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## Fenton-based processes for the regeneration of catalytic adsorbents

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### ABSTRACT

In the present study, natural phyllosilicate clays, Illite and Montmorillonite, were established as efficient adsorbents for the removal of the ionic liquid 1-butyl, 2,3-dimethyl imidazolium chloride, achieving, respectively, 14 and 25 mg/g of adsorption. In addition, the regeneration of both adsorbents was hereby firstly performed by Fenton-based processes, using the catalytic action of the iron naturally present in clays. Two different reactor configurations, with regard to the ratio of adsorbent to liquid phase, were tested: fluidized and fixed bed reactors. The desorption equilibrium was the main limiting factor for the effective regeneration of the Illite clay by electro-Fenton process in the fluidized bed reactor. On the other hand, the fixed bed reactor, based on electrokinetic-Fenton phenomenon, proved to be suitable for the regeneration of the Montmorillonite clay and it would be an appropriate solution for the implementation of adsorbent regeneration by Fenton-based technology at large adsorbent/solution ratios. Both reactor configurations were suitable for the adsorbents regeneration, and 80% of ionic liquid degradation has been accomplished. Additionally, the adsorption capability of both clays was confirmed after the regeneration process, achieving almost the same initial uptake.

### 1. Introduction

Lately, one of the most important topics on environmental research has been water pollution with emerging contaminants [1]. Their removal is difficult via conventional technologies, causing their accumulation into the environment, which may cause chronic toxicity and other effects of environmental concern [2]. Among the different emerging pollutants, the attention is hereby focused onto Ionic Liquids (ILs) which are complex salts [3]. They are being used industrially as solvents, and taking into account their low volatility, ILs have been considered to be a “green” alternative to the traditional organic solvents [4]. However, ILs are not as eco-friendly as expected, as they may accumulate in the environment because they have high chemical and thermal stabilities [5].

The increase of ILs utilization may provoke an augmentation of their presence in the environment, which would exponentially increase if they are not properly treated. Thus, both water bodies and soils are susceptible of being contaminated because ILs usually have strong interactions with aqueous solutions and interlayer clays [6]. Moreover, biological studies have revealed a toxic effect of the presence of ILs in the environment [7]. Thus, the treatment of industrial water streams becomes a necessity for avoiding the presence of these pollutants in the environment.

Adsorption processes can be a feasible alternative due to their simplicity and high efficiency, even in cases where large amounts of

wastewater need to be treated. However, the cost of the adsorbent and its regeneration process are the main shortcomings of this technology. Clays have been already reported as good adsorbents due to their high adsorption capability [8] because of their elevated surface charge and area [9]. Moreover, they are naturally available which makes them an inexpensive alternative to be used as adsorbent materials, avoiding the high operational costs of other materials [10]. However, without regeneration, exhausted adsorbents would require to be disposed as solid wastes, which would not definitely solve the problem but switch it to another phase. In order to reduce this inconvenient and adsorbent costs, regeneration is essential [11].

In recent times, the Fenton-based processes have arisen as a feasible option for remediating the spent adsorbents [12]. These technologies are based on the Fenton’s reaction in which powerful oxidants, mainly hydroxyl radicals, are obtained by the catalytic decomposition of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in presence of iron II (Fe<sup>2+</sup>) in acid medium (Eq. (1)) [13].



This treatment has been satisfactory proved for the regeneration of adsorbents, such as natural clays, polluted with dyes [14]. In addition, the adsorbents can be loaded with iron so it acts as heterogeneous catalysis (Fenton-like process) [15].

The Fenton’s treatment can be also carried out under the action of an electric field (electro-Fenton process) which allows the regeneration

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of the catalyst (Eq. (2)) and the continuous production of  $\text{H}_2\text{O}_2$  (Eq. (3)) due to the air supplied to the system [13]. These two reductions on the cathode avoid the constant addition of reactants needed in the Fenton's process. Until now, this technology has been efficiently applied for the regeneration of carbon-based materials containing organic pollutants [16,17], however, to our knowledge, no studies have been reported in the electro-Fenton treatment of natural clays.



The natural presence of iron and other transition metals (Al, Cu) in clays may act as Fenton catalyst [18,19]. In fact, some metal combinations could enhance the Fenton's process, for instance Al-Fe [20] and Mg-Fe co-presence contributed synergistically to the catalytic activity [21].

Spent adsorbents are typically treated in aqueous suspensions on batch electrochemical reactors. However, this configuration is difficult to be scaled up because of the high ratio liquid:adsorbent (100:1-400:1 [22,23]). Therefore, in this study, the treatment of a highly polluted spent adsorbent will be also evaluated by electrokinetic-Fenton process. In this treatment, the electric field is used to introduce the reactants in the adsorbent matrix by electroosmotic flow (EOF) [24]. This process has been formerly tested as an alternative to conventional soil treatments based on its peculiar advantages, such as the capability of treating fine and low-permeability materials (like clays), which would not otherwise be efficiently treated due to the challenging delivery of the oxidant into the substrate [18]. Thus, the electrokinetic-Fenton process would be applied to the polluted adsorbent, in order to facilitate the oxidant ( $\text{H}_2\text{O}_2$ ) distribution along the clay and its activation by the naturally present iron. This may also induce simultaneous oxidative/reductive reactions directly into the clay [25].

The purpose of this study is to test the adsorption capability of two natural clays (Illite and Montmorillonite), for the removal of the IL 1-butyl-2,3-dimethylimidazolium chloride ([bdmim]Cl). Afterwards, the regeneration of these adsorbents will be performed under Fenton-based treatments. For this purpose, two different reactor configurations, with regard to the adsorbent : liquid ratio, fluidized and fixed bed reactors, will be assess for electro-Fenton and electrokinetic-Fenton treatments, respectively.

## 2. Materials and methods

### 2.1. Reagents

The IL [bdmim]Cl (99%) has been purchased from Io-li-tec GmbH. Both citric acid (99%) and sodium sulphate anhydrous (99%) were acquired from Sigma-Aldrich to be used as buffer and electrolyte, respectively.  $\text{H}_2\text{O}_2$  (30%) used in the Fenton's reactions was obtained from Foret. Illite and Montmorillonite clays were purchased, respectively, from Argiletz laboratories and Sigma-Aldrich.

### 2.2. Experimental set-up

#### 2.2.1. Kinetic studies

To evaluate the adsorption kinetics, 50 mL of [bdmim]Cl aqueous solution (500 mg/L) were mixed with 1 g of clay (raw or regenerated). The mixture was maintained at 25 °C and 150 rpm by means of a shaker (MaxQ 8000, Thermo Scientific) and liquid samples were taken periodically in order to analyse the variation of the [bdmim]Cl concentration. The experimental data was fit to pseudo-first (Eq. (4)) and pseudo-second order models (Eq. (5)) by these linearized equations. The pseudo-first order adjustment fits sorption processes ruled by homogeneous sorbents and physical sorption [14] while the pseudo-second order adjustment fits more heterogeneous surfaces [26].

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_{1st}}{2.303} \cdot t \quad (4)$$

$$\frac{t}{Q_t} = \frac{1}{K_{2nd} \cdot Q_e^2} + \left( \frac{1}{Q_e} \right) \cdot t \quad (5)$$

Where  $Q_t$  and  $Q_e$  (mg/g) are the [bdmim]Cl uptakes at time  $t$  and equilibrium, respectively.  $K_{1st}$  and  $K_{2nd}$  are the rate constants of pseudo-first ( $\text{min}^{-1}$ ) and pseudo-second (g/mg-min) orders, respectively.

#### 2.2.2. Isotherm studies

To obtain adsorption isotherms, 50 mL of [bdmim]Cl solutions at different concentrations (50, 100, 250, 500, 750 and 1000 mg/L) were mixed with 1 g of clay. The mixture was maintained at 25 °C and 150 rpm by means of the shaker during 24 h. Then, several isotherms adjustments, Langmuir (Eq. (6)), Freundlich (Eq. (7)) and Temkin (Eq. (8)), were tested by using Sigma Plot 11.0.

$$Q_e = \frac{Q_{max,L} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (6)$$

$$Q_e = K_F \cdot C_e^{1/n} \quad (7)$$

$$Q_e = \frac{R \cdot T}{b} \cdot \ln(K_T \cdot C_e) \quad (8)$$

$Q_{max,L}$  (mg/g) is the maximum amount of [bdmim]Cl adsorbed within a monolayer.  $K_L$  (L/mg) is the Langmuir dissociation constant, which is related to the adsorption energy [27].  $K_F$  is Freundlich's constant and  $1/n$  is the affinity parameter which indicates the adsorbent-adsorbate interaction [28]. The units of  $K_F$  are in volume/mass but may vary depending on the value of  $n$ .  $RT/b$  is a factor related to the heat of adsorption whereas  $K_T$  is the Temkin equilibrium constant (L/mg) [29].

#### 2.2.3. Statistical analysis

The adjustment of both kinetic and isotherm curves was established by the value of correlation coefficient ( $R^2$ ) and the Standard Error of Estimate (SEE) (Eq. (9)) as it measures the concordance between experimental and theoretical data [26]. In the equation,  $n$  is the number of measurements.  $Q_e$  and  $Q_{et}$  are, respectively, the uptake value obtained experimentally and by the adjustments.

$$SEE = \sqrt{\frac{\sum (Q_e - Q_{et})^2}{n - 2}} \quad (9)$$

#### 2.2.4. Evaluation of Fenton's catalytic activity of the studied adsorbents

Preliminary tests were performed to analyse the feasibility of both adsorbents to be used as heterogeneous Fenton's catalyst. 2 g of the adsorbent were mixed with 100 mL of [bdmim]Cl (500 mg/L) at pH 3 [13], 25 °C and in presence of  $\text{H}_2\text{O}_2$  (290 mM). This higher concentration, regarding the iron content of the adsorbent clays, was selected following the good performance obtained by previous researchers [15,16]. The mixture was stirred during 24 h and then [bdmim]Cl concentrations were measured (both in liquid media and clay). As control assay, an experiment without adsorbent was performed at the same conditions with the aim of evaluating the stability of the [bdmim]Cl in presence of  $\text{H}_2\text{O}_2$ .

#### 2.2.5. Regeneration assays using fluidized bed electro-Fenton reactor

A diagram of the fluidized bed electrochemical reactor (E-F reactor) is detailed in Fig. S1 (a). It consists on a 150 mL glass-cylindrical reactor magnetically stirred. 7.5 g of spent adsorbent (2.5 mg/g) were mixed with 150 mL of aqueous solution at pH 3 and 25 °C. The [bdmim]Cl concentration was selected in order to ensure the IL is strongly linked to the adsorbent active sites. For all assays,  $\text{Na}_2\text{SO}_4$  0.1 M was added as electrolyte. The cathode (carbon felt,  $19.5 \times 6$  cm) was placed surrounding the inner wall of the reactor whereas the anode (Boron Doped

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