

Taking advantage of iron contained in natural volcanic ash for catalytic degradation of Rhodamine 6G

Antoine Tiya-Djowe^{1,*}, Patrick N. Lemougna^{2,3,*}, Alphonse Emadak¹, Melanie Pitap-Mbowou¹, Samuel Laminsi¹, Uphie Chinje-Melo^{2,3}

¹ Laboratory of Applied Physical and Analytical Chemistry, University of Yaounde 1, P.O box 812, Yaounde, Cameroon.

² Laboratory of Applied Inorganic Chemistry, University of Yaounde 1, P.O. Box 812, Yaounde, Cameroon.

³ Local Materials Promotion Authority (MIPROMALO), P.O. Box 2396, Yaounde, Cameroon.

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Abstract : Using Fe-containing silica-alumina materials as heterogeneous catalyst for Fenton-like degradation of organic pollutants has attracted a lot of attention during the last decades. In this work the catalytic activity of an iron-rich natural silica-alumina material (namely volcanic ash) for the abatement of Rhodamine 6G (Rh6G) has been evaluated. The X-ray diffraction (XRD) and Scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS) results showed that such material contains about 13wt% of iron mainly present in augite and ferroanforsterite crystalline phases. Such iron content was sufficient to activate hydrogen peroxide via Fenton process. Indeed, 78% of Rh6G was degraded after 120 min of reaction in the presence of volcanic ash ([VA] = 5 g/L; [Rh6G] = 25 mg/L and initial pH = 3). The dye abatement efficiency increased with decrease of initial dye concentration, and with increase of catalyst dosage. However, the process was efficient only in acid medium (pH = 2.5 – 3) in which the leaching of the catalyst could not be avoided. As a consequence, a drastic decrease in abatement efficiency was observed during the recyclability test. This suggests that the studied volcanic ash can be used as low cost material for wastewater treatment. However it needs to be pre-treated for efficient use as heterogeneous catalyst.

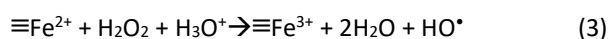
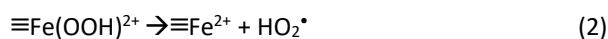
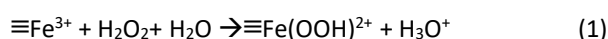
Keywords: Volcanic ash; Fenton-like process; Dye degradation; Wastewater treatment.

1. Introduction

The rising population, industrialization, and higher standards of living are leading to an increase in water consumption. At the same time, the amount of clean drinking water in the world is decreasing due to drought, deforestation, soil erosion and water pollution. Undesirable characteristics of polluted water include soluble organic compounds, recalcitrant organic compounds, turbidity, heavy metals and colour. The colour produced by organic dyes in water can affect plan life and destroy ecosystems. For this purpose, it is necessary to treat dyes containing polluted waters before their disposal in the environment.

During the last decades, heterogeneous Fenton system has been widely used as advanced oxidation process (AOP) for the degradation of organic pollutants in wastewater. In such system, the highly oxidizing HO[•] radicals (E⁰= 2.8 V/SHE) are produced from the breakdown of hydrogen peroxide catalysed by iron containing solid materials such as bulk iron oxides/hydroxides, or zero valent iron, or iron ions stuck onto supports (e.g zeolite, clay, activated carbon, alumina, etc.) [1-5]. Bi-functional mixed oxides such as FeVO₄ were also used as heterogeneous Fenton catalysts [6]. The degradation mechanism of organic dyes via heterogeneous Fenton reaction has been

described by equations (1) – (4) where the symbol (≡) represents the solid surface of the catalyst [7].



Recent studies established that the performances of iron supported catalysts in Fenton-like degradation of organic pollutants depend on the type of support. Specially, materials containing silica and/or alumina have proven to be more efficient catalysts, and have the advantage to be active even at neutral pH [8, 9]. For this purpose, the use of clays which are aluminosilicate materials have been intensively considered as support for the synthesis of heterogeneous Fenton catalysts [10-13]. However, it would be an asset to take advantage of using natural aluminosilicate materials which already contain a considerable quantity of iron capable of catalysing the Fenton reaction.

In this study, the performances of a natural volcanic ash with Fe-containing minerals were evaluated in heterogeneous Fenton reaction. Volcanic ashes are vitreous pyroclastic materials produced by violent

* Corresponding authors: antoine.tiyadjowe@yahoo.com (A. Tiya-Djowe); lemougna@yahoo.fr (P.N. Lemougna)

eruptive volcanic action [14]. In Cameroon, many cones of volcanic ashes exist and the valorisation of such material is currently limited to its use as raw material for the production of building materials including ceramics and geopolymers, and many deposits remain unexploited [15-17]. Horwell et al. has studied the surface reactivity of volcanic ash from Soufrière Hills volcano (West Indies) in order to probe the main health hazard in the ash, and they concluded that iron is a major factor that needs to be considered in assessing the health hazard of volcanic dusts [18]. This work is thus directed on the valorisation of volcanic ashes in heterogeneous catalysis for environmental management, taking into account the fact that they contain a relative high iron content that can activate hydrogen peroxide via the Fenton-like process for pollutants abatement. For this purpose, we aim at investigating whether such materials are able to act as heterogeneous Fenton-like catalysts for the degradation of Rhodamine 6G (Rh6G), a highly toxic triphenyl-methane dye which is very resistant to biodegradation and photodegradation [19].

The objective of this work is twofold. First, we wish to evaluate the ability of iron species present in volcanic ash to act as catalysts for conversion of hydrogen peroxide into HO[•] radical capable of oxidizing the Rh6G

dye molecules. To this end, the effect of some reaction parameters (namely the initial dye concentration, initial pH, catalyst dosage and the presence of HO[•] radicals' scavengers) will be screened. Secondly, we wish to investigate whether such material acts as heterogeneous or homogeneous catalyst. More precisely, the idea is to find the more favourable conditions for the abatement of Rh6G using volcanic ash as catalyst, and to study the stability of such material as heterogeneous catalyst.

2. Materials and Methods

2.1. Materials

The volcanic ash used in this study was collected in the deposit of Foubot (west region of Cameroon). Before use, the material was ground to pass a 400 µm sieve and washed several times with distilled water in order to remove soluble impurities. The bulk chemical composition of the material as presented in Table 1 shows that it contains very high percentages of silica (43.39%) and alumina (15.33%). It also contains other metal oxides among which iron oxide has a higher weight percentage (12.5%). Rhodamine 6G dye selected as model pollutant was obtained from Sigma-Aldrich (Belgium) and was used without any purification.

Table 1

Chemical composition of the volcanic ash from Foubot as obtained by X-ray fluorescence spectroscopy

Oxides	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	SUM
Wt%	43.39	15.33	12.5	11.15	6.85	4.46	1.70	2.92	0.90	0.19	99.39

2.2. Ash characterization

The bulk chemical composition of the volcanic ash was determined by using a WDX-Ray fluorescence spectrometer (S4 Pioneer, Bruker). The material was further characterised by X-ray diffractometry and SEM/EDS analysis. The X-ray diffraction patterns were recorded on a Philips PW1700 equipment with a computer-controlled goniometer and graphite monochromator with Co K_α radiation, 2θ scan range of 4 to 80°. Scanning electron micrographs and EDS maps were determined in the backscattered mode on sample coated with 16 nm of carbon using a Jeol JSM 6500F microscope operated at 15.0 kV.

2.3. Catalytic performances measurement

Experimental runs were carried out at 25°C in a conical flask containing a 250 mL aqueous solution of Rh6G at a given concentration. In a typical run, the solution pH was adjusted to the desired value by the addition of few drops of 0.1 M solution of NaOH or H₂SO₄. A given amount of volcanic ash was then introduced into the dye solution. The reaction started when 1.14 mL of H₂O₂ (50%) were added to the flask. At specific time intervals, 2 mL aliquots of the solution were withdrawn from the reaction mixture, filtrated using a

0.2 µm PTFE membrane and analysed using an Ultraviolet-Visible JENWAY spectrophotometer. The remaining concentration of Rh6G was evaluated by measuring the absorbance at a maximum wavelength of 513 nm. The measured absorbance was then converted into concentration by using a calibration curve. All the measures were done in triplicate and the mean of three values were used to evaluate the degradation process. The dye abatement efficiency E (%) was calculated using equation 5, in which C₀ and C_t respectively represent the initial concentration and the residual concentration after t min in the solution.

$$E(\%) = \left(1 - \frac{C_t}{C_0}\right) \times 100 \quad (5)$$

The amount of total iron (Fe^{II} and Fe^{III}) leached in the reaction mixture after catalytic tests was determined by a coulometric method as described in our previous work [17]. Briefly, a 5 mL solution was withdrawn from the mixture after 120 min of reaction and filtrated. Three drops of Spectroquant[®] reagent (Merck Millipore) for the detection of iron were then added to such solution. After 3 min, the solution was transferred to a cuvette which was placed afterward to the UV-Vis spectrophotometer for absorbance measurement at 560 nm.

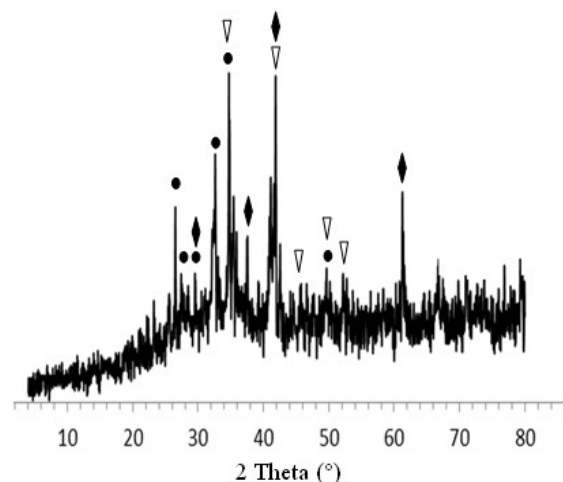
3. Results and discussion

3.1. XRD and SEM-EDS characterization of the ash

The X-ray patterns of the volcanic ash (Fig.1) showed a large amount of amorphous material, in addition to the crystalline minerals augite/diopside ($\text{Ca}(\text{Mg,Fe,Al})(\text{Si,Al})_2\text{O}_6$, PDF no. 41-1483), ordered anorthite, $((\text{Ca, Na})(\text{Al,Si})_2\text{Si}_2\text{O}_8$, PDF no. 20-528) and ferroanforsterite $((\text{Mg,Fe})_2\text{SiO}_4$, PDF no. 31-795). These results hence indicate that iron in volcanic ash is mainly contained in augite and ferroanforsterite minerals. The material could also contain amorphous iron oxides, since a Mossbauer spectroscopy analysis undertaken on a similar sample in previous study has shown the presence of two types of ferrous iron, accounting respectively for 55 and 23%, together with 23% of ferric iron mainly located in the amorphous phase [16].

The results of SEM and EDS analysis presented in Fig.2 revealed a relatively widespread distribution of iron element in the ash particles. The element mass percentage of iron was found to be about 13%, relatively close to the mass percentage of Fe_2O_3 obtained by the chemical analysis. Considering some interesting results obtained in previous studies on Fenton-like system using catalysts prepared with materials containing approximately 2.5 and 6.8 wt% iron [20], the amount of iron present in the current volcanic ash is enough to provide a good reactivity in Fenton-like system, provided

their chemical and mineralogical state in the ash are suitable for the process. Besides, in case of good suitability for Fenton-like process, volcanic ash based catalysts are expected to be lower cost because of no requirement of iron enrichment as often the case for some aluminosilicates based catalysts used for Fenton process [20, 21].



▽ = aluminian augite, $\text{Ca}(\text{Mg, Fe, Al})(\text{Si, Al})_2\text{O}_6$ (PDF n° 41-1483)
 ● = sodium anorthite, $((\text{Ca, Na})(\text{Al, Si})_2\text{Si}_2\text{O}_8$ (PDF n° 20-528)
 ◆ = ferroan forsterite, $((\text{Mg, Fe})_2\text{SiO}_4$ (PDF n° 31-795)

Fig.1. X-ray diffraction patterns of volcanic ash showing crystalline phases of Fe-containing minerals.

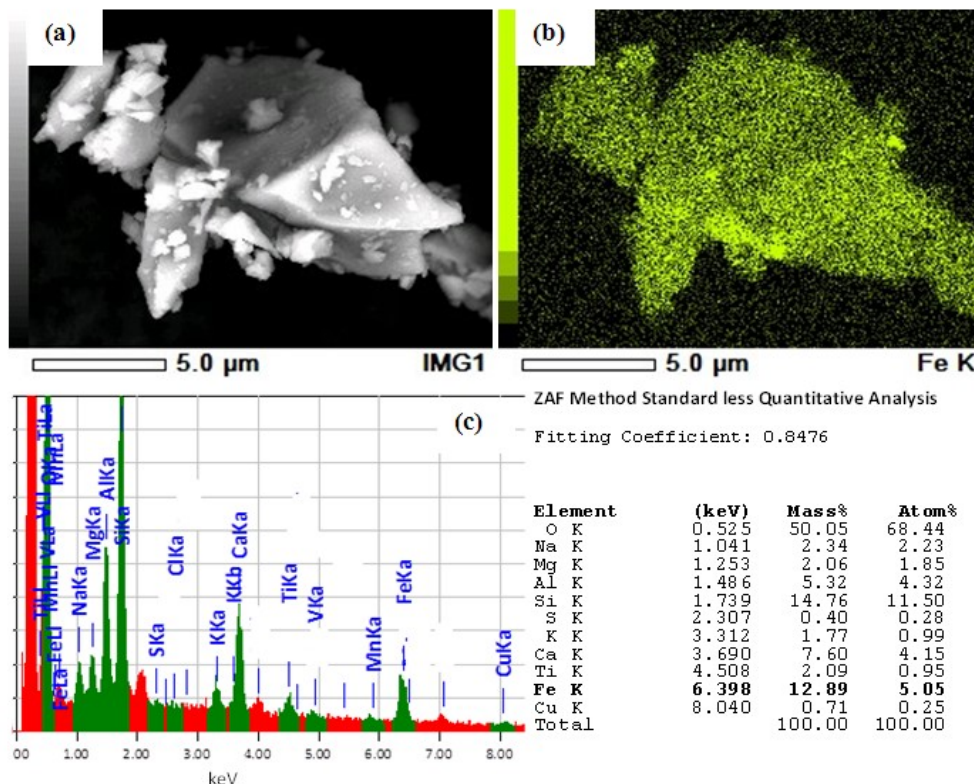


Fig.2. SEM image (a), surface Fe mapping (b) and EDS results (c) of a volcanic ash particle highlighting the presence of iron on the ash particles.

3.2. Catalytic abatement of Rh6G

The Rh6G abatement was first evaluated by recording the UV-Vis spectra of the dye solution from 330 to 800 nm (Fig.3a). The spectrum of the starting solution presents two resolved bands: the first one in UV region ($\lambda_{\text{max}} = 351$ nm) and the second one in the visible region ($\lambda_{\text{max}} = 513$ nm). As the reaction proceeds, the band at 513 nm gradually decreases owing to progressive degradation of dye. Furthermore, the overlay of all the spectra shows an isobestic point at 450 nm, suggesting that the total concentration of both dye and degradation by-products is constant at this point, and that the dye abatement favours the formation of products that absorb in the UV region. As a consequence, it was difficult to discuss on the behaviour of the peak at 351 nm during the process.

The kinetics of Rh6G abatement was also studied. As shown in Fig.3b, 78% dye was degraded within 120 min in the presence of both H_2O_2 and volcanic ash (i.e. H_2O_2 -VA system). Furthermore 14% of dye was degraded in the presence of H_2O_2 alone, while only 7% of dye was removed by adsorption process onto volcanic ash surface. The sum of abatement efficiencies obtained with the non-catalytic oxidation process and with the adsorption process is lower than that obtained with the H_2O_2 -VA system, suggesting that the 78% abatement percentage obtained with such system is not due to a combined effect of adsorption and non-catalytic

oxidation, but to a catalytic activation of H_2O_2 via a Fenton-like process. This result is confirmed by the HO^\bullet radicals scavenging results. As shown in Fig.3c, the abatement efficiency of Rh6G decreased markedly from 78% to 20% in the presence of 20 mM of methanol. Indeed, aliphatic alcohols have been successfully used as selective radical scavengers to evaluate the contribution of HO^\bullet radicals for organic pollutant abatement [22]. The effect of the initial dye concentration on the abatement efficiency was also investigated. Experiments were conducted with various concentrations of dye (10, 20, 25, 30 mg/L) at solution pH = 3 in the presence of 5 g/L of volcanic ash. It can be seen from Fig.3d that the abatement decreases from 100% to 39% with an increase initial concentration from 10 to 30 mg/L. Moreover, Table 2 also shows that the abatement reaction is faster for low initial dye concentration. Indeed, the half-time $t_{1/2}$ (i.e., the time to reach 50% of abatement) increases with increasing initial dye concentration. A similar result was obtained by Rajoriya et al. during the degradation of Rh6G using hydrodynamic cavitation. These authors attributed the lower abatement efficiency/rate at initial concentration of Rh6G higher than 10mg/L to the insufficient generation of HO^\bullet radicals to degrade the dye, suggesting that the relevant proportion of total amount of HO^\bullet radicals and dye molecules is a significant factor [23].

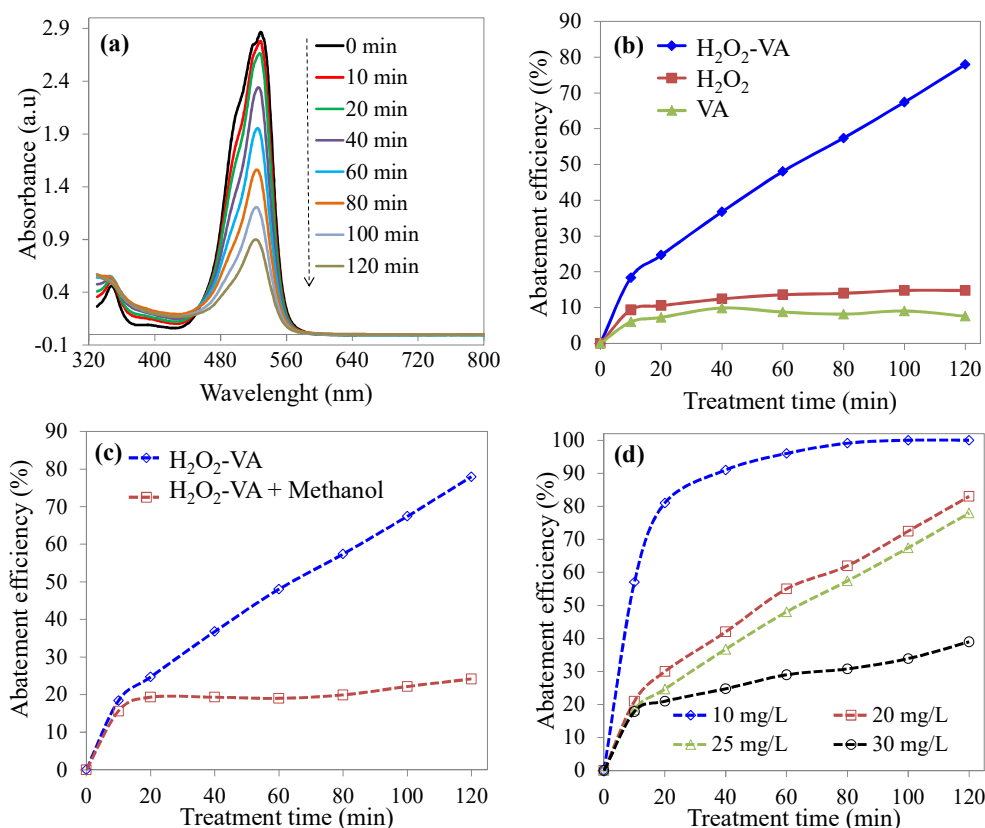


Fig.3. Abatement efficiency of Rh6G using VA catalyst (a) UV-Vis spectral change and (b) evolution of abatement efficiency as a function of treatment time ([VA]=5 g/L; [Rh6G]=25 mg/L and initial pH=3); (c) Effect of HO^\bullet scavenger on the abatement efficiency ([VA]=5 g/L; [Rh6G]=25 mg/L, [Methanol]=20 mM and initial pH=3) and (d) Abatement kinetics as a function of initial dye concentration ([VA]=5 g/L and initial pH=3).

Table 2*Rh6G degradation efficiency and reaction half-time as a function of initial dye concentration*

Initial Rh6G concentration (mg/L)	Abatement efficiency after 120 min (%)	Half-time $t_{1/2}$ (min)
10	100	8
20	83	52
25	78	64
30	39	n.d

3.3. Effect of initial pH and catalyst dosage on Rh6G abatement

The effect initial pH solution on the degradation efficiency of organic pollutants via a heterogeneous catalysed Fenton reaction has been intensively studied. Most of the results showed the quasi pH dependence of heterogeneous Fenton process which, in the most cases was more efficient in acidic than in basic or neutral medium. Nevertheless, while using silica-alumina as catalyst support, several researches showed that the catalyst was still active even at near neutral pH, thanks to the contribution of the solid acidity of the support [8,9,13]. In this work, the effect of initial solution pH was also studied. The results obtained (Fig.4a) reveal a drastic decrease of the abatement efficiency when the

initial pH was increased from 2.5 to 10. The higher abatement efficiency (92%) was obtained at pH = 2.5 and was probably a consequence of the contribution of homogeneous catalytic process. Indeed, at such pH value, the active species can be leached from the solid phase, and then contribute to the activation of H_2O_2 via a homogeneous Fenton process (Eq.6 and Eq.7). This result corroborates those reported by He et al. [24] and Kakavandi and Babaei [25]. However, such process is normally not hoped since it contributes to the catalyst deactivation which disables it reuse.

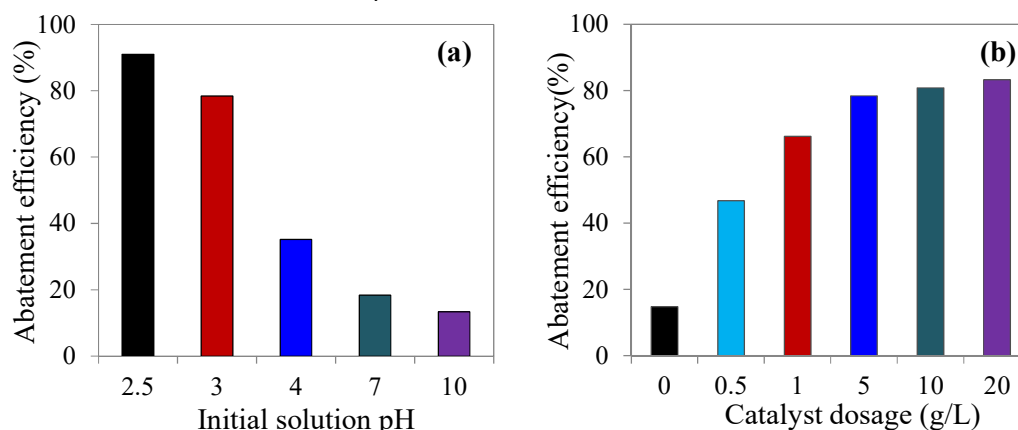
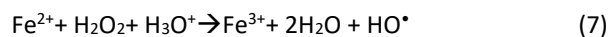
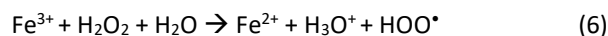


Fig.4. Effect of (a) initial solution pH ([VA] = 5 g/L; [Rh6G] = 25 mg/L) and (b) catalyst dosage ([Rh6G] = 25 mg/L; initial pH = 3) on the Rh6G abatement efficiency after 120 min.

The abatement of Rh6G in the VA- H_2O_2 system was also evaluated with various volcanic ash loadings. It can be observed from Fig.4b that during the process, the efficiency of Rh6G removal increased from 51% to 78% when the catalyst dosage increased from 0.5 to 5 g/L. This is mainly due to (i) the increase of active sites which improves the decomposition of H_2O_2 into HO^* radicals, and (ii) the providing of additional surface area for the adsorption of dye molecules on the catalyst [26,27]. Beyond 5 g/L loading, no remarkable change in Rh6G abatement was observed, suggesting that the maximum catalyst dosage for the abatement of such dye should be 5 g/L. The removal efficiency for optimum catalyst dosage remains lower than that previously obtained by Dökkancı and collaborators [28]. Indeed, those authors succeeded to totally degrade Rh6G after 120 min of treatment by a Fenton process using CuFeZSM-5 zeolite catalyst. Nevertheless, our system is

most efficient for Rh6G degradation than the hydrodynamic captivation coupled with H_2O_2 as presented by Rajoriya et al. who obtained only 54% of discolouration [23].

3.4. Catalyst recyclability

The second aim of this work was to investigate on the heterogeneous catalytic behaviour of volcanic ash. Since an important characteristic of heterogeneous catalyst is its potential reuse, the recyclability tests were undertaken during Rh6G degradation in VA- H_2O_2 system. For this purpose, the dye abatement was investigated for four consecutive runs. After each run, the catalyst was separated from the solution, washed with distilled water, dried in an oven at 110°C for 3 hours before being used for the next run. The results presented in Fig.5 show a drastic decrease in the abatement efficiency from the first to the third run. This

drop in abatement efficiency could be explained by (i) the mass loss of volcanic ash during the filtration/washing process and (ii) the leaching of the iron species from the solid support with reduces the number of active sites of the catalyst. The second explanation would be more representative. Indeed, 0.005mmol of iron was leached in the medium after 120 min during the first run. Furthermore, no decreased of abatement efficiency was observed between the third and the fourth run, suggesting that most of the soluble iron phases were removed after the third run. This could open a new route for pre-treating volcanic ash based on washing such material with acidified solution for its efficient use as recyclable Fenton-like catalysts.

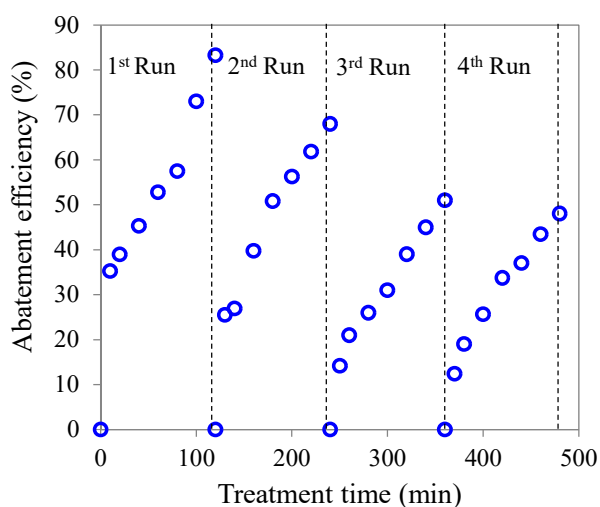


Fig.5. Effect of Volcanic ash reuse times on Rh6G abatement ([VA] = 5 g/L; [Rh6G] = 25 mg/L and initial pH = 3).

4. Conclusion

The aim of this study was to evaluate the properties of a natural volcanic ash from Foumbot (west-Cameroon) for its potential use as heterogeneous Fenton catalyst. The characterization of such material showed that it contains some iron-based minerals (namely augite and ferroanforsterite). The Fe content of such material was sufficient to initiate the Fenton-like abatement of Rhodamine 6G. Its catalytic performances were dependent on the initial dye concentration and initial solution pH. The higher abatement efficiency was obtained at pH = 2.5 and was due to the contribution of homogeneous catalyzed reaction by the leached iron species. A deactivation of the catalyst due to the leaching of active species was observed during the recyclability tests. This study led to establish that volcanic ash from Foumbot deposit can be used as a cheap efficient Fenton-like catalyst for the treatment of organic dyes containing wastewater. Nevertheless, this material needs to be pre-treated in order to avoid or to limit the iron leaching process, aiming at improving its efficient recyclability.

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