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## Efficient removal of Orange G using Prussian Blue nanoparticles supported over alumina

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### ABSTRACT

Prussian Blue nanoparticles (PBNP) synthesized and adsorbed onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> spheres were prepared and characterized by transition and scanning electron microscopy (TEM, SEM), energy dispersive X-ray spectroscopy (EDS) and sorptometry. Adsorption and reaction runs were performed using aqueous solutions of a model azo dye Orange G. The adsorption capacity of the PBNP/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 323 and 343 K at initial pH 3 and 6 was studied. The presence of PBNP increased the adsorption capacity of the support and this effect was more pronounced at initial pH 6. However, since the adsorbent life time was narrow and its regeneration quite difficult, PBNP/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was tested as a heterogeneous Fenton-like catalyst. The catalytic activity and stability for oxidation of Orange G were investigated in terms of discolouration, TOC and oxidant conversion.

At the best operating condition studied (343 K and pH<sub>0</sub> = 3), complete dye discolouration and 60% of mineralization were attained while reaction largely overcomes adsorption. At this temperature the catalyst activity and its characteristics remained almost invariable during 9 cycles of 5 h each and iron leaching occurred in low extent.

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### 1. Introduction

The removal of dyes from textile wastewater is considered an environmental challenge because even a small quantity of organics in water can be toxic and highly visible. The term “dyes” includes a vast number of compounds that commonly present chromophore groups, responsible for producing the colour, and auxochrome groups which enhance the affinity of the dye towards the fibres. Usually, dyes can be classified into cationic, anionic and nonionic dyes. Cationic dyes are basic dyes while the anionic dyes include direct, acid and reactive dyes [1]. Cationic and anionic dyes present in textile liquid effluents could be remediated by Fenton or Catalytic Wet Peroxide Oxidation (CWPO) processes under reasonably mild conditions of temperature and pressure [2]. Therefore, increasing efforts have been made regarding the development of heterogeneous Fenton catalysts, given their easy removal and reusability. Soon and Hameed [3], provides a review of different kind of iron

catalysts immobilized on inorganic supports (i.e. zeolite, clay, activated carbon, alumina, fly ash, etc.) for synthetic dyes removal. Nevertheless, the main problem associated with these catalysts arises from the leaching of the iron active phase [4].

In particular, few researchers used alumina as solid catalyst support in Fenton system. Bautista et al. [4] showed that Fe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was more effective than Fe/AC catalyst for the treatment of cosmetic wastewaters. In a more recent work, Bautista et al. [5] reported good catalyst stability testing Fe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst on phenol solutions.

Prussian Blue (Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]<sub>3</sub>) (PB) is a prototype of mixed-valence compounds with well-known electrochromic and electrocatalytic properties [6], although recently its catalytic behaviour was also demonstrated by Liu et al. [7]. These authors showed that the mixture of PB colloids and hydrogen peroxide can function as a heterogeneous Fenton reagent. Later, Wang et al. [8] reported excellent catalytic activity towards the oxidation of Methylene Blue.

In this contribution, Prussian Blue nanoparticles (PBNP) adsorbed onto granular  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were prepared, characterized and tested for the peroxidation of Orange G, an anionic azo dye that possesses two bulky sulfonic groups. This catalytic system was selected given Prussian Blue has shown remarkable stability when it is adhered as a solid phase to metal oxides [9]. Moreover, as its

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solubility at low pH is very small [10], stability under reaction conditions may be favoured. To our knowledge, the deposition of PBNP over alumina and its use as Fenton like catalyst was not previously reported.

## 2. Experimental methods

### 2.1. Catalyst preparation and characterization

The  $\gamma$ - $\text{Al}_2\text{O}_3$  spheres (SASOL,  $d_p = 2.5$  mm) used as support, were washed with distilled water at room temperature and dried for 12 h at  $110^\circ\text{C}$ . PBNP were synthesized following a procedure based on the reaction between  $\text{FeCl}_3$  and  $\text{K}_3\text{Fe}(\text{CN})_6$  using  $\text{H}_2\text{O}_2$  as reducing agent. An aqueous solution of  $\text{FeCl}_3$  13 mM and  $\text{K}_3[\text{Fe}(\text{CN})_6]$  10 mM at pH 2–3 was prepared. Then, the  $\gamma$ - $\text{Al}_2\text{O}_3$  spheres and  $\text{H}_2\text{O}_2$ , in a slight substoichiometric ratio, were added suddenly to produce the PBNP and immediately adsorb them onto the support. Alumina spheres were left in contact with the PBNP suspension for 1 h under orbital shaking. Thereafter,  $\gamma$ - $\text{Al}_2\text{O}_3$  spheres containing adsorbed PBNP were separated by screening, washed and dried in air at room temperature.

All chemicals used for catalyst preparation and oxidation tests were analytical grade without any further purification.

The iron content in the fresh and used catalysts was quantified using the following procedure: a sample of the solid (200 mg) was calcined at  $700^\circ\text{C}$  to degrade the PBNP; then, the formed iron oxide was extracted by adding 5 ml of boiling concentrated HCl for five times. The extract was transferred to a 100 ml volumetric flask and diluted with bi-distilled water to fall within the range of the calibration curve. The standards were prepared using  $\text{FeNH}_4(\text{SO}_4)_2 \times 12\text{H}_2\text{O}$  (PM:482) and adjusting the pH to 1 with HCl. The standard solutions and the sample were diluted 1:2 with KSCN 0.01 M to form the characteristic red complex. Absorbance at 475 nm was used for quantifying the dissolved Fe(III), using a SHIMADZU UV-1800 spectrophotometer and contrasting with the absorbance of the standards.

Specific areas of the support and the prepared PBNP/ $\gamma$ - $\text{Al}_2\text{O}_3$  were determined from  $\text{N}_2$  adsorption isotherms at 77 K.

The morphology of the catalyst was examined by transmission electron microscopy (TEM) and scanning electron microscopy (SEM); the superficial iron distribution was mapped with Energy Dispersive X-ray Spectroscopy (EDS).

### 2.2. Adsorption and CWPO experiments

The performance of the prepared PBNP/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst was studied in the Fenton-like oxidation of a model azo dye Orange G (OG). The following experiments were carried out:

- Decomposition of OG with  $\gamma$ - $\text{Al}_2\text{O}_3$  support (with and without  $\text{H}_2\text{O}_2$ ) at  $\text{pH}_0 = 3$  and  $T = 323$ – $343$  K.
- Decomposition of OG with  $\text{H}_2\text{O}_2$  (in darkness or exposed to natural light) at  $\text{pH}_0 = 3$  and  $T = 323$  K.
- Adsorption and/or reaction of OG with PBNP/ $\gamma$ - $\text{Al}_2\text{O}_3$  at  $\text{pH}_0 = 3$ – $6$  and  $T = 323$ – $343$  K.
- Reaction stability tests at  $\text{pH}_0 = 3$  and  $T = 343$  K.

Runs were conducted in a thermostated stirred glass batch reactor with 200 mL capacity. Solid was placed into a basket to mitigate particles abrasion arising from the stirring. To start each test, 175 mL of an OG aqueous solution was placed into the reactor. Assays at  $\text{pH}_0 = 6$  (original pH of OG solution) and  $\text{pH}_0 = 3$  were performed. When it was necessary, the initial pH ( $\text{pH}_0$ ) was adjusted by using 1 M  $\text{H}_2\text{SO}_4$  or 1 M NaOH and it was measured with a pH-metre from HANNA instruments. No pH control was performed

during the experiments. Reaction was initiated by adding a calculated amount of  $\text{H}_2\text{O}_2$  and the basket containing the catalyst into the reactor. The operating conditions were:  $T = 323$ – $343$  K;  $[\text{PBNP}/\gamma\text{-Al}_2\text{O}_3] = 6.5$  g/L and  $[\text{OG}]_0 = 0.2$  mM. The effect of initial pH ( $\text{pH}_0 = 3$ – $6$ ) for a stoichiometric initial oxidant concentration ( $[\text{H}_2\text{O}_2]_0 = 9$  mM) was assessed. The catalytic activity was evaluated by measuring discolouration, pH,  $[\text{H}_2\text{O}_2]$ , Total Organic Carbon (TOC), carboxylic acids and the UV–vis spectra along the 5 h reaction time. Liquid samples were taken out periodically and analyzed at once. Results reported here represent the mean of at least three identical experiments.

The UV–vis spectra of samples were recorded from 190 to 800 nm using a SHIMADZU UV-1800 spectrophotometer. The maximum absorbance wavelength ( $\lambda_{\text{max}}$ ) of OG is in the visible range, at 492 nm. To assess mineralization, Total Organic Carbon was measured using a SHIMADZU TOC-V CPN Total Organic Carbon analyzer. Hydrogen peroxide concentration was determined by a Glycemia enzymatic test (Wiener Lab.).

Carboxylic acids were measured by ion-exclusion HPLC (VWR Hitachi ELITE LaChrom) fitted with a Rezex<sup>TM</sup> ROA-Organic Acid H+ (8%) 300 mm  $\times$  7.8 mm (Phenomenex) column. It was operated at 298 K and in isocratic mode using 0.005 N sulphuric acid at a flow rate of 0.5 mL/min as mobile phase. The samples injection volume was 10  $\mu\text{L}$  and the DAD (L-2455) was set at  $\lambda = 210$  nm.

### 2.3. Determination of lixiviated active phase

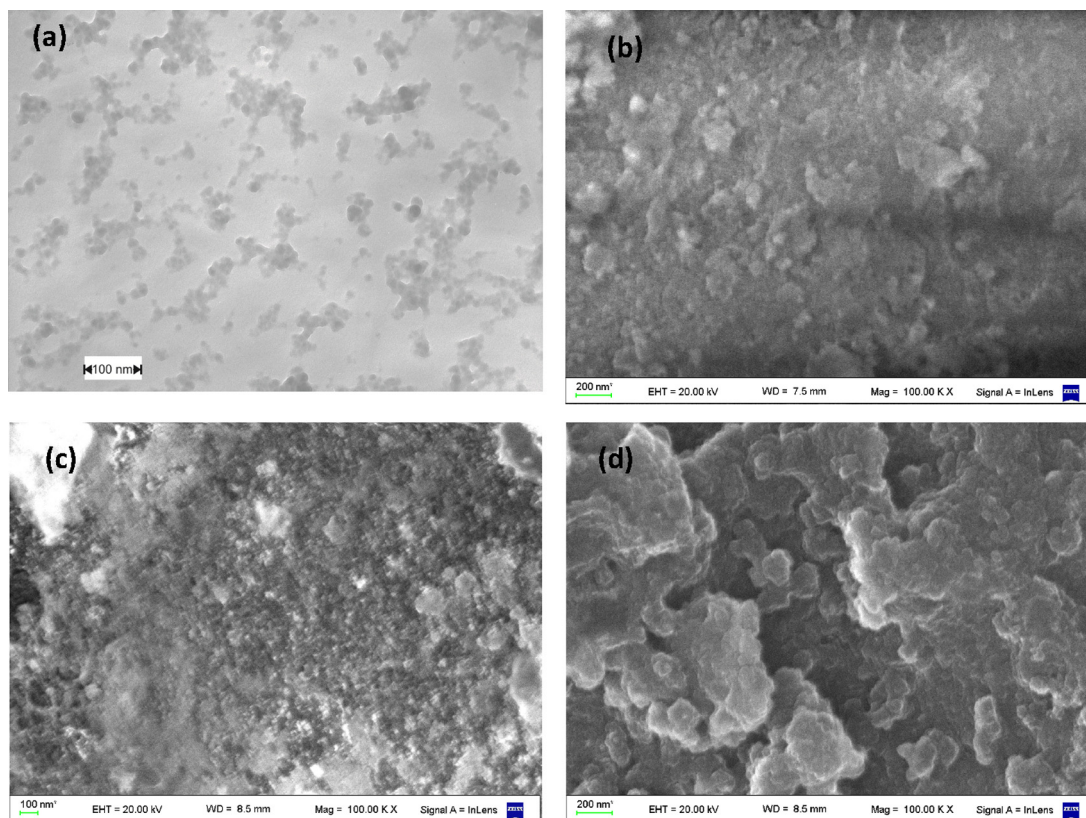
Prussian Blue nanoparticles, ferrocyanide–ferricyanide ions or “free” iron cations may be released into treated solutions. Total “free” iron was measured with the HACH FerroVer method. The presence of PBNP and ferrocyanide–ferricyanide ions was monitored by UV–vis spectroscopy. PBNP shows a broad band at around 700 nm. The mixture ferrocyanide–ferricyanide ions can be tracked at  $\lambda$  260 and 420 nm, as demonstrated by Chakrabarti and Roberts [11].

## 3. Results and discussion

### 3.1. Catalyst characterization

The total Fe content in the prepared catalyst is 0.38 w%, as determined spectrophotometrically after solid degradation. BET surface area measured for the support is 224  $\text{m}^2/\text{g}$ , whereas for the catalyst is 190  $\text{m}^2/\text{g}$ . A slight decrease (around 20%) of the catalyst BET surface area with respect to  $\gamma$ - $\text{Al}_2\text{O}_3$  area is observed and could be attributed to partial blockage of the porous net.

Fig. 1 shows TEM and SEM photographs of the PBNP and the catalysts surface. The PBNP formed by the described preparation procedure are shown in Fig. 1(a), to illustrate the size and shape of the particles which are adsorbed onto the alumina. The alumina surface inspected by SEM is shown in Fig. 1(b) to compare with the texture of the fresh and used catalyst surface (Fig. 1c and d). The fresh catalyst surface evidences the roughness introduced by the adsorbed PBNP. After using the catalyst for nine cycles, the surface appears slightly less wrinkled. The distribution of the Fe atoms over the catalyst surface, determined by EDS points to a fairly homogeneous and concentrated distribution of active sites. One bead of catalyst was divided into halves and inspected visually to disclose the distribution of the active phase. The catalyst has a white core and a blue egg shell. The PBNPs are concentrated mainly on the outer surface of the catalyst grains (a shell of approximately 30  $\mu\text{m}$  width as estimated from the map of Al and Fe atoms obtained by EDS on the border of the inner bead half). The iron content determined by EDS on the external shell is about 6% in weight.



**Fig. 1.** (a) TEM photograph of the PBNP; (b) SEM photograph of the alumina surface; (c) SEM photograph of the fresh catalyst surface; (d) SEM photograph of the surface of a bead used in 9 consecutive reaction cycles.

**Table 1**

Experiments performed at  $\text{pH}_0 = 3$ ,  $[\gamma\text{-Al}_2\text{O}_3] = 6.5 \text{ g/L}$  and  $[\text{OG}]_0 = 0.2 \text{ mM}$ .

	$\text{H}_2\text{O}_2$ (mM)	Solid	$T$ (K)	% Discoloration	%TOC
Room light	0	$\gamma\text{-Al}_2\text{O}_3$	323	–	–
Room light	9	$\gamma\text{-Al}_2\text{O}_3$	323	5 (1 h) 46 (5 h)	–
Room light	9	–	323	4 (1 h) 48 (5 h)	–
Dark	9	–	323	–	–
Room light	9	$\gamma\text{-Al}_2\text{O}_3$	343	26 (1 h) 98 (5 h)	5

### 3.2. Preliminary runs

#### 3.2.1. Support effect

In order to evaluate the effect of the  $\gamma\text{-Al}_2\text{O}_3$  support on OG degradation, preliminary experiments at  $\text{pH}_0 = 3$ , with and without hydrogen peroxide were performed. Outcomes are presented in Table 1. In the absence of  $\text{H}_2\text{O}_2$ , colour of fresh model wastewater remained unchanged, whereas 46% and 98% discoloration was gradually attained in presence of  $\text{H}_2\text{O}_2$  (9 mM) after 300 min at 323 and 343 K, respectively. In these experiments, the colour of the support did not change significantly. No TOC was removed in any case, so adsorption could be considered negligible.

Further experiments carried out just with OG and  $\text{H}_2\text{O}_2$  and keeping the glass-reactor in the dark or exposing it to natural light are shown in Table 1. Results confirmed that the oxidant is decomposed with natural light to render hydroxyl radicals that react with the chromophore group.

#### 3.2.2. PBNP/ $\gamma\text{-Al}_2\text{O}_3$ adsorption experiments

A set of experiments were done to explore the adsorption capacity of the PBNP/ $\gamma\text{-Al}_2\text{O}_3$  at 323 and 343 K without addition of  $\text{H}_2\text{O}_2$  at  $\text{pH}_0$  3 and 6. The OG solution (0.2 mM) was left in contact with

the solid during 5 h. For both  $\text{pH}_0$  values at 323 K, 96% of discoloration was attained at 5 h, whereas the TOC was reduced in around 85%. This points to a quantitative adsorption of the dye; the 10% discrepancy between TOC and discoloration values can be assigned to analytical uncertainties. The UV–vis spectra profiles (not shown) evidenced the gradual disappearance of OG from the solution. Moreover, visual observation of the outer part of the catalyst revealed a distinct colour change from blue to brown after these assays, whereas the colour inside the grain turns from white to bright orange. This fact clearly indicates that adsorption is the governing process related to OG depletion from the liquid phase.

The adsorption runs were performed over consecutive cycles. The solid was dried overnight at room temperature and used again in contact with fresh OG solution. Experiments were repeated until saturation was reached. The amount of dye adsorbed onto the catalyst at the end of each cycle,  $q_c$  (mg/g), was calculated as:  $q_c = (C_0 - C_c)/W$ ; where  $C_0$  is the initial dye concentration (mg/l),  $C_c$  is the dye concentration measured at the end of each 5 h cycle (mg/l) and  $W$  is the concentration of solid used (g/l).

Outcomes are shown in Fig. 2 for different  $\text{pH}_0$  and temperature values. For  $\text{pH}_0 = 3$  and 323 K, the solid adsorbed approximately 16.2 mg/g of OG in two consecutive cycles. After that, no OG was removed from the solution, so the solid was virtually saturated. In experiments performed at the same temperature but at  $\text{pH}_0 = 6$ , the amount of OG adsorbed over 4 cycles was 44.7 mg/g. Clearly, the amount of dye adsorbed increased with pH. The lower adsorption capacity observed at initial pH 3 may be attributed to a decrease in OG dissociation. This results in a lower sulfonate groups concentration available to interact with the catalyst surface [12]. Vieira et al. [13] stated that the pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization and speciation of different pollutants.



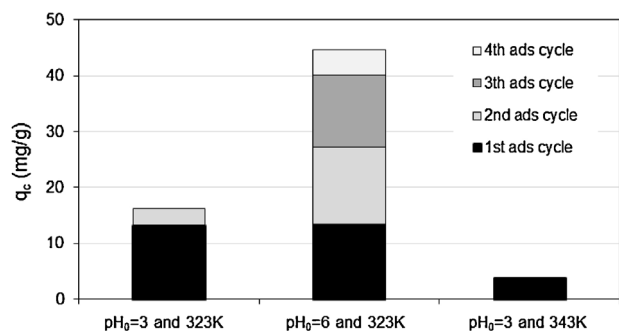


Fig. 2. Amount of dye adsorbed onto the PBNP/ $\gamma$ - $\text{Al}_2\text{O}_3$  in consecutive adsorption cycles for different  $\text{pH}_0$  and temperature.  $[\text{H}_2\text{O}_2]_0 = 0$  mM,  $[\text{PBNP}/\gamma\text{-Al}_2\text{O}_3] = 6.5$  g/L.

At 343 K and  $\text{pH}_0$  3, the amount of OG adsorbed was less than 5 mg/g and solid saturation was attained in a single run (Fig. 2). The high temperature resulted in a decrease in the adsorption capacity with a 27% discolouration in 5 h. The observed trend may indicate that the adsorption is an exothermic process [1]. This tendency has also been observed by Gupta et al. [14], who argued that dye molecules may tend to escape from the solid phase to bulk phase with increasing temperature.

As a whole, while the alumina support presents nil adsorption capacity, when the PBNP are synthesized over the alumina, the adsorption capacity of the solid is greatly enhanced. This could be related to the crystalline structure of PBNP, which generally exhibits vacancies, capable to accommodate neutral molecules or composites with anionic hosts [15,16].

The possibility of regenerating the PBNP/ $\gamma$ - $\text{Al}_2\text{O}_3$  adsorbent was investigated. The solid used in a single run with 0.2 mM of OG at  $\text{pH} = 6$  and 323 K was immersed in a known volume of bidistilled water at  $\text{pH}_0 = 6$  and 323 K. The mixture was shaken for 48 h, until no changes in the liquid dye concentration were observed. Desorption efficiency was found to be less than 10%.

Since electrostatic interaction of OG with the solid surface can be minimized at pH values higher than 10 [12], a run at pH 11 using bidistilled water as solvent was carried out. At this condition, OG but also PB were desorbed from the alumina. This confirmed that Prussian Blue is not stable at higher pH values [9].

### 3.3. Catalytic experiments

As shown previously, under certain experimental conditions the synthesized PBNP/ $\gamma$ - $\text{Al}_2\text{O}_3$  particles can be used as an adsorbent. However, the adsorbent life time is narrow and its regeneration is difficult. So, further experimental work was performed using PBNP/ $\gamma$ - $\text{Al}_2\text{O}_3$  as a heterogeneous Fenton-like catalyst. Test were carried out with  $[\text{catalyst}] = 6.5$  g/L and  $[\text{OG}]_0 = 0.2$  mM at  $\text{pH}_0$  3 and 6, and  $T = 343$  K.

Briefly, for initial  $\text{pH} = 6$ , the addition of  $\text{H}_2\text{O}_2$  had negligible influence on neither discolouration nor TOC removal. Moreover, no improvement was observed after adding  $\text{H}_2\text{O}_2$  to a PBNP/ $\gamma$ - $\text{Al}_2\text{O}_3$  sample previously saturated at  $\text{pH}_0$  6. So, the subsequent experiments were performed at  $\text{pH}_0$  3, other conditions particularly specified.

### 3.4. Peroxidation experiments

The discolouration as well as the mineralization of OG were investigated in experiments performed at  $\text{pH}_0 = 3$  and 323 K and 343 K using the stoichiometric amount of  $[\text{H}_2\text{O}_2]$ . For all experiments, the pH remained constant at around 3 and no induction period was observed. Discolouration, TOC and  $\text{H}_2\text{O}_2$  profiles are

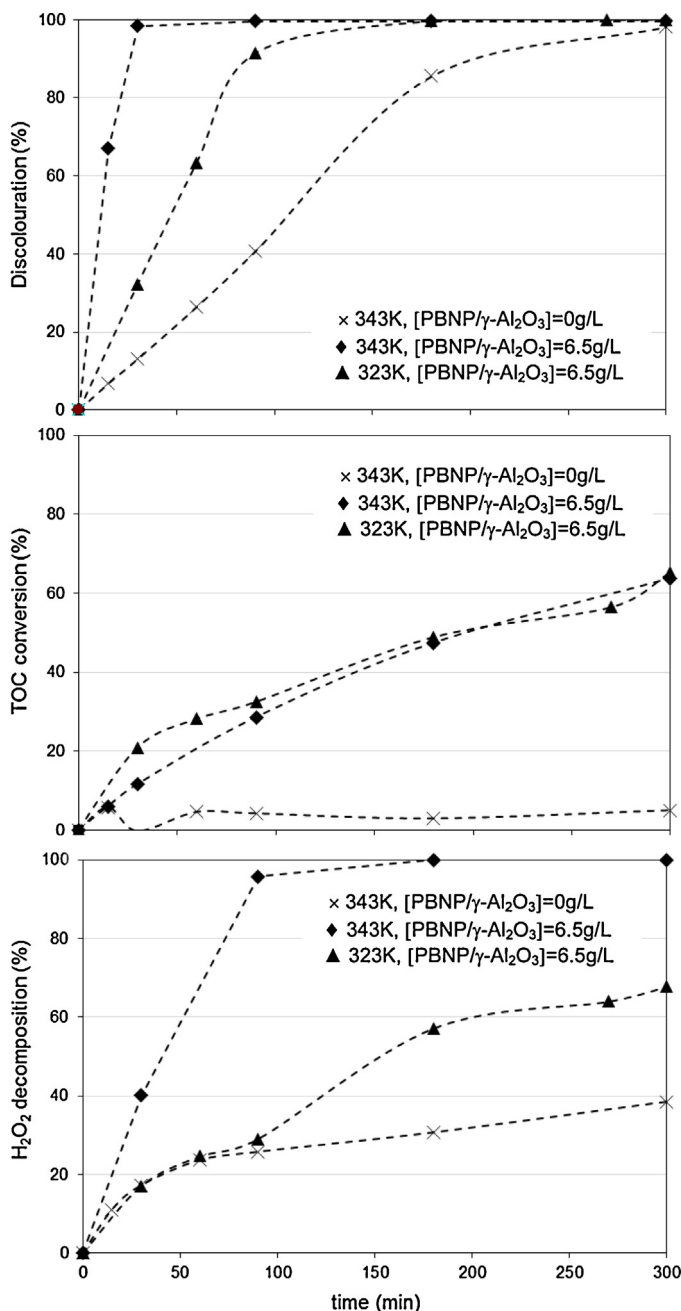


Fig. 3. Temporal evolution of colour removal, TOC conversion and oxidant decomposition for different temperatures.  $[\text{H}_2\text{O}_2]_0 = 9$  mM,  $[\text{OG}]_0 = 0.2$  mM,  $\text{pH}_0 = 3$ .

shown in Fig. 3. In all figures, profiles attained in a blank run at 343 K without catalyst are shown for the sake of comparison.

At 323 K, complete discolouration is achieved at 180 min and about 63% of TOC removal is attained within 300 min. The presence of  $\text{H}_2\text{O}_2$  enhanced discolouration rate but decreased the TOC conversion reached during adsorption experiments, probably because intermediate reaction products are less adsorbable and remain in solution contributing to the measured TOC. Only the 68% of the initial  $\text{H}_2\text{O}_2$  is decomposed. Furthermore, the inner colour of the catalyst turns from white to light orange after usage. This evidences the co-existence of adsorption and oxidation processes.

On the other hand, at 343 K, oxidant is completely consumed within 180 min; almost complete discolouration is attained within 30 min and 63% of initial TOC is removed at the end of the experiment. There are no significant differences between the TOC profiles

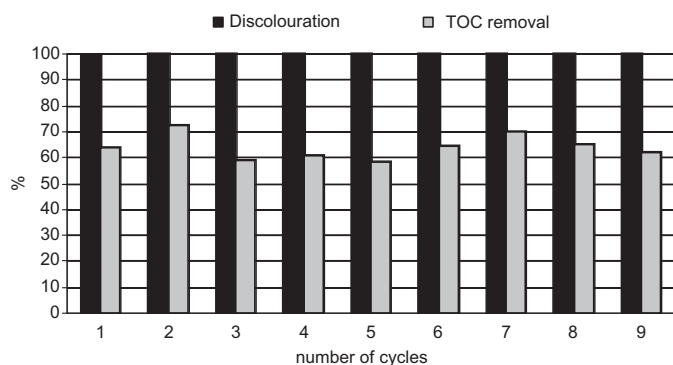


Fig. 4. Outcomes obtained at the end of each 5 h-cycle.  $T = 343$  K,  $pH_0 = 3$ .

attained for the two temperatures studied; however at 343 K oxidation apparently prevails since the colour of the catalyst remained unchanged after 300 min (white core and blue shell).

The decomposition rate of hydrogen peroxide, as expected, is enhanced at higher temperatures. A decrease in the oxidant decomposition rate in the presence of OG is observed (outcomes not shown), probably due to the competition of the organic species for the generated radical's propagation [17,18].

### 3.5. Stability

For this anionic dye, best catalytic performance was obtained at the lower pH studied and the catalytic capacity of the solid was enhanced at higher temperatures. Based on these findings, further experiments were performed at  $pH_0 = 3$  and 343 K to examine catalyst stability. The solid was recovered from the solution after the reaction, dried at room temperature and tested again for the peroxidation of fresh OG solution at the same reaction conditions. For all cycles, fresh OG solution was almost completely discoloured within 60 min. Oxidant consumption was beyond 98% at the end of each cycle and pH was almost constant along time. Discolouration and TOC conversions attained at 5 h in runs with a  $H_2O_2$  concentration of 9 mM and 343 K are presented in Fig. 4. Activity in terms of discolouration and TOC removal was maintained after the 9 cycles of 5 h in values higher than 99.6% and 60% respectively.

After 9 cycles, the beads were visually inspected and their appearance seemed not to be affected, showing a white core and blue egg shell. Fig. 1d shows a SEM photograph of a used bead revealing no significant morphological/textural changes. BET surface remained practically constant ( $180\text{ m}^2/\text{g}$ ).

Moreover, at the end of each cycle, a colourless solution (with no solids in suspension nor precipitated) was attained. The total Fe content in the used catalyst (determined after solid thermal degradation) was 0.32 w/w%. Total “free” iron lixiviated gradually

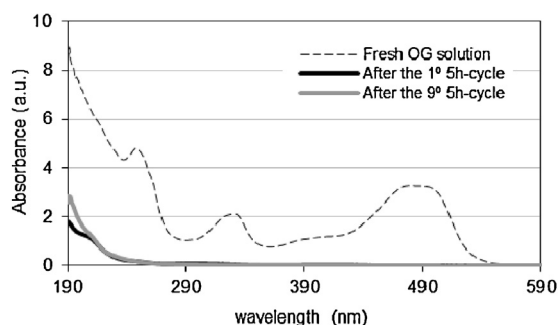


Fig. 5. UV-vis spectral changes for the original fresh OG solution and at the end of the first and the ninth cycle.  $T = 343$  K,  $pH_0 = 3$ .

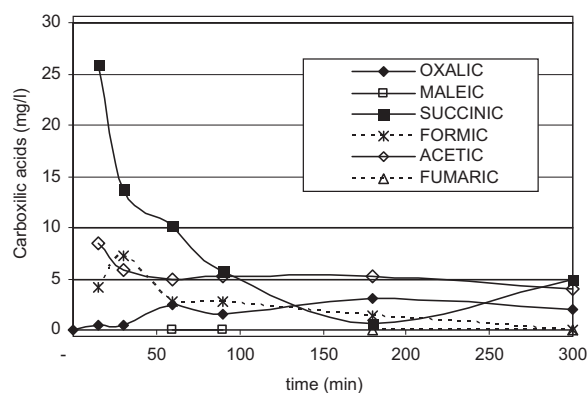


Fig. 6. Carboxylic acids produced during OG oxidation.  $[H_2O_2]_0 = 9$  mM,  $[OG]_0 = 0.2$  mM,  $pH_0 = 3$ , 343 K,  $[PBNP/\gamma\text{-}Al_2O_3] = 6.5$  g/L.

decreased during the first 4 cycles from 0.7 mg/l to 0.3 mg/l, and then remained constant.

Fig. 5 presents the evolution of UV-vis absorption spectra along the consecutive runs performed with  $PBNP/\gamma\text{-}Al_2O_3$  and  $H_2O_2$ . The absorbance axis is presented in arbitrary units (a.u.). At time 0, the peak at 492 nm is associated to the azo groups ( $N=N$ ) and the peaks at 248 and 331 nm in ultraviolet region are related to the benzene and naphthalene rings of the dye, respectively [19]. The presence of hydrogen peroxide is reflected in the spectra at the beginning of the experiment through a higher absorbance measured between 190 and 240 nm. As the reaction proceeds, the decrease in the intensity of the peaks at 200 nm is related to the decomposition of  $H_2O_2$ . The characteristic peaks of OG decreases indicating that the azo bonds and the aromatic rings are gradually broken. At the end of each run,  $H_2O_2$  is almost completely depleted. The negligible leaching of  $PBNP$  is confirmed since no absorbance was measured beyond 600 nm.

No absorbance is measured in visible region, however, remnant peaks are observed at UV region. Signals in the UV region can be related to aromatic and carboxylic acids formed from the dye degradation. In addition, traces of ferricyanide and ferrocyanide ions lixiviated along reaction might contribute.

The presence of carboxylic acids was confirmed by ion-exclusion HPLC analysis in samples obtained during the first cycle of reaction at 343 K,  $pH_0 = 3$ . The results allowed only the identification of the following carboxylic acids: maleic, succinic, fumaric, oxalic, formic and acetic. Their evolution is presented in Fig. 6. As can be seen, succinic, formic and acetic acids are the earliest species formed, while oxalic acid is formed progressively along the reaction course. Only traces of fumaric and maleic acids were detected.

## 4. Conclusions

$PBNP$  were prepared via the reaction between  $FeCl_3$  and  $K_3Fe(CN)_6$  adding suddenly  $H_2O_2$  as the reducing agent and adsorbed onto  $\gamma\text{-}Al_2O_3$  beads; forming a kind of egg-shell catalyst. Our study shows that  $PBNP/\gamma\text{-}Al_2O_3$  effectively oxidizes Orange G in the presence of  $H_2O_2$ . Under the best operating condition tested ( $[PBNP/\gamma\text{-}Al_2O_3] = 6.5$  g/L,  $[OG]_0 = 0.2$  mM, 343 K and  $pH_0 = 3$ ), complete dye discolouration and 60% of mineralization was attained. Under these conditions, reaction largely overcomes adsorption. Maleic, succinic, fumaric, oxalic, formic and acetic acids were identified as intermediates in the OG degradation. The catalyst has shown to maintain its catalytic performance after 9 cycles of 5 h. Total “free” iron loss was less than 15%. The  $PBNP$  were not detected in aqueous solution and the lixiviation of ferrocyanide–ferricyanide ions was almost negligible.

PBNP/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> proved to be an active and stable catalyst for the CWPO of a model anionic azo dye water contaminant at mild oxidation conditions.

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