hosting aluminosilicate are stabilized upon thermal treatment in a swollen form, delivering a nanostructured wafer-shaped set of channels available for adsorption and catalysis. Since they can be usually prepared from natural clays quite abundant worldwide, the resulting modified materials display remarkable applicability to solve environmental problems at big scale, under low cost.

Therefore, several works have been recently devoted to optimize some variables for the preparation of Al/Fe-PLCs like the hydrolysis ratio (HR, the molar ratio hydroxyl/metals) [11] and the atomic metal ratio (AMR, the amount of a pillaring metal referred to the total amount of them in mixed pillaring solutions) [12]. However, the method of preparation still needs to be further improved in order to efficiently work on concentrated suspensions. Conventional procedures for preparation of pillared clays involve slow dropping of low concentrated metal oligomeric solutions (typical total metal concentration <0.1 mol/dm³) on diluted clay suspensions (commonly, 2–5%, w/v), consuming significant volumes of water [15]. Although some investigations have recently faced on this problem applying microwaves or ultrasound [16,17] along the step of clay intercalation in concentrated suspensions with promising results, it obviously implies the consumption of an extra amount of energy. Storaro et al. [18] proposed some time ago that by using a solvent with low dielectric constant like acetone rather than water as suspension medium, the intercalation of completely unrefined Ca-rich smectites was improved, avoiding its gelation along the process even in highly concentrated clay suspensions. It is worth noting that calcium-rich aluminosilicates are one of the most commonly occurring cationic forms of smectites in nature [19]. Moreover, to our best knowledge the use of cheaper, less volatile and more easily handled solvents also featuring low dielectric constant like ethanol, has not been assessed as suspension medium for this preparative approach.

Aiming to contribute in the same sense, some methodologies to generate Keggin-like aluminum oligomeric pillaring precursors under concentrated conditions have been tested. Among others, preparation from concentrated metal solutions [20,21] and generation of a solid polymeric precursor from sulfate precipitation followed by nitrate metathesis [22,23] can be mentioned. Moreover, it has been realized as a big trouble that either, final metal concentrations higher to 0.2 mol/dm³ in the partially hydrolyzed solutions [20] and/or HR values lower than 1.5 [24] conduce to

meaningful decrease in the fraction of the metals forming Keggin-like Al₁₃ pillaring species. Besides, to avoid significant precipitation of the metal hydroxides, the use of high concentrated metal solutions obligates to carry out the hydrolysis step using smaller base amounts and in turn lower final HR values than the typical range found optimal, 2.0–2.5 [24].

Therefore, in the present work pillared clays from both diluted or concentrated ethanol or water/clay suspensions and diluted or concentrated mixed (Al/Fe) metal oligomeric pillaring precursors were prepared. The proper HR value for the preparation of the concentrated mixed metal precursor, while minimizing the metal loss by precipitation, was previously established by Ferron analyses. The resulting materials were examined in the CWPO treatment of raw surface water, recording chemical oxygen demand (COD) and true color depletion profiles. The input stream is currently employed as feedstock of the Pasto (Colombia) city's drinking water treatment plant and satisfies the demand of close to half a million people. The reaction was carried out under semi-batch lab scale at room temperature and atmospheric pressure.

2. Experimental

2.1. Materials

The starting material for the preparation of the clay catalysts was a natural bentonite from the Cauca Valley region-Colombia, already carefully characterized [12,16]. Before the pillaring procedure, the raw mineral was particle-size refined by sedimentation ($\leq 2 \mu\text{m}$ fraction), yielding a material (BV) with cationic exchange capacity (CEC) of 89 meq/100 g (dry basis). The mixed metal oligomeric precursor for pillaring was prepared employing AlCl₃·6H₂O ($\geq 99\%$, from Sigma-Aldrich), FeCl₃·6H₂O ($\geq 99.5\%$, from Mallinckrodt) and NaOH ($\geq 99.8\%$, from Mallinckrodt), all used as received. The clay suspensions were prepared in distilled water or ethanol ($\geq 99.5\%$, ACS reagent, from Sigma-Aldrich).

2.2. Preparation of the Al/Fe-mixed hydrolyzed solutions

Two Al-Fe mixed pillaring precursors, a diluted and a concentrated one, were prepared with identical Fe charge (AMR = 2.0%; Al/Fe molar ratio = 49). For reference purpose, a sample of the starting clay was also pillared with single Al-hydrolyzed solution (sample BVAI-W2), prepared according to the conventional procedure, that is, from diluted both pillaring solution and aqueous clay suspension. The mixed diluted precursor was prepared from a slightly modified conventional method already reported [12]. A couple of 0.2 mol/dm³ AlCl₃·6H₂O and 0.2 mol/dm³ FeCl₃·6H₂O solutions were mixed to reach the desired AMR value. Afterwards, a 0.2 mol/dm³ NaOH solution was slowly added throughout 8 h at 343 K under reflux in proper amount to get a final molar hydrolysis ratio (OH/(Al + Fe)) of 2.0. The obtained solution, having a final metal concentration [Al + Fe] = 0.068 mol/dm³, was then left to cool down till room temperature before being added on the clay suspension.

In the case of the concentrated Al/Fe intercalating precursor, a similar methodology was used, excepting the following features: the mixed aqueous solution of metal chlorides was 2.23 mol/dm³ [Al + Fe], which was thereafter hydrolyzed by a 1.2 mol/dm³ NaOH solution getting a final HR value of 1.6. The final metal concentration [Al + Fe] was 0.628 mol/dm³.

2.3. Preparation of the catalysts

The procedure to prepare the mixed pillared clays was adapted from various literature reports [15,18]. The previously prepared either, diluted or concentrated Al- or Al/Fe-hydrolyzed solution was

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