Hydroxyapatite-supported Silver Nanoparticles and Preliminary Investigations of their Catalytic Potential

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The hydroxyapatite-supported silver nanoparticles were synthesized and used as a new type of catalyst for the discoloration of a model cationic dye in a Fenton-like process. The structure and morphology of the catalyst were investigated by FTIR, TEM and SEM before and after reaction. The main factors that could influence the catalytic activity were summary investigated. The catalytic activity was monitored by evaluating the discoloration degree from the absorbance data recorded in the visible spectra. The results obtained during these preliminary investigations are very promising from applicative point of view.

Keywords: hydroxyapatite, silver nanoparticles, catalysis, dye discoloration

Hydroxyapatite (HAp) is a key inorganic component of the animal endo- and exo-skeletons, and have the stoichiometric formula $Ca_{10}(PO_4)_6(OH)_2$ for a Ca/P molar ratio of 1.67. Due to the particularities of hexagonal-cylinder crystalline structure and ionic radius, HAp shows excellent ion-exchange properties, which in turn conduct to a large variety of Ca/P molar ratios and crystalline forms, either calcium-rich or calcium-depleted, with a general formula $Ca_{10-n}(HPO_4)_n(PO_4)_{6-n}(OH)_{2-n}(H_2O)_n$ [1]. The structural resemblance and good biocompatibility with bones and teeth, the absence of toxicity, facile osteointegration and high versatility for physical and chemical manipulation as well as for integration in composite materials have made from HAp of mineral, synthetic or biologic origins a common, widely used raw material for biomedical applications like bone and dental grafting, healing, reconstruction and repair, tissue engineering and drug delivery [2-5].

However, the particular surface properties like porosity, high surface area, coexistence of acidic and basic sites, strong ion-exchange and adsorptive behavior, the exposure of lattice oxygens and hydroxyls, associated with good thermo-mechanical stability and very low water solubility, have furthermore attracted a high interest in using HAp as catalyst in organic syntheses [6-8] or to eliminate wastewater contaminants like dyes [9, 10], pesticides [11] and heavy metal ions [12]. More recently it was also reported that metal doping or surface deposition of metal and metal oxide nanoparticles like Au, Pd, Sr, Ru, Fe_3O_4, CuO, CeO_2, and ZnO could tune up and enhance the catalytic activity of the resulting material as compared with the initial, unmodified catalysts [13-19].

Silver nanoparticles (AgNPs) were loaded on HAp as well but, although there are numerous reports that confirm the suitability of AgNPs as catalyst or photocatalyst for a series of organic synthesis [20-22] and dyes degradations [23-25], the researches were mainly focused on their antibacterial properties and potential applications as dental materials [26-28]. Nevertheless, valuable catalytic performances have been obtained with AgNPs loaded onto various supports like alumina [29], silica [30], hydrotalcite [31], zinc oxide [32], manganese oxide [33], and nanometric diamond [34].

Such supports could increase the stability of the catalysts and may also act in synergy with the metallic nanoparticles guests, enhancing the overall catalytic efficiency. We have also reported a facile and green way to obtain HAp-supported AgNPs with potential use as dental fillers [35], and it became interesting from applicative point of view to test if such constructs shows a significant catalytic activity as well. In line with some of our previous researches [36], basic blue 41 (BB 41), a very stable basic azo-dye that frequently contaminates the industrial wastewaters from wool weaving and textile production, has been selected as target compound for catalytic degradation.

Experimental part
Materials
The hydroxyapatite mineral support was obtained from Sigma-Aldrich as a reagent grade synthetic powder and used without any further purifications or treatments. Silver nitrate ($AgNO_3$), sodium hydroxide (NaOH) and hydrochloric acid (HCl) of analytical purities were also purchased from Sigma-Aldrich. Sodium lignosulphonate (LS; powder, 93% dry substance) and hydrogen peroxide (H_2O_2; 30% w/w) have been supplied by Carl Roth.

The hydroxyapatite-supported silver nanoparticles catalyst (HAp/Ag) has been obtained as previously described [35]. Briefly, 1 g HAp was stirred with deionized water into a cylindrical glass reactor. After addition of 20 mL LS (2% wt.) and temperature increase to 70°C, 2 mL $AgNO_3$ (0.1M) were poured in dropwise. Reaction was continued for 2 h under vigorous stirring, maintaining the *p*H at 6-6.5 with NaOH (0.1 M). The liquid mixtures were furthermore desiccated under vacuum at 60°C, 12 h, and the resulting solid was extracted and conditioned for another 3 h in an oven at 600°C.

The model cationic azo textile dye, BB 41 (40% dye content; fig. 1), was supplied by Sigma-Aldrich. Ultrapure deionized water was used in all experiments.
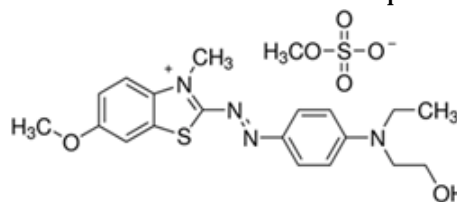

Fig. 1. The chemical structure of BB 41 cationic dye

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Characterization

The structural analysis was carried out on a Fourier transform infrared spectrometer (FT-IR) Vertex 70 (Bruker Optics) by KBr technique (600-4000 cm^{-1} domain). A transmission electron microscope (TEM) HT7700 (Hitachi) and a scanning electron microscope (SEM) Quanta200 (FEI) low vacuum apparatus equipped with an energy dispersive X-Ray (EDX) module for elemental analysis were used to assess the morphology of initial and used catalyst. The AgNPs formation and dye discoloration were evidenced with a LAMBDA 35 (Perkin Elmer) UV-Vis spectrophotometer (300-800 nm scan range), whereas the pH of aqueous solutions was measured with an OP-211 Radelkis Kft pH meter.

Discoloration procedure

All discoloration experiments were run in 250 mL Erlenmeyer flasks, under occasional shaking. In a standard test, dye samples of 100 mg L^{-1} were treated with 2 mL H$_2$O$_2$ (30% w/w) in the presence of 100 mg catalyst, at room temperature and pH 6.0. Furthermore, a summary evaluation of the main factors that could significantly influence the discoloration rate and degree was made by changing the concentrations of catalyst (50 mg; 200 mg), dye (50 mg L^{-1}; 200 mg L^{-1}) and H$_2$O$_2$ (0 mL; 1 mL), the reaction temperature (4; 60^{0}C) and pH (4; 8). Dye samples treated with H$_2$O$_2$ only were also analyzed for comparison.

The evolution of discoloration degree was followed by monitoring the variation of absorbance registered at λ = 611 nm, and comparing the results with the values given by known dye concentrations ranging from 0.005 to 0.05 mg mL^{-1}, within the linearity domain of correspondence.

The discoloration degree (%) was calculated according with formula:

$$Discoloration\ (\%)\ = \frac{C_0 - C_t}{C_0} \cdot 100\ ,$$

where C_0 is the initial dye concentration and C_t represents the dye concentration at time t as results from the absorbance standard calibration curve.

Results and discussions

The successful formation and deposition of AgNPs on HAp fragments was evidenced before calcination by recording the TEM images (fig. 2) and scanning the UV-Vis spectra of the resulted colloidal solutions (maximum absorbance at ~ 400 nm; fig. 3), which confirms the presence of relative spherical AgNPs less than 20 nm in diameter [35, 37], well anchored on HAp surface.

The employment of various metal-based nanoparticles supported on inorganic minerals in catalytic processes was extensively studied in the last years as part of the sustained efforts for greener synthesis and a cleaner environment. In the case of dye elimination the very most studies carried out on such catalysts have been focused on photocatalytic and adsorptive processes. However, due to the specific
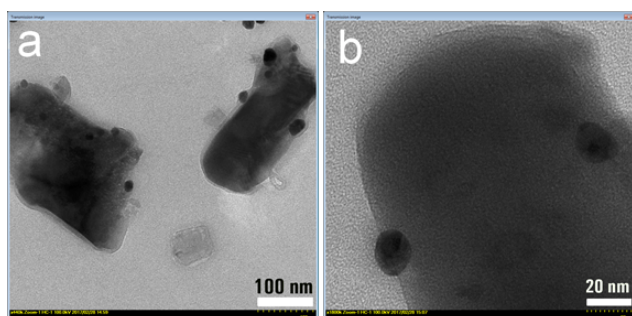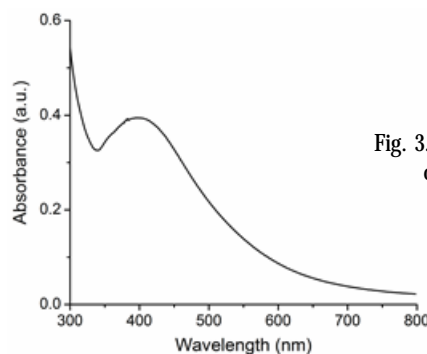

Fig. 3. Typical UV-Vis spectra of HAp/Ag colloids

properties of AgNPs combined with the surface characteristics of HAp, a Fenton-like degradation was considered for the initial testing of the HAp/Ag catalyst.

The preliminary tests regarding the HAp/Ag catalytic potential were focused on the discoloration of the BB 41 dye model, and have started with the assessment of the influence of catalyst concentration both in the absence and presence of H$_2$O$_2$ Fenton reagent (fig. 4). Either H$_2$O$_2$ or HAp/Ag alone has a limited efficiency in discoloration, but HAp/Ag performs significantly better than H$_2$O$_2$. Nevertheless, the maximum discoloration degree was attained for the HAp/Ag/H$_2$O$_2$ system (~39-50% after 1 hour and 94-96% after 1 day, as compared with ~29-42%, and 55-75% respectively in the absence of H$_2$O$_2$, where the highest values correspond to the highest HAp/Ag concentrations). In the absence of catalyst, H$_2$O$_2$ gives significantly lower results (10% after 1 h and 33% after 1 day). It must be noted that, as shown in the picture taken after 24 h (fig. 5), the HAp/Ag/H$_2$O$_2$ system is the single one that achieved a virtually complete discoloration.
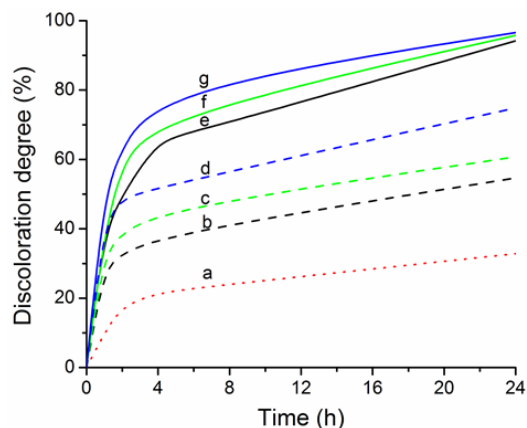

Fig. 4. BB 41 discoloration degree in the presence of: (a) H$_2$O$_2$; (b) 50 mg, (c) 100 mg, (d) 200 mg HAp/Ag; H$_2$O$_2$ and (e) 50 mg, (f) 100 mg, (g) 200 mg of HAp/Ag

Fig. 5. Visual presentation of BB 41 solutions at 24 hours: untreated (a); discolored with H$_2$O$_2$ (b), HAp/Ag (c), and HAp/Ag/H$_2$O$_2$ (d)

The increasing amounts of catalysts improve the discoloration rate especially in the first hours, but with lower yields. It was also observed that higher H$_2$O$_2$ amounts do not furthermore improve the discoloration rate and degree, and even display slight inhibitory effects (table 1). On the other hand, the rising dye amount substantially

Fig. 2. TEM micrographs of HAp/Ag at different magnifications

Time (h)	1mL H$_2$O$_2$ + HAp/Ag	1mL H$_2$O$_2$	2 mL H$_2$O$_2$ + HAp/Ag	2 mL H$_2$O$_2$
	Discoloration (%)	Discoloration (%)	Discoloration (%)	Discoloration (%)
1	41.52	9.65	39.51	9.95
2	49.49	12.63	48.68	17.95
4	65.96	14.08	64.48	21.45
6	67.62	19.66	65.18	22.94
24	96.31	26.97	94.23	32.83

Table 1
THE EFFECT OF H$_2$O$_2$ CONCENTRATION ON DISCOLORATION

Time (h)	BB 41, 100mg/L		BB41, 200mg/L	
	Discoloration (%)	mg/g catalyst	Discoloration (%)	mg/g catalyst
1	58.80	15.53	52.55	46.91
2	69.49	23.82	60.19	53.03
3	77.28	28.94	72.86	60.78
4	83.80	35.53	80.39	64.40

Table 2
THE EFFECT OF DYE CONCENTRATION ON DISCOLORATION

Fig. 6. The influence of temperature on discoloration

Fig. 7. The influence of pH on discoloration
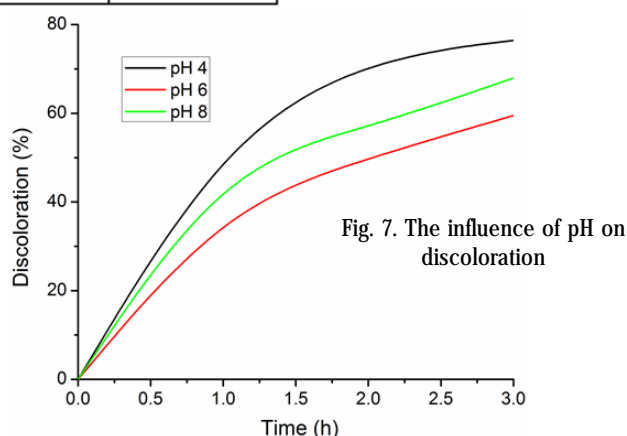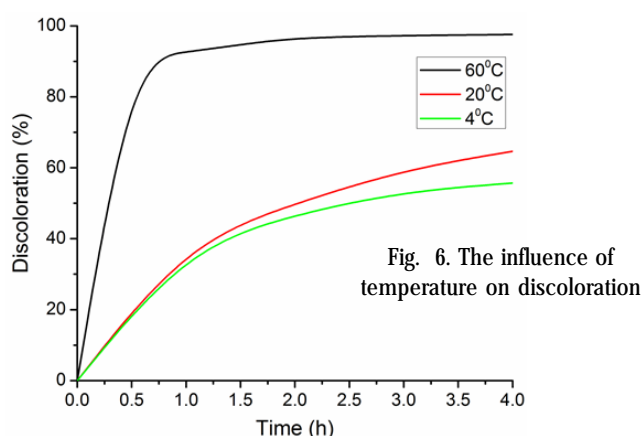
improves the HAp/Ag/H$_2$O$_2$ efficacy (expressed as mg discolored dye / g catalyst), with only a minor reduction in the discoloration degree (table 2).

As expected, the temperature has a strong influence on the reaction rate, a discoloration degree of 90.8% being achieved after only 30 minutes at 60^{0}C (fig. 6). From applicative point of view is also important that lowering the reaction temperature to 4^{0}C inhibit only in a low extent the discoloration process as compared with 20^{0}C. An acidic *p*H of 4.0 has conducted to better results than a slight basic or acidic one (fig. 7), but the pH range should be extended to find an optimum. In fact, the aim of this work was to report the applicative potential of a new catalyst in Fenton-like degradation reactions. The elucidation of the reaction mechanism, an optimization process and other catalytic applications are currently under investigations.

The stability of the HAp/Ag was examined by FTIR and SEM. The infrared data (not shown) indicate almost no changes in the absorption of specific HAp bands, suggesting only a very slight increase in the amount of hydrates corroborated with a questionable faint loose in phosphates. Moreover, the SEM images taken at two different magnifications (fig. 8) do not show any visible differences between the unreacted HAp/Ag and those previously used with H$_2$O$_2$ or alone as catalysts.
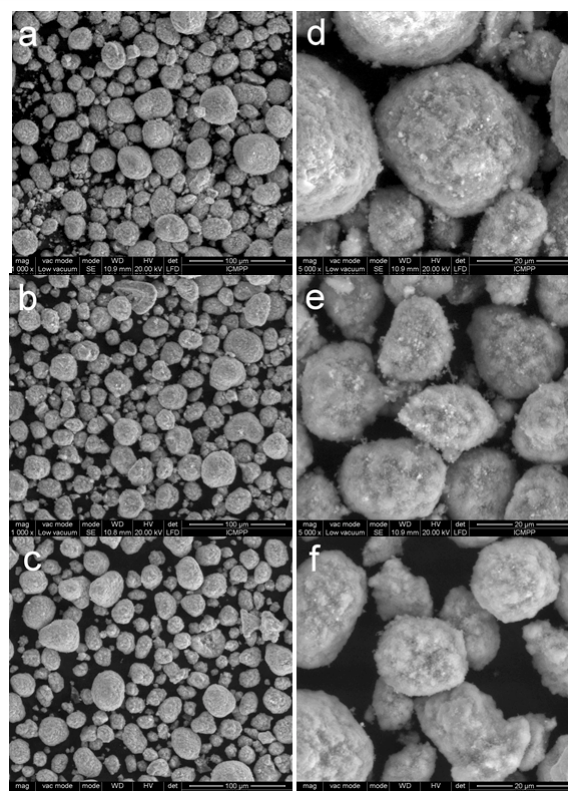

Fig. 8. SEM images of HAp/Ag catalysts after 24 h incubation in pure deionized water (a, d); BB 41 (b, e) and BB 41 + H$_2$O$_2$ (c, f) reaction mixtures

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In a previous papaer were studied silver nanoparticles used for obtain cellulosic materials with antibacterial properties [38].

Conclusions

The synthesized hydroxyapatite-supported silver nanoparticles could be successfully used as a new type of catalyst for the discoloration dyes in Fenton-like processes. This work suggests that is stable enough in the reaction conditions and could give well to excellent results at relative low concentrations. The H_2O_2 concentrations required for obtaining high discoloration rates and degrees should be also limited at low to very low levels. An acidic pH seems to be more effective than a slight acidic or basic. A relative mild temperature of 60^0C tremendously speeds up the discoloration rate. Still, the $HAp/Ag/H_2O_2$ catalytic system seems to be efficient at high dye concentrations. All these results are very promising from applicative point of view, but an extensive optimization work is highly needed and is currently underway.

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