Science of the Total Environment 622–623 (2018) 556–562

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Kaolinite adsorption-regeneration system for dyestuff treatment by Fenton based processes

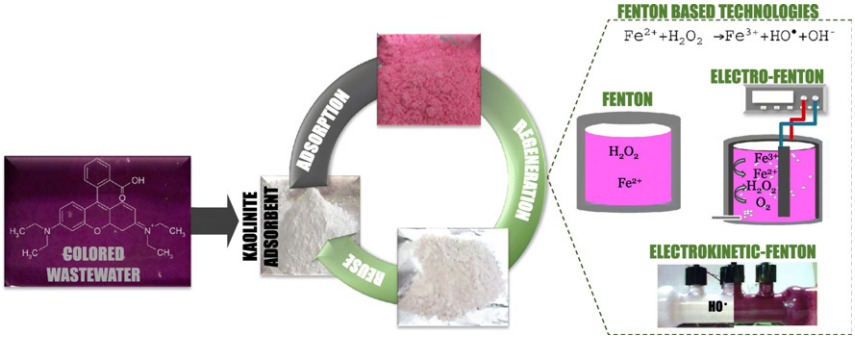
Emilio Rosales [a,*], Delia Anasie [a,b], Marta Pazos [a], Iuliana Lazar [b], M. Angeles Sanromán [a]

[a] Department of Chemical Engineering, University of Vigo, Campus As Lagoas-Marcosende, 36310 Vigo, Spain
[b] Faculty of Engineering, "Vasile Alecsandri" University of Bacau, Calea Marasesti 157, 600115 Bacau, Romania

HIGHLIGHTS

- Kaolinite proved to be a viable low cost adsorbent in the removal of dye from wastewater.
- Feasible regeneration of spent adsorbent by Fenton techniques using different solid:liquid ratios
- Adsorption-degradation cycles were successfully carried out.
- No alteration of the kaolinite was detect after the successive cycles.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 September 2017
Received in revised form 17 November 2017
Accepted 26 November 2017
Available online xxxx

Keywords:
Spent adsorbent
Adsorption-degradation system
Fenton
Electro-Fenton
Electrokinetic-Fenton

ABSTRACT

The regeneration and reuse of adsorbents is a subject of interest nowadays in order to reduce the pollution and the wastes generated in the adsorption wastewater treatment. In this work, the regeneration of the spent kaolinite by different advanced oxidation processes (Fenton, electro-Fenton and electrokinetic-Fenton) was evaluated. Initially, it was confirmed the ability of a low cost clayey material, kaolinite, for the adsorption of model dye such as Rhodamine B showing Freundlich isotherm fitting. Then, the regeneration and consequent degradation of the pollutant in the adsorbent by Fenton based processes was carried out. The role of different parameters affecting the regeneration process (H_2O_2:Fe^{2+} ratio, liquid:solid ratio) were evaluated. Working at 100:1 H_2O_2:Fe^{2+} ratio and 30 min near complete dye removal (around 97%) from kaolinite was obtained by Fenton treatment. After that, a two-stage treatment for adsorption-regeneration was evaluated during five treatment cycles demonstrating its viability for regeneration of the adsorbent through dye degradation. Based on the successful application of Fenton technique, the improvement of the treatment by electro-Fenton and electrokinetic-Fenton were studied for different solid:liquid ratios achieving satisfactory regeneration values.

1. Introduction

Water is an essential element of life and one of the pillars of the sustainable development. The effect of human activities in water bodies (wetlands, rivers, lakes, *etc.*) is a subject of concern. Different industries such as textile, tannery, paper and pharmaceuticals are characterized by

* Corresponding author.
E-mail address: emiliorv@uvigo.es (E. Rosales).

https://doi.org/10.1016/j.scitotenv.2017.11.301
0048-9697/

the consumption of high amount of chemicals, but not all of them are completely consumed in the processes and their release generate environmental issues. Among them, dyes represent a problem due to their impact in the aquatic ecosystems for their coloration affecting to photosynthesis processes and the carcinogenic and mutagenic properties of these compounds (Cruz-Rizo et al., 2017).

Nowadays, many biological and physical-chemical processes have been proposed for the treatment of wastewater (Wang et al., 2006). Adsorption is one of the more commonly applied technique due to its simplicity, efficiency and easy design (Ahmed et al., 2015; Omorogie et al., 2016). However, this process presents some disadvantages such as adsorbent cost. For this reason, low-cost adsorbents (clays, agroindustrial wastes, *etc.*) have been proposed as alternatives to more expensive and widely applied activated carbon (Crini, 2006; De Gisi et al., 2016; Kurniawan et al., 2006; Rosales et al., 2015; Stawinski et al., 2017a).

In addition, the disposal of the adsorbents once exhausted is also a matter of concern due to their hazardous content and the possibility of leaching the adsorbates in the environment after dumping (Omorogie et al., 2016). There is a lot of literature about the new adsorbents with good performance for adsorption process, but scarce information is available about their regeneration for their reuse or safe disposal (Stawinski et al., 2017a, b). The regeneration of the adsorbents is a possible solution in order to reduce the impacts of the generated wastes, the economic cost of the treatment and the valorization of the wastes. Several alternatives based on chemical, biological or physical processes have been proposed as solutions in the regeneration of spent adsorbents (Omorogie et al., 2016; Stawinski et al., 2017a; Wang et al., 2006). Thermal treatment is the most widely used technique for the elimination or regeneration task of adsorbents spent with organic compounds, but requires the transport of the adsorbent to treatment plants and an expensive treatment procedure. Therefore, alternative cost-effective techniques are required focused in the treatment of the spent adsorbent facilitating the operational process.

Advanced oxidation processes have arisen as a promising alternative in the degradation of several organic compounds due to the generation of highly oxidant species able to remove a wide range of pollutants. Among them, Fenton, electro-Fenton and electrokinetic-Fenton processes have attracted great attention due to operational conditions at room temperature, easily handling, the reagents are readily available and usually quick reactions with short treatment times. These techniques are based on the use of H_2O_2 in presence of iron to generate the hydroxyl radicals according to the Eq. (1).

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + {}^{\cdot}OH + H_2O \quad (1)$$

The aim of this work is the design of a combined process adsorption-regeneration for dyestuff treatment. Thus, a low cost clayey material, kaolinite, was used to removal the dye present into a simulated effluent and the spent adsorbent was regenerated by dye degradation using Fenton based processes. At the beginning, a brief study of the adsorption process was carried out. Then, the regeneration process was evaluated using Fenton treatment and the working parameters related to the process were studied. Finally, the enhancement of spent adsorbent regeneration by electro-Fenton and electrokinetic-Fenton techniques was performed in order to overcome the drawbacks of Fenton treatment.

2. Materials and methods

2.1. Reagents

Kaolinite, citric acid and sodium sulphate were purchased from Sigma-Aldrich. Hydrogen peroxide (30% w/w) was obtained from Foret. Rhodamine B (RhB), and Fe^{2+} as iron sulphate ($Fe_2SO_4 \cdot 7H_2O$) were purchased from Panreac.

2.2. Adsorption assays

Kaolinite (5 g) was added to a 100 mL solution of different RhB concentrations taken in 250 mL Erlenmeyer flasks. The solution was stirred in thermostatic shaker at a constant speed of 150 rpm/min at a given temperature 25 °C. The experiments were performed at the natural pH of the solution 6.7. Samples were taken at different time intervals and the adsorbent was separated by centrifugation.

The amount of dye adsorbed (q) and the percentages of removal (D) were calculated using the following equations:

$$q = (C_i - C_f) \cdot V/M \quad (2)$$

where q is the dye uptake (mg/g); C_i and C_f the dye concentration at initial and through time, (mg/L) respectively; V is the solution volume (L); M is the mass of adsorbent (g).

$$D = 100 \cdot (m_i - m_f)/m_i \quad (3)$$

where m_i and m_f the mass of dye in the adsorbent at initial and through time (mg) and D the percentage of dye removal (%).

2.3. Regeneration of spent adsorbent

2.3.1. Fenton assays

Glass vial (12 mL) was used and 1, 2 or 4 mL of Fenton solution were added to 1 g of kaolinite polluted with different amounts of RhB. Two different ratio H_2O_2: Fe^{2+} were tested: 2.9 mM H_2O_2:0.29 mM Fe^{2+} and 29.0 mM H_2O_2:0.29 mM Fe^{2+} and the experiments were carried out in a multi-purpose tube rotator (Selecta Mobile-Rod) at pH 3. The contact time was optimised between 0 and 24 h.

All the assays were always performed in duplicates. The results correspond to the medium values and the standard deviation was lower than 5%.

2.3.2. Electro-Fenton assays

These experiments were carried out in a 250 mL cubic cell with a working volume of 150 mL and double-side boron-doped diamond/Nb anode (2500 ppm B, Neocoat SA) and graphite carbon (Carbon-Lorraine, RVG 2000) were selected as anode and cathode, respectively (Sandu et al., 2016). Then, 7.5 g kaolinite were added to the system and mixed with 150 mL of an electrolyte solution Na_2SO_4 (0.01 M), the pH fitted to value of 3, and a constant voltage of 5 V was applied using a power supply (Agilent 3502). In order to assure the oxygen saturation of the system, air was pumped into the system with a flow of 1 L/min.

Control Fenton experiments were performed mixing 7.5 g of the same polluted kaolinite with 150 mL of the H_2O_2:Fe^{2+} solution at the evaluated H_2O_2: Fe^{2+} ratio. These assays were carried out at pH 3 under magnetic stirring.

In all cases, the results correspond to the medium values of triplicated and the standard deviation was lower than 5%.

2.3.3. Electrokinetic-Fenton assays

The regeneration of the adsorbent was performed in a column of 70 mL loaded with 100 g of the spent adsorbent (Sandu et al., 2016). Two chambers were included at both sides of the column in order to locate the graphite electrodes. The electrochemical delivery of the oxidant, H_2O_2 10% added in the anode and cathode, was performed applying a voltage of 3 V/cm. Na_2SO_4 (0.1 M) was added as electrolyte and when necessary citric acid (0.1 M) was used as buffering (pH 2) and complexing agent.

2.4. Adsorption-regeneration cycles of adsorbent

Several adsorption and degradation cycles were performed. The adsorption studies were done using 1 g of kaolinite and 2 mL of a solution