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Catalysis

Copper-Based Hybrid Polyion Complexes for Fenton-Like Reactions

Mathieu Mestivier, Jun Rong Li, Aurèle Camy, Camille Frangville, Christophe Mingotaud, Florence Benoît-Marquié,* and Jean-Daniel Marty*^[a]

Abstract: An innovative strategy allowing the development of a new generation of easy-to-prepare and easy-to-use nano-sized catalysts with high tenability is presented. This strategy is based on the formation of hybrid polyion complexes (HPICs) from the complexation of copper with a block copolymer consisting of an ionizable complexing block and a neutral stabilizer block. These complexes have a well-defined structure and size with a hydrodynamic diameter

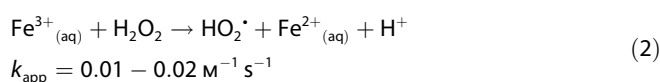
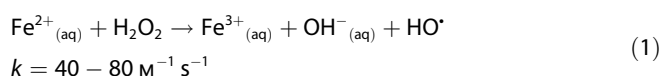
around 29 nm. They are stable in aqueous solution over a pH range from 4 to 8 and are not sensitive to NaCl salt addition or dilution effects. As a proof-of-concept the degradation of naphthol blue black in water through the use of the Fenton or photo-Fenton reaction is studied. Their performances are comparable to a classical homogeneous reaction, whereas HPICs are easily recyclable by simple dialysis.

Introduction

Nanostructures have been recognized as promising catalysts owing to their high surface-to-volume ratio and high catalytic selectivity.^[1] The use of shape- and size-controlled nanocatalysts facilitates quasi-homogeneous catalysis, thus merging the benefits of homogeneous (higher activity) and heterogeneous catalysis (better separation).^[2] Different families of nanocatalyst have been developed. Metal or metal oxide nanoparticles (Pt, Pd, Au, TiO₂,...),^[3,4] zeolites,^[5] metal-organic frameworks (MOFs)^[6] are by far the most studied. Nevertheless, their synthesis often requires tedious conditions with specific stabilizing agents that hamper the development of multicatalytic systems.^[1] The development of metal-supported systems that are easy to prepare, highly tunable, and with high colloidal stability is still a requirement. In this context, supramolecular metal-containing polymeric structures, like hybrid polyion complexes (HPICs), also called coacervates, can be of great interest. Their formation has been achieved through the simple mixing of charged polyvalent metal ions (e.g., Cu^{II}, Zn^{II},...) to a solution of double hydrophilic block copolymers (DHBCs).^[7–9] The obtained nanoobjects have a hydrodynamic diameter around 20 nm and present a high colloidal stability in aqueous solution. Such objects have been used as highly powerful contrast agents by using Gd ions^[10] or as templates to promote the

preparation of metal hydroxide, oxide, or sulfide nanoparticles of different shapes (plate-like, elongated, spherical) and controlled sizes.^[11,12] Hence, the size- and properties-controlled formation of inorganic-organic HPIC micelles based on DHBCs is now well understood but no uses as catalysts have been reported.

In this article, an innovative strategy based on the use of HPICs allowing the development of a new generation of easy-to-prepare and easy-to-use nano-sized catalysts with high tenability will be presented. As a proof-of-concept, the degradation of a pollutant in water through the use of the Fenton reaction will be studied.^[13,14] The Fenton reaction makes it possible to produce hydroxyl radicals (HO[•]) from hydrogen peroxide by oxidation of iron(II) salts. The cascade reaction of regeneration of Fe²⁺ ions in the Fenton reaction system is given below [Eqs. (1), (2)]:



Although this reaction effectively produces hydroxyl radicals, it has drawbacks that limit its application in water depollution. The first disadvantage is the relatively small pH range (0–4) for the dissolution of iron ions. At a higher pH, precipitation of iron(III) oxide is favored, which prevents the regeneration of iron(II) (2).^[15,16] The second is the value of the rate of regeneration of ferrous ions [k_{app} in Eq. (2)], which is low compared to k [Eq. (1)]. These ions are therefore consumed much faster than they are regenerated and therefore the production of hydroxyl radicals slows down over time.^[15] The third is the need to be

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able to extract and sometimes reuse the catalyst (iron salts) from the water after treatment.

Therefore, to expand the reaction range towards neutral pH values, iron is replaced here by copper. Copper enables a Fenton-like reaction to occur,^[17] favoring oxidation in the presence of photons to accelerate the regeneration of the reduced species and to limit the formation of organometallic complexes with the radical byproducts produced during oxidation. Then, the formation of HPICs based on the interaction of copper with block copolymers comprising an ionizable complexing block and a neutral stabilizer block, that is, poly(ethylene oxide)-block-poly(acrylic acid)—PEO_{6k}-*b*-PAA_{3k}—as the coordinating polymer will be studied. Interestingly, the metal ions themselves will drive the formation of the HPICs in addition to their functions as catalysts. The obtained HPICs will be used as homogeneous catalysts for the degradation of naphthol blue black (noted later as AB1), which will be chosen as a model reaction in water and at room temperature. Their performance will be compared with a classical homogeneous reaction obtained with free copper ions.

Results and Discussion

Formation of HPICs and study of their colloidal stability

To obtain HPICs, copper ions are added to a 0.1 wt% aqueous solution of the diblock PEO_{6k}-*b*-PAA_{3k} copolymer. In the following, the ratio, $R = 2[\text{Cu}^{2+}]/[\text{AA}^-]$, between the positive charge arising from the divalent Cu^{2+} ions and the potentially available negative charges from the ionized or ionizable carboxylic acid monomer units (AA) of the polymers will be used. The interaction of copper ions with PEO_{6k}-*b*-PAA_{3k} polymers was followed by measuring the absorbance at 700 nm related to the d-d transition of Cu^{2+} ions complexed by carboxylate functions (Figure 1A). This band is also compared with the band relative to free Cu^{2+} ions observed at 800 nm (Figure S1 in the Supporting Information). As can be shown, a linear increase of the absorbance at 700 nm is observed for molar ratio values R from 0 to 1. For higher values of R , a plateau is reached. This increase thereby highlights the expected interactions of Cu^{2+} ions with carboxylate groups from the PAA block. When all carboxylate groups were complexed by Cu^{2+} ions, the absorbance as expected does not evolve anymore. The interaction speed of Cu^{2+} ions with PEO_{6k}-*b*-PAA_{3k} was evaluated through the monitoring of the absorbance at Abs(700 nm) as a function of time for a chosen fixed ratio $R = 1$ (see Figure 1B). Cu^{2+} ions were added under stirring for 7 s after the start of the acquisition time. An exponential fit equation was arbitrarily applied to assess a characteristic time constant, τ , which represents the time after which 63% of the plateau value is reached. This led to an evaluation of τ equal to 1.5 s, characteristic of a fast interaction between Cu^{2+} ions and the PAA block.

DLS measurements were then recorded to assess the colloidal structure resulting from these polymer/metal ions interactions. As shown in Figure 2, the light scattering intensity remains low when $R < 0.5$, increases linearly for $0.5 < R < 1$, and then remains constant. These results suggest the formation of

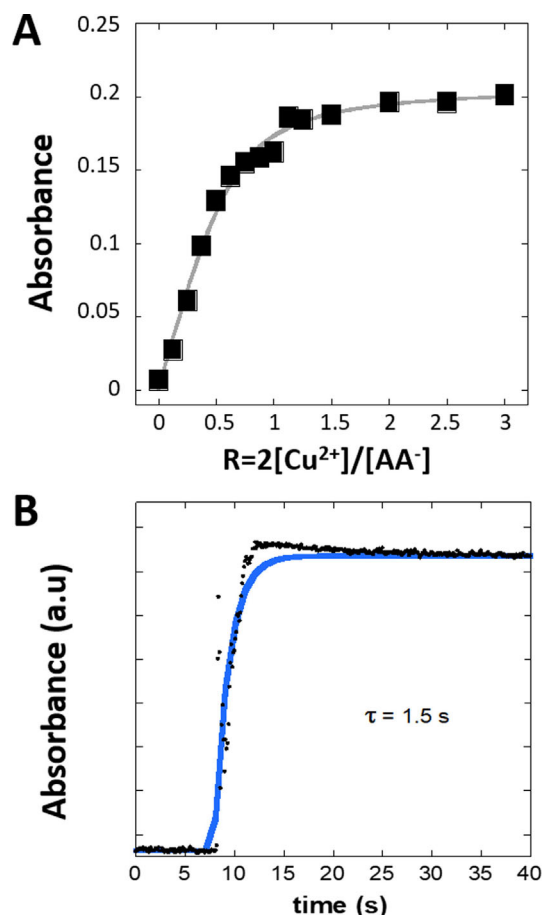


Figure 1. (A) Absorbance at 700 nm as a function of $R = 2[\text{Cu}^{2+}]/[\text{AA}^-]$. (B) Absorbance at 700 nm as a function of time after addition at $t = 7$ s of copper to a 0.1 wt% solution of polymer (with $R = 1$).

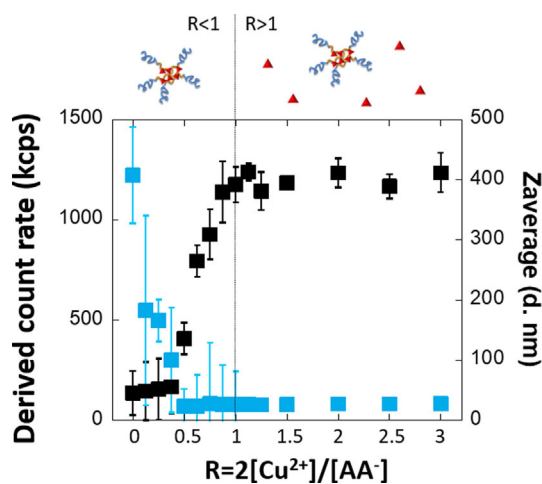
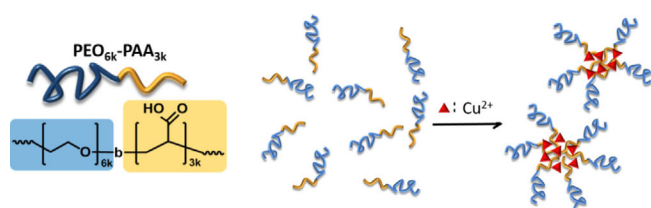


Figure 2. Scattered light intensity (full squares) and Z-average size (full circles, in terms of diameter given in nm) measured for mixed Cu^{2+} /polymer solutions as the ratio, R , is varied (see the Supporting Information, Figure S2 for the corresponding correlograms). The Z-average size data for low values of R is poorly defined (presumably because of self-association of the copolymers in pure water) and are differentiated with open circles. The polymer concentration was 0.1 wt% with the pH adjusted to 7 at room temperature.

colloids, triggered by the addition of copper ions and completed upon achieving electro-neutrality. Analysis of these correlograms in term of *Z*-average size (Figure 2 and Figure S2 in the Supporting Information) also shows two regimes: for $R < 0.5$ the correlograms were poorly defined; accordingly, the calculated *Z*-average values are poorly reproducible. No colloids are formed yet. For R larger than 0.5, the constant value of the *Z*-average size, 33 ± 6 nm, strongly suggests the presence of large polymeric nanoparticles with a constant diameter. The size distribution of the colloidal structures is monomodal for R equal to or higher than 1. The determination of hydrodynamic diameter by a non-negative least squares (NNLS) method led to 32 ± 9 nm (intensity averaged) or 23 ± 5 nm (number averaged). Multi-angle light scattering analysis (Figure S3 in the Supporting Information) enabled us to determine a value of 29 ± 2 nm for the hydrodynamic diameter. The obtained values are comparable to the one obtained for HPICs formed from Gd^{3+} and $\text{PEO}_{6k}\text{-b-PAA}_{3k}$.^[10]

Transmission electronic microscopy (TEM) of dried solutions shows small domains of high contrast with an average diameter of 8 ± 2 nm (Figure S4 in the Supporting Information). These domains presumably arise from the copper ions at the polymer complex core, which will be surrounded by a polymer corona. The zeta potential was measured as a function of R to evaluate the surrounding electric potential of the colloidal objects (Figure S5 in the Supporting Information). Pristine $\text{PEO}_{6k}\text{-b-PAA}_{3k}$ polymer solutions were found to have an overall negative zeta potential value of about $\zeta = -25$ mV at pH 7, a charge which is due to the ionized carboxylate block of polymers in solution. Addition of Cu^{2+} ions then induces the decrease of the zeta potential until $R=1$ where a plateau value of about $\zeta \approx 0$ mV is reached. Data from DLS and zeta potential support the formation of HPICs as follows: for $R < 0.5$, added Cu^{2+} ions interact quickly with the PAA block without the formation of colloidal objects. When the R ratio is greater than 0.5, these interactions led to the formation of HPIC nano-objects with a PAA core crosslinked by copper ions surrounded by a PEG shell as depicted in Scheme 1. The formation of hybrid inorganic/polymeric nanoparticles is complete when the ratio R is close to unity. For higher R ratios, HPICs nanostructures coexist with free Cu^{2+} ions.

When increasing the R ratio from 0 to 3, the amount of free Cu^{2+} ions was assessed by using induced coupled plasma-mass spectroscopy (ICP-MS) analysis and the Zincon back titration method (see the Experimental Section and Figures S6 and S7 in the Supporting Information). For this, HPICs obtained at different R molar ratios were filtered with 3 kDa cut-off centri-



Scheme 1. Synthesis of hybrid polyion complexes (HPICs).

fugal filter devices to collect free Cu^{2+} ions. The filtrates were then analyzed by the addition of the colorimetric probe Zincon. The absorbance corresponding to the Zincon-Cu band at $\lambda = 625$ nm enabled us to evaluate the amount of free Cu^{2+} ions thanks to a calibration curve (see the Experimental Section). The measured concentrations of free Cu^{2+} ions are displayed in Figure 3. For molar ratios R from 0 to approximately 1, no detection of free Cu^{2+} ions was observed, which is consistent with the former observations of bounded Cu^{2+} ions with carboxylate groups of $\text{PEO}_{6k}\text{-b-PAA}_{3k}$ polymers. Further addition of Cu^{2+} for $R > 1$ resulted in an increase of free Cu^{2+} ions in solution, which is consistent with the saturation of carboxylate groups from PAA block.

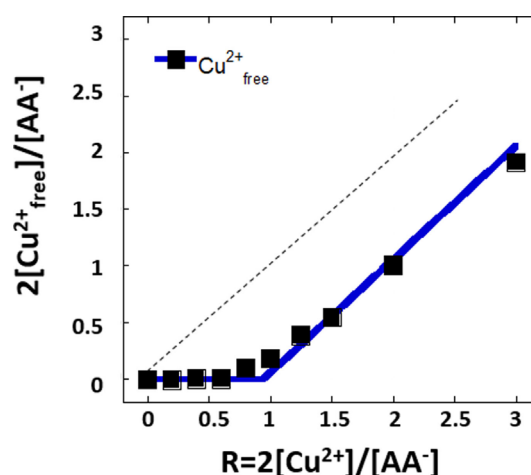


Figure 3. Evaluation of free copper remaining in solution as a function of $2[\text{Cu}^{2+}_{\text{tot}}]/[\text{AA}]$ ratio. The $2[\text{Cu}^{2+}_{\text{free}}]/[\text{AA}]$ ratio is presented as a function of $2[\text{Cu}^{2+}_{\text{tot}}]/[\text{AA}]$. (The dashed line represents the theoretical increase of free Cu^{2+} ions).

The colloidal behavior of HPICs was further assessed over a period of 2 months in high ionic strength conditions by addition of NaCl solution (1 mol L^{-1}). No aggregation was observed through DLS measurements over a two-month period. This result joined with the quasi-null zeta potential values indicates that the colloidal stability of these HPIC objects does not rely on electrostatic stability but rather on steric stabilization supported by hydrated PEGylated chains on the outer corona of the HPIC architecture. The integrity of the HPICs is also maintained with high dilution (up hundred times). Stability over this range of dilution suggests that the NPs are not in equilibrium with free copolymer and Cu^{2+} ions. UV/Vis spectroscopy and DLS measurements were then performed to probe the HPICs colloidal stability for pH values from 8 to 2 (see Figure S8 in the Supporting Information). The amount of released copper as a function of pH was measured thanks to the Zincon method and are reported in Figure 4. HPICs solutions displayed a decrease in the absorbance at 700 nm as well as the derived count rate from scattered light intensity when the pH values decreased from 8 to 5. No release of free Cu^{2+} ions was evident through colorimetric Zincon titration. Below pH 4.5, a sharp decrease of absorbance at 700 nm and derived count

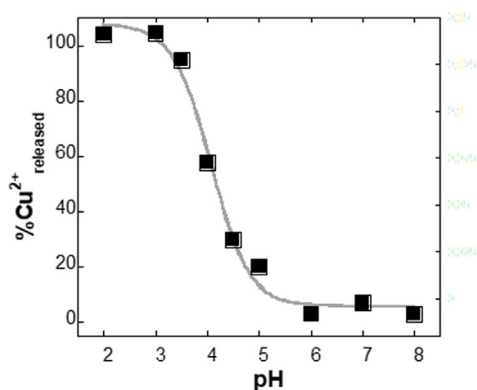


Figure 4. Amount of copper released from HPICs as a function of pH. The evaluation of free copper was performed by using the Zincon method with $[\text{Zincon}] = 4.2 \times 10^{-5} \text{ M}$ and MTEN buffer (MES 100 mM, Tris 50 mM, ethanolamine 50 mM) with Zincon-Cu calibration at pH 9. The amount of free copper was calculated from the measurement of absorbance at 625 nm (see Figure S7 in the Supporting Information).

rate were found. Additionally, free Cu^{2+} ions were found to increase and about 100% Cu^{2+} release was found for pH 2–3. At those pH values, the UV/visible spectra show only a weak band centered around 800 nm, associated with the free hydrated copper ions. These results confirm that the interactions between Cu^{2+} ions and carboxylate groups are the driving forces for their assembly. However, although a $\text{p}K_{\text{a}}(\text{PAA})$ value was reported at 4.5, the half equivalence points of $\text{Cu}^{2+}/\text{PEO}_{6k}\text{-}b\text{-PAA}_{3k}$ systems from the three different analyses techniques were collected at about pH 3.5. The interactions of Cu^{2+} ions with $\text{PEO}_{6k}\text{-}b\text{-PAA}_{3k}$ block copolymers seem consequently to stabilize the carboxylate groups and harden their neutralization through protonation. However, Figure S9 in the Supporting Information provides evidence for a fast disruption ($\tau = 3.0 \text{ s}$) of Cu^{2+} ions interactions with the carboxylate groups of the PAA block below pH 4.5, associated with a full Cu^{2+} ion release along with a disassembly of HPICs colloids. It is noteworthy that preliminary studies on iron-based HPICs have also demonstrated that a decomplexation phenomenon also occurred at pH values below 4.5, thus preventing the use of such iron-based HPICs as Fenton catalysts under low pH conditions.

Fenton reaction

As seen in the previous section, copper-based polyionic complexes have the properties required for use as a catalyst in the Fenton reaction: their formation is simple and follows a quick process. Moreover, they have a well-defined structure and size. They are stable in aqueous solution over a pH range from 4 to 8 and are poorly sensitive to salt and dilution effects. Subsequently, and to avoid the presence of free copper ions during catalytic processes, HPICs characterized by a ratio $R = 1$ will be used. Naphthol blue black, noted as Acid Black 1 or AB1, will be used as a model pollutant in this study.^[18] The reaction is performed at pH 7. Based on previous work, hydrogen peroxide, copper ions, and AB1 were added with the molar ratio 40:1:1.^[19] Photo-Fenton reaction was initiated through irradiation

with a halogen reflector lamp as described in Experimental Section. This photo-Fenton type degradation reaction is studied either in its homogeneous version, that is, with an equivalent concentration of copper but in the absence of polymer or in the presence of HPICs. These two conditions, are noted, respectively, photo-Fenton-Cu and photo-Fenton-HPICs. The degradation of AB1 was also studied in the absence of photochemical irradiation in the presence or absence of HPICs (noted, respectively, Fenton-HPICs and Fenton-Cu). The evolutions of pollutant concentration for the different processes were followed by measuring the optical density at 618 nm and are presented in Figure 5.

To perform photo-Fenton or Fenton-like reaction, the pollutant is first added to a solution of copper (complexed or not with a polymer). The reaction was then initiated by the addition of hydrogen peroxide and followed by UV/Vis spectroscopy as illustrated in Figure 6A (Figures S10 and S11 in the Supporting Information). Figure 6B shows the evolution of AB1 concentration C normalized by its initial concentration C_0 through time. This evolution can be roughly modeled by a pseudo-first-order kinetic evolution.^[18] At 5 h, the conversion observed is equal to 38 mol%. It has to be noted that all pre-

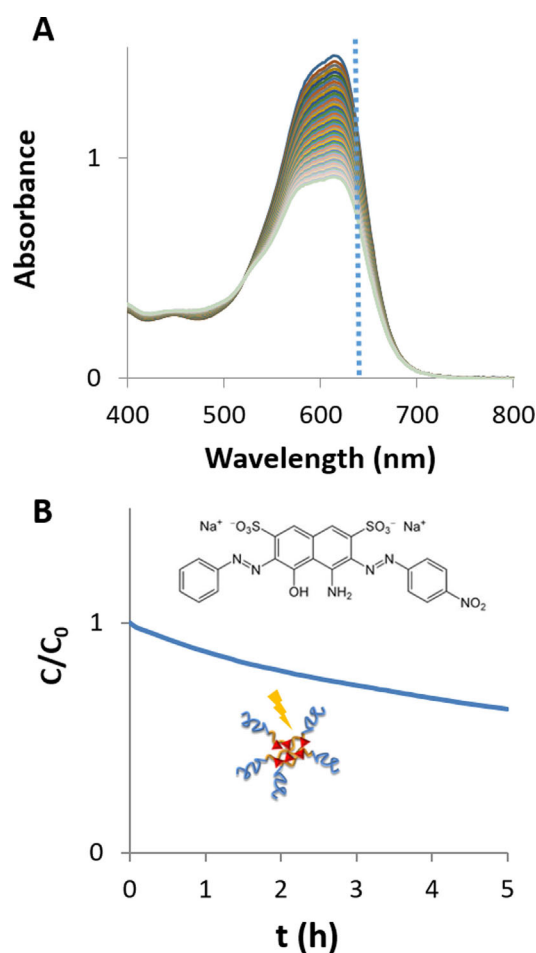


Figure 5. (A) Evolution of the absorption spectrum and (B) evolution of C/C_0 as a function of time at 618 nm of AB1 (structure shown) solution undergoing photo-Fenton degradation in the presence of HPICs.

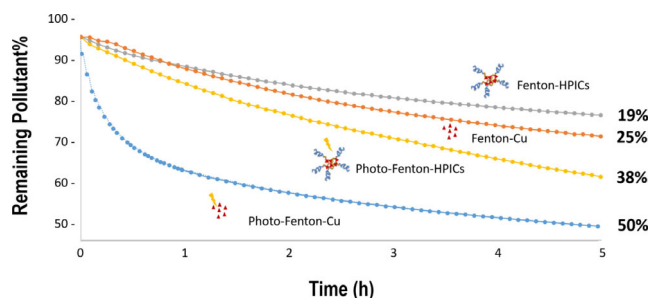
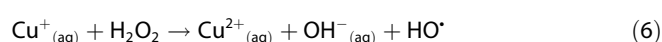
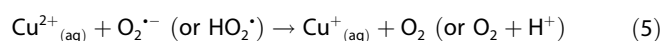
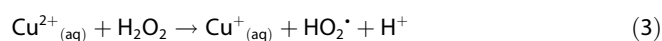


Figure 6. Conversion level of AB1 with a copper/pollutant/ H_2O_2 ratio equal to 1:1:40 under different reaction conditions in the presence of HPICs irradiated or not (noted, respectively, photo-Fenton-HPICs and Fenton-HPICs) or in the absence of HPICs irradiated or not (noted, respectively, photo-Fenton-HPICs-Cu and Fenton-Cu).

liminary experiments of the degradation of AB1 in the presence of H_2O_2 alone, H_2O_2 -photons, or photons alone were carried out and proved to be ineffective. As expected, photo-Fenton reactions are more effective at degrading the model pollutant than their counterparts without photons. Hence, in the case of free copper ions in the model system, whereas a conversion of 50% was observed after 5 h through a photo-Fenton process, these values fall to 25% without photons.

The redox reaction of copper towards hydrogen peroxide is similar to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ Fenton-like systems [Eqs. (3)–(6)]. Without irradiation, the mechanism of the Fenton-like reaction with copper to produce reactive oxidants HO^\bullet can be summarized as follows, in which regeneration of Cu^{2+} thanks to reaction (6) is slower than its consumption as discussed in the Introduction for iron.^[20,21]



Under UV irradiation, the Cu^{2+} complex can also be reduced to Cu^+ with the formation of HO^\bullet .^[22] HO^\bullet is further capable of oxidizing AB1 and further reacts with H_2O_2 (which is in excess) to produce HO_2^\bullet . The produced HO_2^\bullet reduces Cu^{2+} to Cu^+ , which accelerates the generation of reactive oxidants HO^\bullet through a Fenton-like reaction (3–6) and accelerates the rate of regeneration of the Cu^{II} ions.

The complexation of copper ions in the HPICs system led as expected to lower conversion levels with 38% and 19% for the photo-Fenton and Fenton process, respectively. This loss of efficiency is expected because of the higher steric hindrance induced by the presence of the polymer around the copper ions in HPIC systems. Nevertheless, it is noteworthy that the observed rate of degradation for HPIC systems is quite satisfactory in regards to results obtained with heterogeneous systems.^[6] As mentioned above, the mechanism of degradation of AB1 seems to occur through a pseudo-first-order kinetic pro-

cess and leads to the formation of aniline, 4-nitroaniline, and naphthylamine as previously reported.^[18] In addition, the HPIC catalyst system presents one crucial additional advantage compared with free copper ions: this system ultimately behaves like a homogeneous system, in comparison with conventional supported catalysts, which are used in a heterogeneous medium.^[13] Moreover, it has the further advantage of being recoverable through dialysis at the end of the reaction as previously demonstrated with gadolinium-based HPICs.^[10] Hence, no significant loss of catalytic activity is observed after repeated dialysis of the HPIC catalytic system for the studied reaction. The impact of pH on the efficiency of the different catalyst systems was finally evaluated by carrying out the reaction at pH 7 and 3 (Figure S12 in the Supporting Information). Regardless of the studied system, a significant decrease in catalytic efficiency was observed for low pH values. This decrease is essentially linked to the modification of the kinetic processes of the photo-Fenton reaction under these low pH conditions. Thus, for this reason, whereas in the case of the HPIC system the decrease in pH induced disruption of the HPIC system and a release of copper ions, this release does not lead to an increase in the degradation level of AB1.

HPICs act therefore as efficient catalytic systems for the degradation of AB1. Considering this efficiency, a partial degradation of the polymeric part of the HPIC system could not be therefore completely discarded as literature results have shown that such a degradation can occur but on a longer timescale and at higher temperatures than the one used here.^[23] To further assess the effect of the Fenton reaction on the integrity of HPICs, DLS experiments were thus performed at the end of the catalytic process: no significant evolution of correlation function was observed (Figure S13 in the Supporting Information). In addition, no degradation of the pristine polymer can be observed either by size exclusion chromatography or ^1H NMR spectroscopy after one day of irradiation. Thus, the Fenton reaction does not lead to the degradation of the polymer on the timescale of the reaction in the chosen conditions but could not be discarded on longer timescales.

Conclusion

The formation of HPICs based on the complexation of copper with a block copolymer consisting of an ionizable complexing block and a neutral stabilizer block, that is, poly(ethylene oxide)-block-poly(acrylic acid)— $\text{PEO}_{6k}\text{-}b\text{-PAA}_{3k}$ —as the coordinating polymer has been demonstrated. These complexes are obtained by a simple and rapid forming process and have a well-defined structure and size with a hydrodynamic diameter around 29 nm. HPICs are stable in aqueous solution over a pH range from 4 to 8 and are poorly sensitive to NaCl salt addition or dilution effects. No free copper ions are evidenced by the titration method when the charge ratio, R , between the copper ions and acrylic acid monomer around 1 or below. HPICs loaded with copper have been used successfully as the homogeneous catalyst for the degradation of naphthol blue black through a Fenton or photo-Fenton-like process. Their performances are comparable to a classical homogeneous reaction, al-

though HPICs are easily recyclable by simple dialysis. This study demonstrates that HPIC nano-objects previously used as templates for the formation of nanomaterials^[11] or as contrast agents,^[10,24] have also promising applications as catalytic systems. The ability of HPICs to be formed from different ions or mixture of ions opens promising perspectives to get access to multicatalytic “homogeneous” systems for different reactions (Lewis catalyst, Fenton catalysis).

Experimental Section

Materials

PEO_{6k}-*b*-PAA_{3k} was purchased from Polymer SourceTM and used as received. CuSO₄·5H₂O was purchased from Acros Organics Co. Ltd. Zincon monosodium salt (2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene monosodium salt) was purchased from Sigma-Aldrich Co. Ltd. at the highest purity available (≥99%) and used as received. All other reagents and solvents were purchased from Acros, Fluka, or Aldrich and used as received. Water was purified through a filter and ion exchange resin by using a Purite device (resistivity 18.2 MΩ cm).

Characterization

UV/Vis spectra were recorded with a HP 8452A diode array spectrometer or an Analytik Jena SPECORD S600. The spectra were recorded at room temperature, with 10 mm pathlength quartz cuvettes. Dynamic light scattering (DLS) measurements were conducted by using a Zetasizer Nano-ZS (Malvern Instruments, Ltd., UK) with integrated 4 mW He-Ne laser, $\lambda = 633$ nm. Light scattering intensity (at 173°) was measured with instrumental parameters set to constant values for all the samples. The correlation function was analyzed by the cumulant method to get the Z-average size of the colloids and by the general-purpose method (NNLS) to obtain the distribution of diffusion coefficients of the solutes. The apparent equivalent hydrodynamic diameter was then determined by using the Stokes–Einstein equation. Mean diameter values were obtained from three different runs of the number plot. Standard deviations were evaluated from diameter distribution. Multiangle dynamic light scattering measurement was performed on a LS spectrometer from LS instrument. For the zeta potential measurements, the Doppler anemometry technique was used whereby an electric field was applied across the sample solution. All measurements were carried out at 25 °C by using folded capillary cells (DTS 1060) and the Zetasizer Nano-ZS (Malvern Instruments, Ltd., UK) apparatus. ICP-AES was performed with an ULTIMA 2 inductively coupled plasma atomic emission spectrometer from Horiba Jobin Yvon Technology. To enable analyses, a specific nebulizer (PTFE Mira Mist Nebulizer, supplied by Horiba Jobin Yvon Technology) was used to introduce the solution into the ICP-AES. The nebulizer was inserted into a glass cyclonic chamber and operated at a maximum sample flow rate of 1 mL min⁻¹ and with a maximum total dissolved solute of 300 g L⁻¹. The optical wavelength for each element was determined to optimize the limits of quantification through calibration curves with 0–10 ppm concentrations (5 points). The sample was introduced into the ICP-AES instrument with a peristaltic pump. Carbon-coated copper TEM grids (Ted Pella Inc.) were analyzed with a MET Hitachi HT7700 transmission electron microscope operating at 80 kV accelerating voltage.

Methods

HPICs formation was investigated with a constant concentration of PEO_{6k}-*b*-PAA_{3k} (0.1 wt%) and increasing amount of CuSO₄ such that $R = [\text{Cu}^{2+}]/[2\text{AA}]$ from 0 to 3. The polymer (2 mL) was prepared in 10 mm pathlength quartz cuvettes and μ -addition of a concentrated stock solution of Cu was added such that $\Delta R = 0.125$.

Cu-loading kinetics were monitored by UV/Vis spectroscopy by adding stock solutions of CuSO₄ (10 μ L) such that $\Delta R = 1$ into a solution of PEO_{6k}-*b*-PAA_{3k} (2 mL, 0.1 wt%). Measurements were performed at room temperature. The variation of DO with time was adjusted to an exponential function leading to the time constant τ .

Concerning pH-triggered Cu release, a stock solution of HPICs was prepared with $R = [\text{Cu}^{2+}]/[2\text{AA}] = 1$ by adding an appropriate amount of a CuSO₄ stock solution to a solution of PEO_{6k}-*b*-PAA_{3k} (0.1 wt%) dissolved in water. This stock solution was then divided into eight aliquots of 2 mL and the pH was adjusted in each aliquot in the pH range from 2 to 8 with dropwise addition of NaCl (1 mol L⁻¹) and HCl (1 mol L⁻¹). The solutions were incubated for 2 h at 37 °C and UV/Vis spectroscopy measurements were also performed at 37 °C.

The dosage of free copper was determined by using the Zincon process as follows: two MTEN buffers were first prepared with MES (2-(*N*-morpholino)ethanesulfonic acid, 2.172 g, 100 mmol L⁻¹), Tris (tris(hydroxymethyl)aminomethane, 0.606 g, 50 mmol L⁻¹), and ethanolamine (2-aminoethanol, 305 μ L, 50 mmol L⁻¹) in Milli-Q water (100 mL), buffered at pH 9 and pH 5 with NaOH (1 mol L⁻¹) and HCl (1 mol L⁻¹). Then, 2 mL solutions of Cu²⁺/PEO_{6k}-*b*-PAA_{3k} were prepared in the appropriate conditions (increasing concentration of Cu²⁺ for loading monitoring, pH adjusted (with HCl (1 mol L⁻¹) and NaOH (1 mol L⁻¹) for aliquots from a 20 mL stock solution Cu²⁺/PEO_{6k}-*b*-PAA_{3k} ($R = 1$; [PEO_{6k}-*b*-PAA_{3k}] = 0.1 wt%) for the pH-triggered release study) in Milli-Q water. These samples were then filtered with centrifugal filters (molecular weight cut-off 3 kDa; Ultracel®-3K, Millipore Ireland Ltd.) at 6500 rpm over 40 min. Then, 13 μ L (for Cu²⁺ loading) or 40 μ L (for Cu²⁺ pH-triggered release) of filtrates were mixed with Zincon (30 μ L, 3 mmol L⁻¹) and completed to 2 mL with MTEN buffer, pH 9. The samples were transferred on a microplate and analyzed by UV/Vis spectroscopy. Abs(620 nm) and Abs(532 nm) were collected to assess the free metal ion concentrations by using calibration curves previously established.

The chemical degradation of AB1 was studied as follows. Four stock solutions in water were first prepared: a solution of CuSO₄·5H₂O (2.02×10^{-3} mol L⁻¹), a solution of block copolymer PEO_{6k}-*b*-PAA_{3k} (1.08×10^{-5} mol L⁻¹), a H₂O₂ solution (9.79×10^{-2} mol L⁻¹) prepared from a commercial solution at 30 wt%, and a solution of AB1 (4.38×10^{-5} mol L⁻¹). The samples analyzed by UV were prepared by adding polymer solution (390 μ L), Cu solution (41.3 μ L), and dye solution (2000 μ L). The cell was then inserted into the spectrophotometer, and the pH was adjusted. After adding 35 μ L of the H₂O₂ solution, the acquisition was started. For a photo-Fenton reaction, an optical fiber was placed on top of the cell. To ensure the consistency of the optical path, a plastic wedge was applied to the end of the fiber so that it can be placed against the cell and stabilized from one experiment to the next. The source of irradiation for the photo-Fenton reaction was a SCHOTT KLC 1500 LCD lamp equipped with a halogen reflector lamp type EFR (power 6, aperture E, 600 lumen). Temperature changes during experiments were conducted by a temperature control accessory connected to the UV/Vis spectrometer. For our experiment, the spectrum range followed was 190–800 nm with a spectrum every 5 min for 5 h. The schematic diagram is shown in Figure S10 in the

Supporting Information. Recycling experiments were performed by dialyzing HPICs against pure water (molecular weight cut-off 3 kDa of dialysis bag). After dialysis, HPIC solutions were used for further reactions.

Acknowledgments

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Conflict of interest

The authors declare no conflict of interest.

Keywords: catalysis · Fenton reaction · hybrid polyion complexes · nanomaterials · photo-Fenton

- [1] L. L. Chng, N. Erathodiyil, J. Y. Ying, *Acc. Chem. Res.* **2013**, *46*, 1825–1837.
- [2] V. Polshettiwar, R. S. Varma, *Green Chem.* **2010**, *12*, 743–754.
- [3] M. Beija, E. Palleau, S. Sistach, X. Zhao, L. Ressler, C. Mingotaud, M. Destarac, J.-D. Marty, *J. Mater. Chem.* **2010**, *20*, 9433–9442.
- [4] J. Keilitz, S. Nowag, J.-D. Marty, R. Haag, *Adv. Synth. Catal.* **2010**, *352*, 1503–1511.
- [5] B. M. Weckhuysen, J. Yu, *Chem. Soc. Rev.* **2015**, *44*, 7022–7024.
- [6] M. Cheng, C. Lai, Y. Liu, G. Zeng, D. Huang, C. Zhang, L. Qin, L. Hua, C. Zhou, W. Xiong, *Coord. Chem. Rev.* **2018**, *368*, 80–92.
- [7] N. Sanson, F. Bouyer, C. Gérardin, M. In, *Phys. Chem. Chem. Phys.* **2004**, *6*, 1463–1466.
- [8] N. Sanson, F. Bouyer, M. Destarac, M. In, C. Gérardin, *Langmuir* **2012**, *28*, 3773–3782.
- [9] J.-P. Chapel, J.-F. Berret, *Curr. Opin. Colloid Interface Sci.* **2012**, *17*, 97–105.
- [10] C. Frangville, Y. Li, C. Billotey, D. R. Talham, J. Taleb, P. Roux, J.-D. Marty, C. Mingotaud, *Nano Lett.* **2016**, *16*, 4069–4073.
- [11] G. Layrac, M. Destarac, C. Gerardin, D. Tichit, *Langmuir* **2014**, *30*, 9663–9668.
- [12] N. M. Pinkerton, L. Behar, K. Hadri, B. Amouroux, C. Mingotaud, D. R. Talham, S. Chassaing, J.-D. Marty, *Nanoscale* **2017**, *9*, 1403–1408.
- [13] N. Wang, T. Zheng, G. Zhang, P. Wang, *J. Env. Chem. Eng.* **2016**, *4*, 762–787.
- [14] P. V. Nidheesh, *RSC Adv.* **2015**, *5*, 40552–40577.
- [15] A. D. Bokare, W. Choi, *J. Hazard. Mater.* **2014**, *275*, 121–135.
- [16] S. A. Wang, *Dyes Pigm.* **2008**, *76*, 714–720.
- [17] O. Primo, M. J. Rivero, I. Ortiz, *J. Hazard. Mater.* **2008**, *153*, 834–842.
- [18] M. T. Ball, J. Hay, H. M. Masrouji, J. K. Sugden, *Dyes Pigm.* **1992**, *19*, 51–57.
- [19] M. Haddou, F. Benoit-Marquié, M.-T. Maurette, E. Oliveiros, *Helv. Chim. Acta* **2010**, *93*, 1067–1080.
- [20] F. L. Y. Lam, A. C. K. Yip, X. Hu, *Ind. Eng. Chem. Res.* **2007**, *46*, 3328–3333.
- [21] U. J. Ahile, R. A. Wuana, A. U. Itodo, R. Sha'Ato, R. F. Dantas, *Sci. Total Environ.* **2020**, *710*, 134872.
- [22] H.-J. Lee, H. Lee, C. Lee, *Chem. Eng. J.* **2014**, *245*, 258–264.
- [23] A. Neira, M. Tarraga, R. Catalan, *J. Chil. Chem. Soc.* **2007**, *52*, 1314–1317.
- [24] M. Yon, C. Billotey, J.-D. Marty, *Int. J. Pharm.* **2019**, *569*, 118577.

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FULL PAPER

Catalysis

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 Copper-Based Hybrid Polyion
Complexes for Fenton-Like Reactions

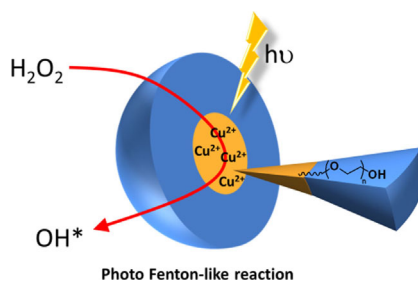


Photo opportunity: An innovative strategy allowing the development of a new generation of easy-to-prepare nanosized catalysts with high tenability is presented. This strategy is based on the formation of hybrid polyion complexes (HPICs) from the complexation of copper ions with a block copolymer consisting of an ionizable complexing block and a neutral stabilizer block. The obtained HPICs are particularly effective for photo-Fenton catalysis.