Total removal of oxalic acid via synergistic parameter interaction in montmorillonite catalyzed ozonation

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ABSTRACT

Oxalic acid ozonation in water at room temperature produced decomposition yields of 50–100% in the presence of Na^+, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} ion-exchanged montmorillonite as catalysts. Among these, Co(II)Mt and Fe(II)Mt displayed the highest performances. The appreciable enhancement of oxalic acid removal as compared to homogenous ozonation and the ozonation yield decay upon heating suggest a significant contribution of adsorption. The initial pH of the reaction mixture, ozonation time and catalyst concentration showed strong influence. A 3^k factorial design with 27 ozonation attempts for each catalyst produced total removal of oxalic acid after 15 min at pH 2.87 with 1.88 g/L of Co(II)Mt, and pH 2.88 with 1.91 g/L of Fe(II)Mt. Because oxalic acid is well known to be a quite refractory intermediate in most oxidation attempts, these results suggest that total mineralization of any hazardous organic pollutants from aqueous media is possible under similar optimum conditions. Higher pH and catalyst amounts were detrimental, presumably due clay compaction, which is supposed to reduce the cation mobility and adsorption contribution. The initial pH was found to act also via synergistic interaction with the other parameters, presumably by enhancing clay exfoliation and adsorption of oxalate anion and ozone.

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Introduction

Chemical, petrochemical, pharmaceutical and food industries, along with agriculture and forestry are major sources of organic pollutant in waste-waters [1–3]. Primary treatments are not sufficiently effective because of residual traces of pollutants [4,5]. Complete decomposition of organic pollutants requires powerful oxidative treatments to avoid the persistent presence of refractory short chain intermediates like oxalic acid (OA). The latter is known to display high chemical stability even in the so-called Advanced Oxidation Processes (AOPs). The main issue to be addressed is that the formation of OA is often the final stage in most oxidation methods [6–9]. Besides, OA is a hazardous compound [10], and shows even more toxicity than most parent pollutants [11].

Notwithstanding that some plants like rhubarb and sorrel contain OA, the latter is recognized as being quite poisonous to the kidneys (nephrotoxic), more particularly when present in drinking water. OA precipitation in the presence of calcium produces kidney stones, which contain calcium oxalate in a proportion of 80%. OA may even be fatal around a median lethal dose (LD50) of 375–380 mg/kg body weight for humans [12–16]. In human and animal metabolism, OA may also form from

excessive use of vitamin C, which is readily oxidized owing to its powerful antioxidizing capacity. This often results in gut lining irritation, rheumatoid arthritis, certain forms of chronic vulvar pains (vulvodynia) and other diseases. However, being quite harmless in low doses, OA is rather regarded as being a precise indicator of incomplete oxidation of organic matter. For this reason, total mineralization of organic pollutants into carbon dioxide (CO_2) without generating any traces of OA or any other short chain compounds has become an essential requirement for effective oxidative water treatments.

So far, attempts to OA oxidative mineralization into CO_2 have received fairly good attention in the published literature, and many advances have been made in this regard [9]. Photocatalysis and photoelectrocatalysis have long been considered promising approaches, but the incomplete decomposition of organic pollutants and high operating costs were still major obstacles for commercial applications [1,3]. AOPs result from continuous improvements of conventional oxidative methods [2]. One of these, namely ozonation, more particularly at elevated pH, has focused interest. Nonetheless, no prospects can be envisaged as long as the issues related to the low solubility of ozone in the liquid media and its weak reactivity as compared to radical species still remain to be addressed. The use of metal cations produce higher effectiveness as compared to the non-catalytic routes, but water contamination by metals turned out to be a major drawback [17–19]. Significant improvements were registered in the presence of

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dispersed solid or supported catalysts. In this regard, ozonation on activated carbon can afford almost total mineralization into carbon dioxide [20–23]. On solid catalysts, the ozonation process is expected to involve both surface phenomena and bulk water reactions between the organic substrate to be decomposed and oxidizing agents. Adsorption appears to play a key-role, because the catalytic activity was found to increase almost linearly with increasing catalyst surface area [24,25].

Among the wide variety of solid catalysts investigated so far, zeolites ion-exchanged with transition metal cations showed interesting performances [26]. However, more available and lower cost materials such as clay minerals appear to be more promising catalysts, which can display almost similar surface properties as zeolites. Besides, their expandable structures allow them to be also used in the decomposition of large size substrates [10,27–31]. Previous attempts with ion-exchanged montmorillonite (Mt) revealed strong individual influences of pH, catalyst and ozone amounts on the decomposition yield [10]. Nevertheless, the role of the parameter interactions has never been tackled so far, and the occurrence of synergistic actions of ozone montmorillonite still remains to be elucidated. The core of the novelty of the present study resides in correlating these interactions with the contribution of the adsorption step through the role of pH in the global ozonation process. This issue has never been tackled and not even been envisaged so far.

For this purpose, montmorillonite ion-exchanged with Na^+, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} cations were employed as catalysts. OA ozonation in water was modeled using a 3^k factorial design of experiments for assessing the contributions of the interactions of the initial pH, ozonation time and catalyst amount. The synergy involving the ozonation reaction and adsorption will be discussed in terms of parameter interactions.

Materials and methods

Catalyst preparation and characterization

A crude bentonite (Sigma–Aldrich) was repeatedly impregnated with 2–5 M aqueous NaCl solutions at 80 °C for 4–5 h, under vigorous stirring, until full ion exchange. After cooling overnight, the clay mineral suspension was repeatedly settled in distilled water at room temperature, under ultrasound exposure. Settling was performed overnight in a polyethylene cylinder obtained by cutting the tip of a large syringe (200 mL). After supernatant removal, the resulting paste was then extruded, dried and fractionated. XRD analysis of the different fractions was used to select a montmorillonite-rich sample, designated as NaMt. The latter was repeatedly dialyzed overnight with distilled water in cellulose bags, until the total disappearance of the NaCl excess using the conventional $AgNO_3$ test.

NaMt was then fully ion-exchanged through repetitive impregnations with aqueous solutions of transition metal salts under vigorous stirring. The resulting Fe(II)Mt, Fe(III) Mt, Co(II)Mt, Ni(II)Mt and Cu(II)Mt samples were then washed, dialyzed and air dried. These catalysts were characterized by Siemens D5000 X-ray diffractometer with Cu Kα, λ = 1.54051 Å, which revealed a broad 001 XRD reflexion for the crude bentonite, but sharp lines for the ion-exchanged montmorillonite samples. This is a common feature of homo-ionic clay minerals, which indicates a perfectly parallel arrangement of the clay sheets. Measurements via ammonium acetate saturation method (AMAS) and Kjeldahl ammonium distillation technique [32] gave a cation exchange capacity (CEC) value of 100 meq/100 g. Deeper insights in the catalyst chemical composition were achieved before and after ozonation through thermal gravimetric analyses (TGA) using a Seiko Instrument Inc., TG/TDA6200 thermal analyzer under a 120 ml min^{-1} air stream at

5 °C/min scanning rate, and energy dispersion X-rays analysis (EDX with an EDAX-Sapphire instrument coupled to the Hitachi S-4300SE/N-VP SEM equipment, using a Si(Li) crystal and an active surface of 10 mm^2).

Ozonation of oxalic acid

Ozonation attempts were performed in a 2 cm × 30 cm cylindrical glass reactor, using a solution with an initial concentration of 10^{-3} M (accuracy: 1%) of OA (99.5% purity, supplied by Anachemia Canada Inc.) and various clay catalyst amounts. Ozone was produced from pure oxygen (supplied by Paraxair Canada Inc.) by a Welsbacher ozone generator and injected into the batch reactor through a bubbler at 6 ± 0.2 mg/min. The ozonation experiments were performed at room temperature by bubbling ozone in an aqueous oxalic acid solution using two different procedures: (1) within a batch reactor, i.e. a flask coupled to a reflux cooling device to avoid liquid loss by evaporation. Periodic COD measurements were made for determining the remaining amount of unconverted oxalic acid. Here, small number of micro-samples were taken from the reaction mixture, so that the total amount removed (less than 10%) does not influence greatly the evolution in time of the ozonation process; (2) When higher number of samples is needed so as the total sample amount exceeds 10%, no sampling was made, and a series of small and similar reaction mixtures were simultaneous ozonated at the same ozone throughput for different bubbling times. The samples were further analyzed through quantitative COD measurements and qualitative HPLC–MS for the identification of the reaction products and intermediates.

The ozonation process was investigated at both intrinsic and adjusted initial pH of the reaction mixture. pH was adjusted using concentrated hydrochloric acid (36.5%) supplied by Caledon Ltd. and sodium hydroxide pills (95% purity) provided by Anachemia Canada Inc. An Accumet 15 pH meter was employed for pH measurements.

Products and intermediates analysis

The reaction mixture was qualitatively analyzed by liquid-chromatography–mass spectrometry (HPLC-MS Agilent-1200 instruments) using a C18 column and a 2:3 methanol:water mixture. After ozonation in optimum conditions, except carbonic acid and carbonates, no traces of any intermediate were detected. In other conditions traces of formic and acetic acid were identified.

The OA conversion yield was evaluated by periodic measurements of the residual amount of unconverted reagent via a standard chemical oxygen demand technique (COD) [33]. For this purpose, concentrated sulphuric acid (98% purity) supplied by Caledon Ltd., potassium dichromate 99.5%, iron(II) ammonium sulphate 99.5%, silver sulphate 99.5% and mercury(II) sulphate 99.5% all provided by Anachemia Canada Inc. were employed. The usual standard deviation (SD) in COD measurement is of 4–5% [34,35]. However, the SD value was reduced to 1% due to the total absence of interfering agents such as halide anions and to the use of triplicate and different blanks, and even down to 1% through COD calibration curve obtained by the introduction of a correction factor assessed by HPLC.

Results and discussion

Effect of catalyst addition

Preliminary observations showed that ozonation without catalyst produces low OA decomposition yield not exceeding 1–2% even after 60 min (Fig. 1). After addition of crude bentonite