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(RESEARCH ARTICLE)

Synthesis of second generation dendrimere PPI (G2) functionalized with 4-hydroxycoumarin effective for the removal of chromium (VI) by adsorption

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Abstract

We report here the preparation of a second generation PPI dendrimer (G2) functionalized by 4-hydroxycoumarin based on the Manich reaction and its use for chromium (VI) removal. The literature review has shown that dendrimers are types of polymer defined by regular branches of a central monomer, which give it a tree molecular structure. Their ends carry functional groups whose arrangement gives rise to cavities that are able to receive other molecules as part of host-guest chemistry. To increase the generation or modify peripheral groupings it is possible to manipulate the properties during the synthesis of the dendrimer.

Coumarins are a set of molecules with multiple beneficial properties including antioxidant, anti-inflammatory, anticancer, antibacterial, antiviral properties. It has also been shown that these molecules are good metal ion chelators and are able to modulate the activity of metrix metalloproteinases (MMPs).

The study of adsorption, on a PPI dendrimer functionalized with Coumarin (C2), trivalent chromium and hexavalent chromium, shows that the kinetics are carried out in two steps with a significant removal efficiency for Cr VI (38.26%) and zero for Cr III.

During this study, we kept the initial chromium concentration, pH, stirring rate, contact time and temperature constant and with the same amount of adsorbent (30 mg).

Keywords: Dendrimer PPI; Coumarin; Chromium (VI); Adsorption; Adsorbent

1. Introduction

Chromium can be released into the environment by various industries, including the metal finishing industry, iron and steel industry, and the production of inorganic chemicals [1]. It exists in several forms: trivalent (chromium III), hexavalent (chromium VI) or as an elemental metal (chromium 0). The toxicity of chromium depends not only on its concentration but also on its degree of oxidation. Indeed, it is commonly accepted that chromium (VI) is much more toxic than chromium (III). The latter is an essential nutrient for living beings since it plays an indispensable role in carbohydrate metabolism as an insulin activator [2].

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Chromium metal is neither toxic nor unstable. Chromium (VI) is the most problematic of all shapes. In the hexavalent form, chromium is very toxic and very soluble in water. It is one of the toxic metals present in certain wastes or sediments, for which inerting solutions are sought that are as durable as possible, as in the case of cement matrices [3]. It has various consequences on human health, fauna and flora [4]. Damage to men's health includes liver necrosis, skin allergies, nasal irritation, nosebleeds and lung cancer [5,6]. The people most exposed to the dangers of chromium VI are those working in the steel and textile industry, but also those who smoke tobacco. In 1978, Adamson and Bowden reported the deaths of twelve people after applying an ointment in which sulfur was replaced by a hexavalent derivative of chromium [7]. The latter is able to cause in animals respiratory problems, a weaker ability to fight diseases, birth defects and infertility or tumor formation.

Metallic water pollution is a growing concern because heavy metals are not biodegradable, toxic even at low concentrations and their bioaccumulation in living organisms can cause damage to the environment and human health. Environmental protection has thus become a major economic and political issue. All countries in the world are concerned with safeguarding freshwater resources, either because they lack water or because they pollute it.

Among the metal pollutants, we can mention chromium which is used by many industries in the manufacture of steel, leather, textile... that discharge into the natural environment releases containing a high concentration of highly toxic hexavalent chromium.

In order to fight against metal water pollution, different techniques have been used, such as : adsorption, precipitation [8], electrolysis [9], ion exchange [10], membrane filtration [11] ... However, there is growing interest in adsorption technology in the removal of heavy metals due to the high capacity of adsorbent materials to trap metals in contaminated water. Physicochemical methods attempt to remove Cr (VI) and electrochemical methods attempt to reduce Cr (VI) to Cr (III). Hence the choice of adsorption on the second generation Dendrimer PPI functionalized by 4-hydroxycoumarin, which has proven its effectiveness for the removal of chromium VI with a percentage of 38.26% under non-optimized conditions.

2. Material and methods

2.1. Equipment

The PPI G1-G5 dendrimers were purchased from SyMO-Chem B. V/University of Heindoven (Netherlands).

The NMR spectra of the compounds were recorded at 400 MHZ for proton 1H and 75.5 MHZ for 13C on a BRUKER AM 400 WB high-field spectrometer from the Centre Régional of Western Physical Measurements (CRMPO) of the University of Rennes 1.

The removal of chromium was carried out with a polymer-based adsorbent synthesized by our team and recorded using a UV spectrophotometer (SPECORD 200 PLUS) for control absorbance at the Laboratory of Electrochemistry of Cheikh Anta Diop University in Dakar, Senegal.

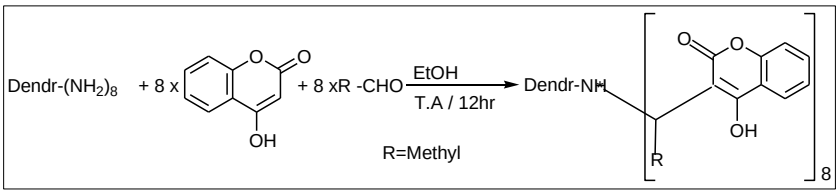
2.2. Procedure for the synthesis of adsorbent (c2)

In 10 mL of absolute ethanol is added to a suspension of 4-hydroxycoumarin in 20 ml of absolute ethanol with magnetic stirring at room temperature previously placed in a light-protected 150 ml Erlenmeyer containing a solution of the second generation Dendr-(NH2)4n. The formation of a white solution is observed as a result of the gradual disappearance of the suspended solid. Then the solution is left stirring for 15 minutes, in order to ensure complete training. This is how acetaldehyde is added using a syringe.

The resulting reaction mixture is then left with magnetic stirring at room temperature for 12 hours away from light.

Thus, the precipitate formed is wrung out, washed with ethanol (2 times) then with petroleum ether (2 times) before drying it in an oven thermostated at 45 °C for 1 hour. Compound C2 was

Prepared according to the diagram below.



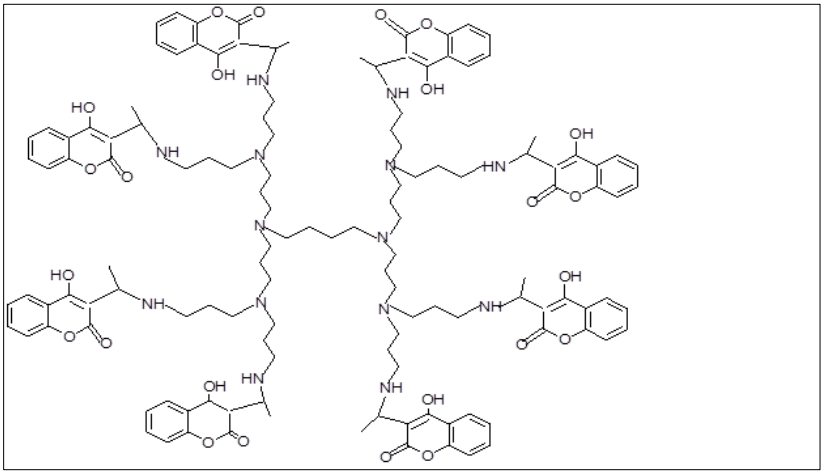


Figure 1 Structure of compound C2

- *Dendri*-$(NH_2)_8$: (107 mg, 0,138 mmol ; 1 éq.) ;
- 4-hydroxycoumarine : (199,54 mg ; 1,23 mmol ; 8,91 éq.) ;
- Acétaldéhyde (0,125 mL ; 2,213 mmol ; 16 eq) ;
- Appearance: solid orange;
- Molecular product formula : $C_{128}H_{160}N_{14}O_{24}$
- Molar molecular weight: M=2276g/mol.
- Mass obtained after drying without any purification operation: 293.83mg;
- Yield: 93.55%.
- Characterization of compound C2 : IR (KBr) ν_{max}/cm^{-1}: 3388 (ν_{O-H}) ; 2054 (ν_{C-H}) ; 2966 (ν_{C-H}) ; 1673 ($\nu_{C=O}$) ; 1607 ($\nu_{C=C}$) ; 1532 (δ_{N-H}) ; 1272 (ν_{C-O}).
  RMN ^1H (DMSO-d_6, 400 MHz): δ (ppm) 7,87 (d, H^{13}-*Coum*, 8H) ; 7,45 (t, H^{15}-*Coum*, 8H) ; 7,21 (d, *J* = 8,4 Hz, H^{16}-*Coum*, 8H) ; 7,16 (t, H^{14}-*Coum*, 8H) ; 4,56 (s, H^9, 8H) ; 2,79 (s, H^8, 16H) ; 2,26 (s, $H^6 + H^5 + H^3 + H^2$, 36H) ; 1,62 (H^7, 16H) ; 1,43 (s, H^{19}, 24H) ; 1,23 (s, $H^4 + H^1$, 12H)
  ^{13}C RMN (DMSO-d_6, 400 MHz) : δ (ppm) 178,9 (d, *J* = 84 Hz, C=O) ; 170,0 (d, *J* = 88 Hz, C-OH) ; 138,4 (d, C^{IV}-coum) ; 133,6 (CH-*coum*) ; 131,3 (C^{IV}-*coum*) ; 130,9 (CH-*coum*) ; 128,2 (CH-*coum*) ; 127,7 (CH-*coum*) ; 127,6 (CH-*coum*) ; 125,3 (CH-*coum*) ; 125,0 (CH-*coum*) ; 111,2 (C^{10}-*coum*) ; 58,7 (RCHN); 19,70 (CH_3) ; 52,2 (t; $N\underline{C}H_2CH_2CH_2\underline{C}H_2N$) ; 50,5 (d, $N\underline{C}H_2CH_2CH_2NH$) ; 44,7 (t, $NCH_2CH_2\underline{C}H_2NH$) ; 22,4 (s, $NCH_2\underline{C}H_2\underline{C}H_2CH_2N$) ; 23,5 (s, $NCH_2\underline{C}H_2CH_2NH$).

2.3. Study of chromium removal by adsorbent c2

2.3.1. Experimental protocol

This study was performed using the adsorption technique using as an adsorbent a second generation PPI dendrimer functionalized with 4-hydroxycoumarin (C2). During this study, we chose to work by the immersion method in the following non-optimized conditions. Thus, in doses of 10 mL of aqueous solutions of K2Cr207 (30 mg / L) optimized at a pH of 2, a mass of 30 mg of the absorbent (based on C2) is added under magnetic stirring.

3. Results and discussion

The evolution of the UV-visible absorption spectrum of the chromium solution as a function of the immersion time of the absorbent was monitored.

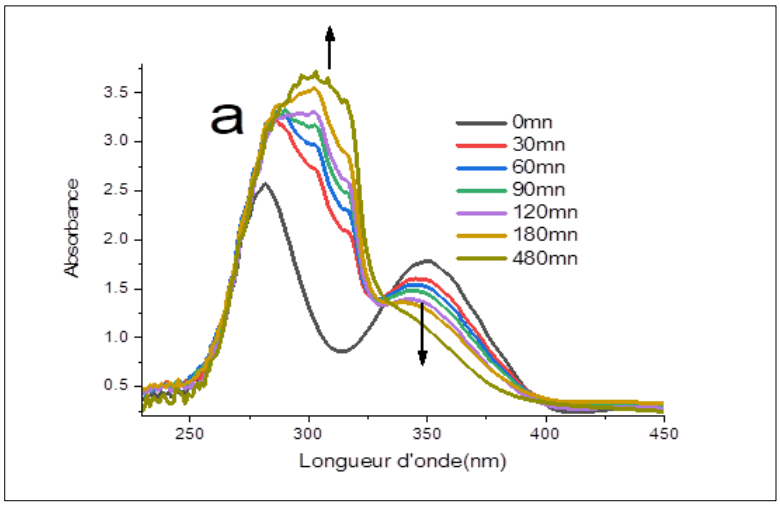


Figure 2 Evolution of the absorbance of a solution of $K_2Cr_2O_7$ 30 mg / L as a function of contact time with (a) compound C2

To better understand the kinetics of chromium VI removal and chromium III formation, we have shown in Figures 2 and 3 the variation in the absorbance of chromium VI and chromium III in solution as a function of contact time with the adsorbent. These resulting curves do not follow any known mathematical distribution of variation as a function of time.

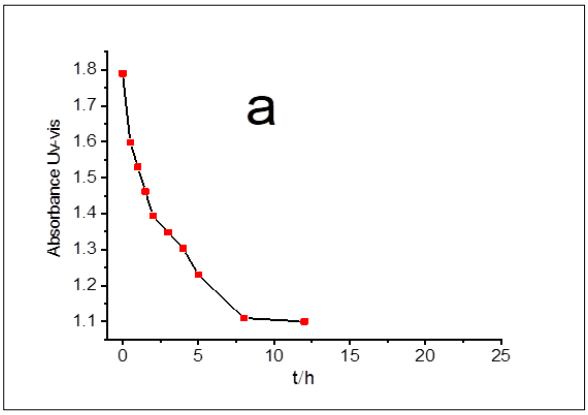


Figure 3 Decay kinetics of the chromium (VI) absorption band at 350 nm, using 30 mg and a pH of 2, of the absorbent (a) compound C2

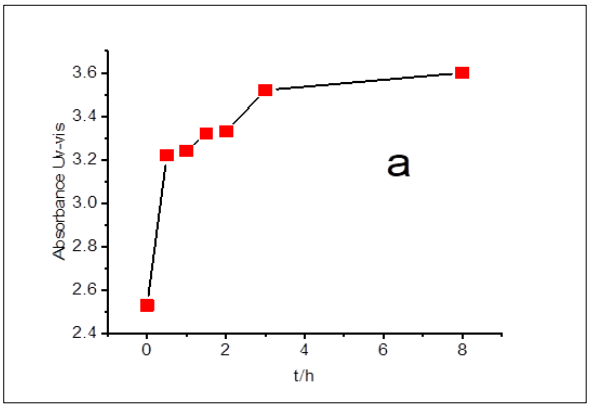


Figure 4 Growth kinetics of the chromium (III) absorption band at 350 nm, using 30 mg and a pH of 2, of the absorbent (a) compound C2

A more detailed study of the kinetics of chromium adsorption by the absorbent leads to a 2nd order kinetics because the curve 1/Ct - 1/C0 as a function of time is strictly linear in all cases (Figure 4 and 5). With an equation of the form y = a. t and a correlation coefficient r2 close to 1. The kinetic parameters are listed in Tables 1 and 2.

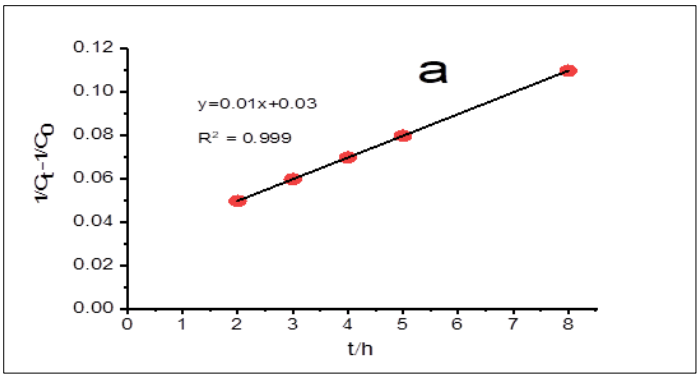


Figure 5 Determination of the second-order rate constant of chromium (VI) adsorption on, absorbent (a) compound C2, under optimized experimental conditions

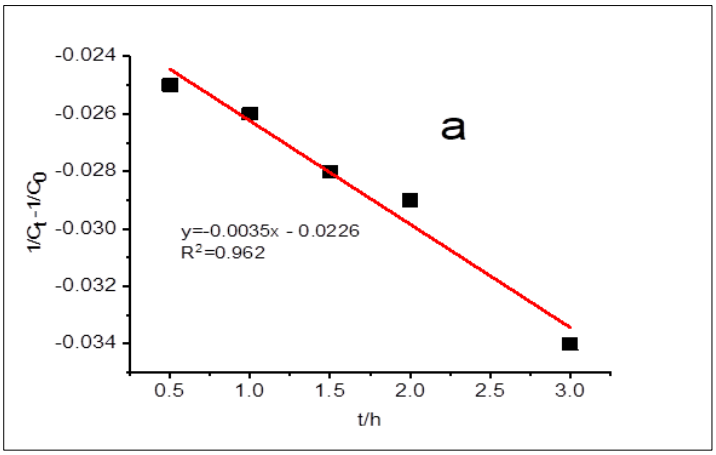


Figure 6 Determination of the second-order rate constant of chromium (III) adsorption on, absorbent (a) compound C2, under optimized experimental conditions

Table 1 Kinetic parameters of the C2 adsorbent on chromium VI.

Adsorbant	R(%)	k2	R2	qe (mg/g)
C2	38.26	0.01	0.999	71.7

Table 2 Kinetic parameters of C2 adsorbents on chromium III

Adsorbant	R(%)	k2	R2	qe (mg/g)
C2	0	0.0035	0.962	0

$q_e = (C_0 - Ce)\ V/\ m$

$R(\%) = (C_0 - Ce)\ /C_0\ x100$ [12]

In Figure 1, we note the presence of two bands around 260 and 350 nm assigned to chromiums III and VI [13]. However, there is a gradual increase in the 260 nm band attributed to chromium III, followed by a successive decrease in that of chromium VI at 350 nm as a function of contact time with the adsorbent C2. Thus this difference in behavior between the two bands could be explained by a phenomenon of conversion or reduction of chromium VI, 500 times more toxic, into chromium III [14,15].

Given the very asymmetrical values of constants of chromium VI removal rate and chromium III formation (0.01 and 0.0035), it can be predicted that in addition to this conversion of chromium VI to chromium III, there may also be a formation of insoluble complex between absorbent and chromium VI.

In this study, we worked with a single amount of adsorbent (30 mg) maintaining the initial chromium concentration, pH, stirring rate, contact time and temperature constant under non-optimized conditions.

4. Conclusion

The objective of this work is the study of chromium removal by adsorption on a second generation PPI dendrimer functionalized by 4-hydroxycoumarin synthesized by our research team. The method used is that of immersion under non-optimized conditions with a single amount of adsorbent (30mg) while maintaining the initial chromium concentration, pH, stirring rate, contact time and temperature constant.

This study showed that the C2 adsorbent has the potential to either remove chromium VI or convert it to chromium III. In view of the percentages of removal of chromium obtained 38.26 for chromium VI and 00.00 for chromium III, it can be concluded that the adsorbent C2 removes chromium VI only.

The study of the adsorption kinetics of chromium on the C2 adsorbent made it possible to specify the order of the reaction. Indeed only one kinetic model was applied, the Lagergren model of the 2nd order. By comparison of the regression coefficients of the curves it can therefore be said that the kinetics of the adsorption reaction of chromium on C2 is most likely of the second order.

In continuity with this work, we will test the optimized method and by varying one or more parameters to verify their influences on adsorption by the adsorbent C2.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

There are no competing interests related to this work.

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