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(RESEARCH ARTICLE)

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Synthesis of a first generation (G1) PPI dendrimer functionalized with 4-hydroxycoumarin effective for the removal of chromium (III) and chromium (VI) by adsorption

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Abstract

The preparation of a first generation (G1) PPI dendrimer functionalized by 4-hydroxycoumarin based on the Manich reaction and its use for chromium removal.

The literature review showed that dendrimers are large tree molecules constructed by iterative processes from a molecule with at least three reactive sites. These hyper-branched and multi-functional macromolecules have a perfectly defined structure whose applications in various fields such as catalysis, materials, or biology, or even medicine are constantly developing. Indeed, these dendrimers allow the development of new organic/inorganic materials with a controlled structure, but also to modify, at the nanoscale, the surface of existing materials. Coumarins form a set of molecules with multiple beneficial properties including antioxidant, anti-inflammatory, anticancer, antibacterial, antiviral properties. These molecules have also been shown to be good metal ion chelators and are able to modulate MMPs activity.

The study of the adsorption of trivalent chromium and hexavalent chromium by the PPI dendrimer functionalized with Coumarin noted C3, shows that the kinetics are carried out in two stages with a high removal yield for Cr (VI) (56.15%) and very low for Cr (III) (12.98%).

In this study, an amount of 30mg of adsorbent is used keeping the initial chromium concentration (30mg/L), pH (2), stirring rate, contact time and temperature constant.

Keywords: PPI dendrimer; Coumarin; Adsorption; Chromium (VI); Chromium (III)

1. Introduction

Humans can come into contact with chromium by breathing, eating, drinking or skin contact. Chromium is present everywhere, in the air, water, our furniture, clothes and shoes. Chromium has 26 isotopes with mass numbers ranging from 42 to 67 and two nuclear isomers. The most stable are four (^{50}Cr, ^{52}Cr, ^{53}Cr and ^{54}Cr) representing almost all the chromium present in nature. The most abundant of these isotopes is $^{52}_{24}Cr$. This element has a standard atomic mass equal to 51.9961 very close to that of $^{52}_{24}Cr$. Without any scientific evidence, chromium $^{50}_{24}Cr$ is rightly or wrongly attested

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to decay by double beta decay (β^+, β^+) to give 50Ti with a half-life period equal to 1.3.1018 years. It is a transitional, hard and steel-silver gray metal belonging to group 6 (or VI) of the periodic table. It exists in several forms : trivalent (chromium III), hexavalent (chromium VI) or as an elemental metal (chromium 0). The toxicity of this element varies greatly according to its chemical form (particle, nanoparticle, ion, oxide, hydroxyl valence …). Chromium metal is neither toxic nor unstable. Chromium III is an essential nutrient for living beings since it plays an indispensable role in carbohydrate metabolism as an insulin activator [1]. It is he who manages the use of energy from sugars and fats absorbed by the human body. It is present in most of our foods (vegetables, fruits, meats, fats and yeasts), and does not pose any danger to the body. Its excessive absorption can cause health problems such as rashes, anemia and even cancer. Chromium VI is the most problematic of all forms. 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 [2]. It has various consequences on human health, fauna and flora [3,4]. 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 [7] reported the death of twelve people after the application of an ointment in which sulfur was replaced by a hexavalent derivative of chromium. The latter is able to cause in animals respiratory problems, a weaker ability to fight diseases, defects at birth and infertility or tumor formation.

Metal pollution of water 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 about 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, textiles ... that discharge discharges into the natural environment containing a high concentration of highly toxic hexavalent chromium.

In order to combat metal pollution of water, different techniques have been used, such as: adsorption [8], precipitation, electrolysis [9], ion exchange [10], membrane filtration [11] ... However, the adsorption technique is increasingly attracting interest in the removal of heavy metals thanks to the high capacity of adsorbent materials to trap metals present in contaminated water. Physico-chemical methods attempt to remove Cr (VI) and electrochemical methods attempt to reduce Cr (VI) to Cr (III). Hence the choice of adsorption on the first generation PPI Dendrimer functionalized by 4-hydroxycoumarin, which has proven its effectiveness for the removal of chromium VI with a percentage of 56.12% 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.

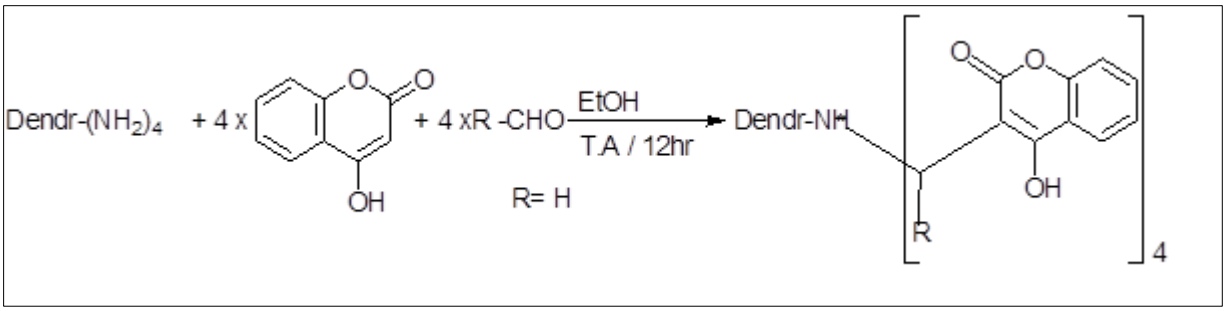
The removal of chromium was carried out with a polymer-based adsorbent synthesized by our team and recorded using a UV spectrophotometer (SPECORD 200 PLUS) for control absorbance at the Electrochemistry Laboratory of Cheikh Anta Diop University in Dakar, Senegal.

2.2. Procedure for the synthesis of adsorbent (c3)

In a 150 ml Erlenmeyer protected from light, a solution of suitable Dendr-(NH2)4n in 10 mL of absolute etahnol is added to a suspension of 4-hydroxycoumarin in 20 ml of absolute ethanol under magnetic stirring at room temperature. The gradual disappearance of the suspended solid observed is marked by the formation of a white solution. In order to ensure complete training, the solution is left stirred for 15 minutes. It is at this time that the aldehyde considered is added with the help of a syringe.

The resulting reaction mixture is then left under 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 being dried in an oven thermostated at 45 ° C for 1 hour. The C3 compound was prepared according to the diagram below :



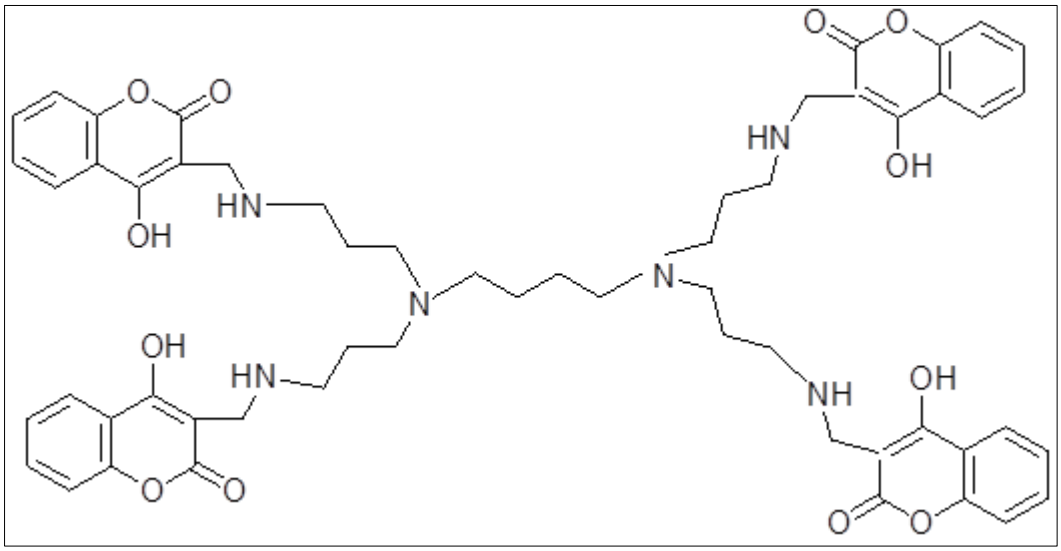


Figure 1 Structure of compound C3

Characterization of compound C3 : IR (KBr) ν_{max}/cm^{-1}:3400 (ν_{O-H}) ;3068 (ν_{C-H}) ; 2964 (ν_{C-H}) ; 1633 ($\nu_{C=O}$) ; 1600 ($\nu_{C=C}$) ; 1569 (δ_{N-H}) ; 1279 (ν_{C-O}).

RMN ^{1}H (DMSO-d_6, 400 MHz): δ (ppm) 7,91 (d, *J* = 7,8 Hz, H^{10}-*Coum*, 4H) ; 7,88 (t, $^3J_{HH}$ = 7.6 Hz, H^{12}-*Coum*, 4H) ; 7,52 (d, *J* = 8,4 Hz, H^{13}-*Coumt*, 4H) ; 7,30 (t, H^{11}-*Coum* 4H) ; 5,55 (s, H^6, 8H) ; 2,91 (s, H^5, 8H) ; 2.40-2,00 (s [2,28 ppm (H^3, 8H) + 2,11 ppm (H^2, 4H)], 12H) ; 1,69 (s, H^4, 8H) ; 1,22 (s, H^1, 4H).

^{13}C RMN (DMSO-d_6, 400 MHz) : δ (ppm) 184,5 (d, *J* = 88 Hz, C=O) ; 178,9 (d, *J* = 84 Hz, C=O) ; 170,0 (d, *J* = 88 Hz, C-OH) ; 138,4 (C^{IV}-Ph) ; 134,3 (d, C^{IV}-*coum*) ; 133,6 (CH-*coum*) ; 131,3 (C^{IV}-*coum*) ; 130,9 (CH-*coum*) ; 128,2 (CH-*Ph*) ; 127,7 (CH-*Ph*) ; 127,6 (CH-*Ph*) ; 125,3 (CH-*coum*) ; 125,0 (CH-*coum*) ; 111,2 (C^{IV}, C^3-*coum*) ; 58,7 (PhCHN) ; 52,2 (t; $NCH_2CH_2CH_2CH_2N$) ; 50,5 (d, $NCH_2CH_2CH_2NH$) ; 44,7 (t, $NCH_2CH_2CH_2NH$) ; 22,4 (s, $NCH_2CH_2CH_2CH_2N$) ; 23,5 (s, $NCH_2CH_2CH_2NH$).

2.3. Study of chromium removal by adsorbent c3

This study was carried out by the adsorption technique using as an adsorbent a first generation PPI dendrimer functionalized by 4-hydroxycoumarin (C3).

During this study, we chose to work by the immersion method under the following non-optimized conditions. Thus, in intakes 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 C3) 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.

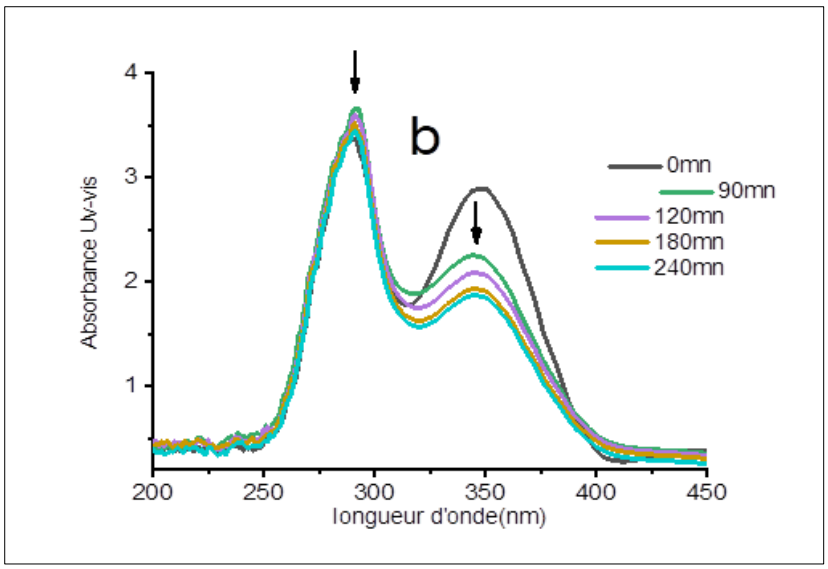


Figure 2 Evolution of the absorbance of a solution of K2Cr2O7 30 mg / L as a function of the contact time with (b) compound C3.

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 different absorbents respectively. These resulting curves do not follow any known mathematical law of variation as a function of time.

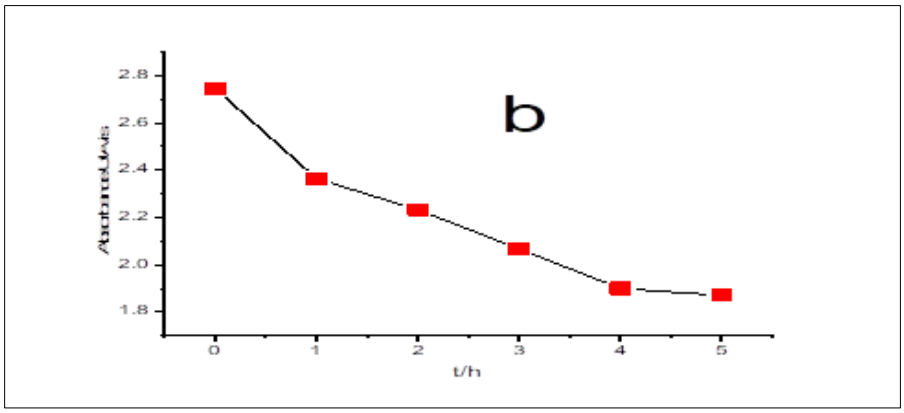


Figure 3 Kinetics of decay of the absorption band of chromium (VI) at 350 nm, using 30 mg and a pH of 2, of the absorbents (b) compound C3.

A more precise study of the kinetics of adsorption of chromium by the absorbent leads to a kinetics of 2nd order 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 r^2 close to 1. The kinetic parameters are listed in Tables 1 and 2.

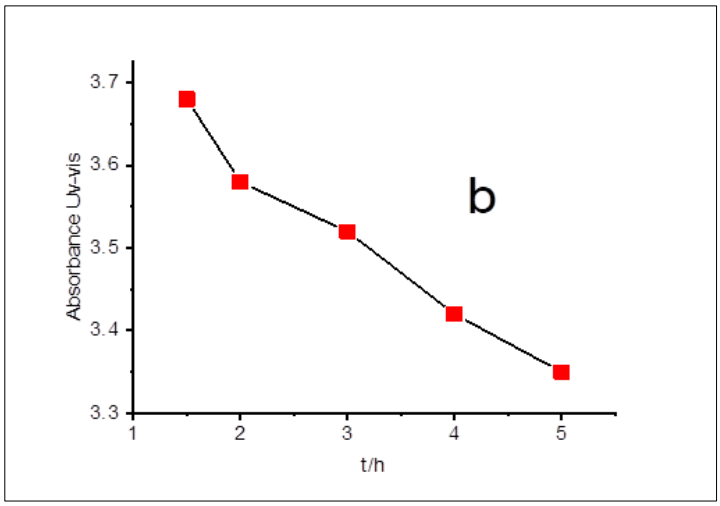


Figure 4 Kinetics of decay of the absorption band of chromium (III) at 350 nm, using 30 mg and a pH of 2, of the absorbents (b) compound C3.

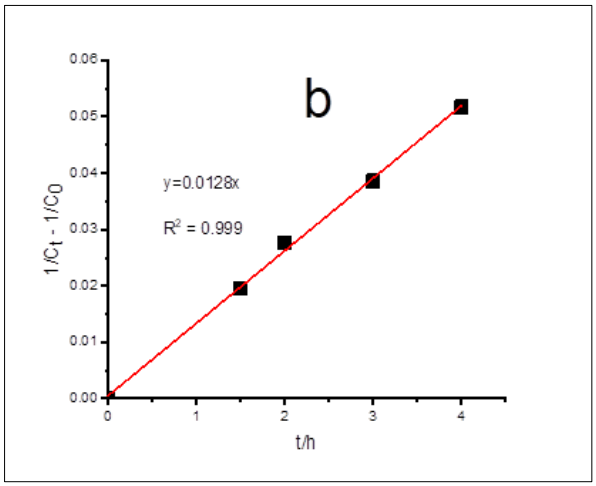


Figure 5 Determination of the velocity constant of the second order of the adsorption of chromium (VI) on, absorbents(b) compound C3, under optimized experimental conditions.

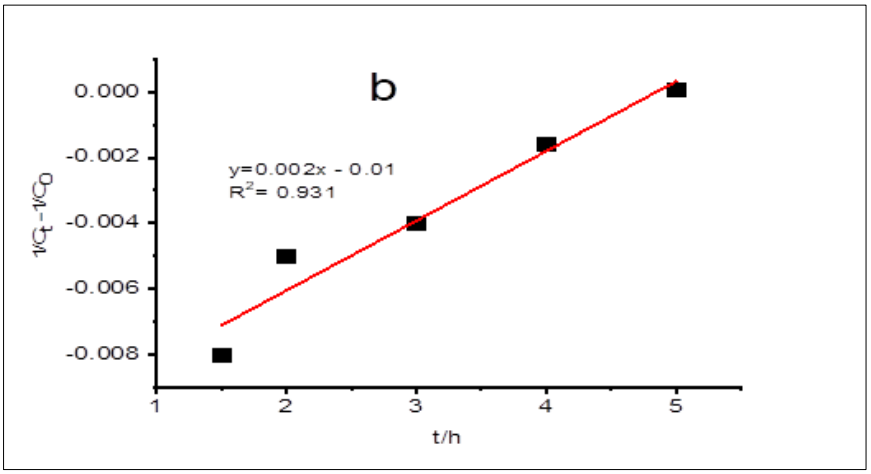


Figure 6 Determination of the velocity constant of the second order of the adsorption of chromium(III) on, the absorbents (b) compound C3, under optimized experimental conditions.

Table 1 Kinetic parameters of adsorbent C3 on chromium VI.

Adsorbent	R(%)	k2	R2	qe (mg/g)
C3	56.152	0.0128	0.999	96.6

Table 2 Kinetic parameters of adsorbent C3 on chromium III.

Adsorbent	R(%)	k2	R2	qe (mg/g)
C3	12.98	0.002	0.931	21.06

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

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

In Figure 1, we note the presence of two bands around 260 and around 350 nm assigned to chromium III and VI [13]. However, it is observed that the two bands of chromium gradually decrease over time. Thus, the gradual decrease of the two bands of chromium in the presence of the absorbent C3, could indicate an elimination of total chromium [14].

The study of these two tables shows that the absorbent C3 can indeed eliminate chromium VI and chromium III according to a kinetics of order 2 with speed constants of 0.0128 and 0.002 respectively. With a speed constant six times higher, the percentage of chromium VI removed (56.152) is also four times greater than that of chromium III (12.98). This indicates greater efficiency in the removal of chromium VI.

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

4. Conclusion

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

This study showed that adsorbent C3 has the ability to eliminate both forms of chromium. In view of the chromium removal percentages obtained of 56.12% for chromium VI and 12.98% for chromium III, it can be concluded that adsorbent C3 removes chromium VI better than chromium III.

The study of the kinetics of chromium adsorption on activated alumina made it possible to specify the order of the reaction. Indeed we applied two kinetic models, the Lagergren model of the 1st and the Lagergren model of the 2nd order. The comparison of the regression coefficients of the curves for determining the velocity constant of chromium (VI) and chromium (III) makes it possible to say that the kinetics of the chromium adsorption reaction on C3 is probably of the second order.

In continuity with this work, it will be proposed to optimize the method by varying one or more parameters in order to verify their influences on the adsorption of chromium by the synthesized dendrimer C3.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

The authors agree no conflict of interest.

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