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Synthesis and kinetic study of the chromium adsorption of a first-generation PPI (polypropylene imine) dendrimer (G1) functionalized by 2-hydroxy-p-naphthoquinone

El Hadji Gorgui Diouf [1*], Talibouya Ndior[1], Alioune Diouf[3], Cheikh Gaye[2], Abdou Karim Diaw[2], Balla Fall[2], Mamadou Kébé[1], Mamadou Latyr Ndour[1], Adama Faye[1], Moussoukoye S. Diop[1]

[1] *Laboratory of Natural Products, Department of Chemistry, Faculty of Science and Technology, Cheikh Anta Diop University of Dakar, Senegal.*
[2] *Electrochemistry Laboratory of Cheikh Anta Diop University in Dakar, Senegal.*
[3] *Department of Chemistry, Organic chemistry and bioorganics laboratory, Faculty of Science and Technology, Cheikh Anta Diop University of Dakar, Senegal.*

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Corresponding authors emails:
elhadjigorgui1.diouf@ucad.edu.sn

Abstract - Résumé

Adsorption on natural or synthetic materials is one of many available decontamination techniques. This process consumes little energy compared to electrochemical processes such as advanced plasma oxidation, electro-photon, photocatalysis, etc. This article discusses the synthesis and evaluation of the adsorbing activity of a first-generation (G1) PPI dendrimer functionalized with 2-hydroxy-p-naphthoquinone. The dendrimers were synthesized by the Manich reaction using a first-generation PPI dendrimer (G1), an aldehyde (acetaldehyde) and 2-hydroxy-p-naphthoquinone. For chromium removal, the method used was immersion under non-optimized conditions. The results of the study of hexavalent chromium adsorption on the PPI dendrimer functionalized with 2-hydroxy-p-naphthoquinone (1a) show that the molecule can remove chromium VI with a removal efficiency of 16.89% using second-order kinetics.

L'adsorption sur matériaux naturels ou synthétiques est l'une des nombreuses techniques de dépollution disponibles. Ce procédé est peu gourmand en énergie par rapport aux procédés électrochimiques tels que l'oxydation avancée par plasma, l'électro photon, la photocatalyse, etc. Cet article traite de la synthèse et de l'évaluation de l'activité absorbante d'un dendrimère PPI de première génération (G1) fonctionnalisé par la 2-hydroxy-p-naphtoquinone. Les dendrimères ont été synthétisés par la réaction de Manich en utilisant un dendrimère PPI de première génération (G1), un aldéhyde (acétaldéhyde) et la 2-hydroxy-p-naphtoquinone. Pour l'élimination du chrome, la méthode utilisée est l'immersion dans des conditions non optimisées. Les résultats de l'étude de l'adsorption de chrome hexavalent sur le dendrimère PPI fonctionn alisé par la 2-hydroxy-p-naphtoquinone (1a) montre que la molécule peut éliminer le chrome VI avec un rendement d'élimination de 16,89 % en utilisant une cinétique de second ordre

1. INTRODUCTION

The generic term "adsorption" is used to designate the accumulation of chemical species at the interface between a liquid or gaseous phase called adsorbate and solid surfaces called adsorbents [1, 2]. When a solid is brought into contact with a solution, each component of the liquid phase, including the solvent, will have a particular tendency to adsorb onto the surface of the solid, so there is competition between the various components for the substrate. The sites where the adsorbate molecules attach is called active sites. Adsorption can occur on organic matter, clays, carbonates, iron oxides and hydroxides [3, 4, 5].

Depending on the binding energies involved, two types of adsorptions can be distinguished: physical adsorption and chemical adsorption [6, 7].

What's more, it is reversible, so the adsorbed molecule can be recovered [8] and the adsorbent regenerated.

The main adsorbents used in industrial applications are activated carbons, clays (bleaching earths), zeolites, silica gels and activated alumina [9].

Knowledge of adsorption kinetics is of considerable practical interest in the optimal implementation of an adsorbent during an industrial operation, and in knowing which factors to optimize in order to manufacture or improve an adsorbent leading to the fastest possible kinetics [10]. During the adsorption of a species on to a solid, the transfer of matter takes place from the fluid phase to the active sites of the adsorbent, and this process takes place in three stages [11]:

- External matter transfer: the molecules pass through the boundary layer of fluid around the adsorbent grains to reach their surface;
- Internal microporous matter transfer: the molecules migrate within the macropores and mesopores of the adsorbent, from the surface to the interior of the grain;
- Internal microporous matter transfer: molecules diffuse into micropores.

The aim of this work is firstly to develop a molecule based on a PPI dendrimer functionalized with 2-hydroxy-p-naphthoquinone using the "onepot" synthesis based on the Manich reaction, and then to carry out a kinetic study of chromium adsorption on this molecule. The latter proved effective in eliminating chromium VI, with a percentage of 16.89% under non-optimized conditions.

2. MATERIALS AND METHODS

2.1. Materials

PPI G1-G5 dendrimers were the main organic compounds used in this study. They were purchased from SyMO-Chem B.V/University of Heindoven (Netherlands).

The products were synthesized using the Mannich reaction based on one-pot synthesis.

The spectra were recorded on a BRUKER AM 400 WB high-field spectrometer at the Center Regional Measures Physiques of West the center regional of western physical measurements (CRMPO) at the University of Rennes1, at 400MHZ for the proton^1 H and at 75.5 MHZ for C^{13}.

To remove chromium, the immersion absorption method was used under non-optimized conditions using a control absorbance UV spectrophotometer (SPECORD200PLUS) at the Electrochemistry Laboratory of Cheikh Anta Diop University in Dakar, Senegal.

2.2. Synthesis protocol for a first-generation PPI dendrimer (G1) functionalized with 2-hydroxy-p-naphtoquinone (1a)

In a 150 mL Erlenmeyer flask protected from light, a solution of the appropriate Dendr-(NH2)n in 10 mL absolute ethanol was added to a suspension of naphthoquinone in 20 mL absolute ethanol with magnetic stirring (at 300 rpm) at room temperature. The gradual disappearance of the suspended solid observed was marked by the formation of a white solution. To ensure complete formation, the solution was left to stir for 15 minutes. At this point, the aldehyde in question was added using a syringe.

The resulting reaction mixture was then left under magnetic stirring at room temperature for 12 hours, protected from light.

The precipitate formed was then wrung out, washed with ethanol (2 times) and then with petroleum ether (2 times) before being dried in a thermostatic oven at 45°C for 1 hour. Compound 1a was prepared according to the scheme below:

2.3. Study of the kinetics of chromium adsorption on PPI dendrimers operated with 2-hydroxy-pnaphtoquinone(1a)

This work was carried out using the immersion method under the following non-optimized conditions. A mass of 30 mg of the adsorbent (1a) was added to 10 mL of optimized aqueous solutions of $K_2Cr_2O_7$ (30 mg/L) at a pH of 2 with magnetic stirring (at 300 rpm) .

3. RESULTS AND DISCUSSION

3.1. Synthesis results and characterization

The molecule 1a was obtained during the synthesis. Its molecular structure is shown in Figure 2.

Spectroscopic data were used to propose the molecular structure of 1a.

- **NMR^{1}H(DMSO-d6,400MHz)**: **δ(ppm)**16.80(br.s,OH);8.95(s,NH);7.90(d,JHH^3=6.8Hz, H^{11}-*Napht*,4H); 7.83(d,J^{3}HH=6.4Hz, H^{14}-*Napht*, 4H);7.68(t,J^3 HH=7.6 Hz, H^{12}-*Napht*, 4H); 7.56 (t, J^3 HH = 7.2 Hz, H^{13}-*Napht*, 4H); 4.56 (q, J^3 HH = 4.4 Hz, H^6, 4H);2.81(s,H^5,8H);2.40-1.95(s[2.23ppm(H^3,8H)+2.14ppm (H^2,4H)],12H); 1.61(s,H^4,8H);1.43(d,*J*=4.4Hz,H^{17},12H);1.22(s,H^1,4H).
- **NMR^{13} C (DMSO-d6, 75.5MHz): δ(ppm)** 184.7 (d, *J* = 28 Hz, C=O); 178.9 (d, *J* = 20 Hz,C=O);170.2(t, *J* = 64Hz,C-OH);134.6(d;C^{IV}-*Napht*);133.7(*CH-Napht*);131.3(C^{IV}-*Napht*);130.8(*CH-Napht*);125.4(*CH-Napht*);125.1(*CH-Napht*);111.6(C^7);52.5(s,C^2);51.3(s,C^6)50.7(s,C^3);43.6(d,C^5);23.6(C^1);23.0(C^4);17.42(s;C^{17}).

- **Mass(ESI/ $_{CH3OH-CH3}$Cl-95:5).**m/z theoretical [found (uncertainty)] **[M-4H+3Na]$^-$ (C H $_{N6468612}$ O$_{Na3}$)** 1181.45938 [1181.4594 (0 ppm)].

3.2. Kinetic study

The curves representing the evolution of the UV-visible absorption spectrum of the chromium solution as a function of the adsorbent immersion time are shown below.

For a better understanding of the kinetics of chromium VI elimination and chromium III formation, the absorbance curves for chromium VI and chromium III in solution as a function of contact time with the adsorbent with the compound 1a are shown in Figures 4 and 5. The curves obtained are neither linear nor affine.

A detailed study of the kinetics of adsorption of chromium by adsorbent 1a leads to kinetics of 2nd order because the curve 1 /Ct - 1/C0 as a function of time is strictly linear in all cases (figures 6 and 7). The equation obtained is of the form y=a.t with a correlation coefficient r^2 close to1. The kinetic parameters are presented in Tables 1 and 2.

The two formulae below were used to determine the parameters and yields, and the results are listed in Tables 1 and 2:

$$qe=(C0-Ce)V/ m$$

$$R(\%)=(C0-Ce)/C0x100$$ [12]

With:

- qe(mg/g and Ce (mg/l) the equilibrium adsorbate concentration in the solid and liquid phase respectively,
- C0 (mg/l) is the initial concentration of the adsorbent
- V is the volume of metal ion solution (L)
- m(g) is the weight of the adsorbent.
- R is the efficiency of metal ion removal

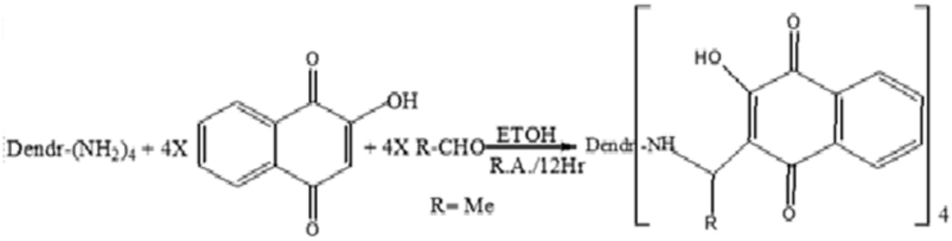

Figure 1: Equation for the reaction to obtain compound 1a.

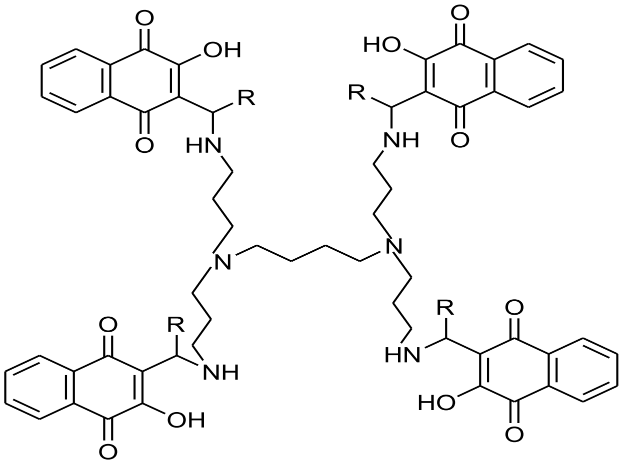

Figure 2: Structure of compound 1a

The absorption spectrum of the $K_2Cr_2O_7$ 30mg/L solution as a function of contact time with (d) compound (Figure 3)1a shows the presence of two bands. The first at around 260nm is assigned to chromium III and the second at around 350 nm corresponds to chromium VI [13].

Analysis of these two bands shows that the band at 260 increases progressively while the bandat 350nm decreases. This can be explained by a conversion or reduction of chromium VI, which is 500 times more toxic than chromium III [14].

In view of the highly asymmetrical values of the rate constants for the elimination of chromium VI and the formation of chromium III (0. 0008 and 0.0045), it is plausible to predict that in addition to this conversion of chromium VI to chromium III, there may also be the formation of a non-soluble complex between the absorbent and the chromium VI.

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

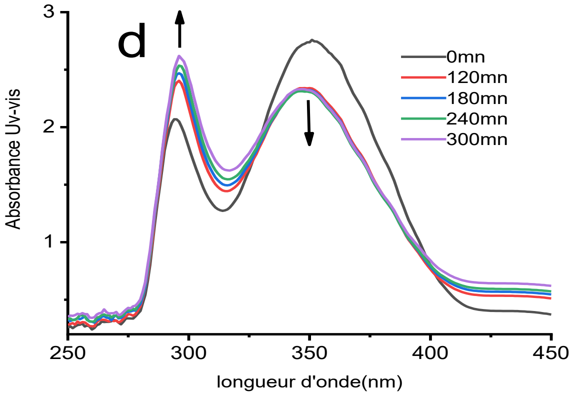

Figure 3: Change in absorbance of a solution of $K_2Cr_2O_7$ 30mg/L as a function of contact time with (d) Compound 1a.

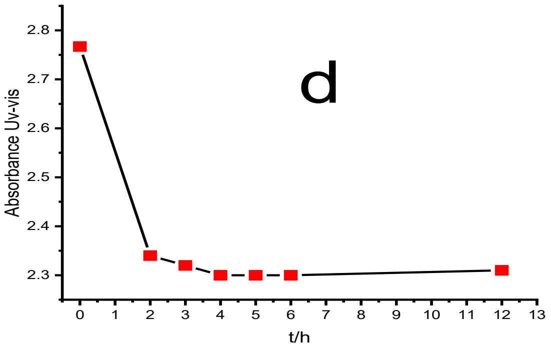

Figure 4: Decay kinetics of the chromium(VI) absorption band at 350nm, using 30mg and a pH of 2, adsorbent (d) Compound 1a

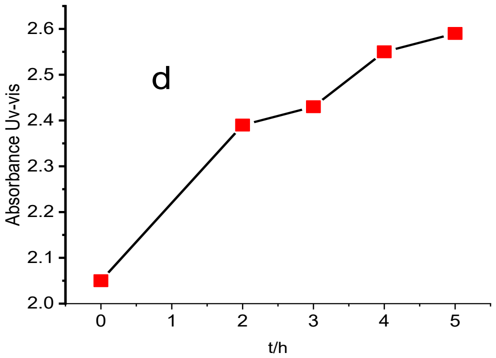

Figure 5: Growth kinetics of the chromium(III) absorption and at 350 nm, using 30 mg and a pH of 2, adsorbent (d) Compound 1a.

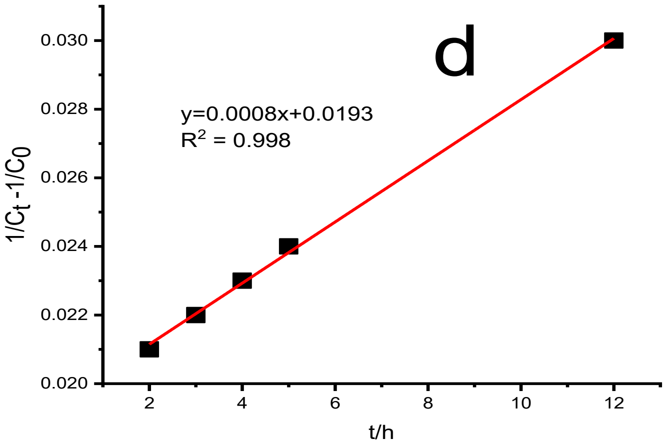

Figure 6: Determination of the second-order rate constant for the adsorption of chromium(VI) on to (d) Compound 1a under optimized experimental conditions.

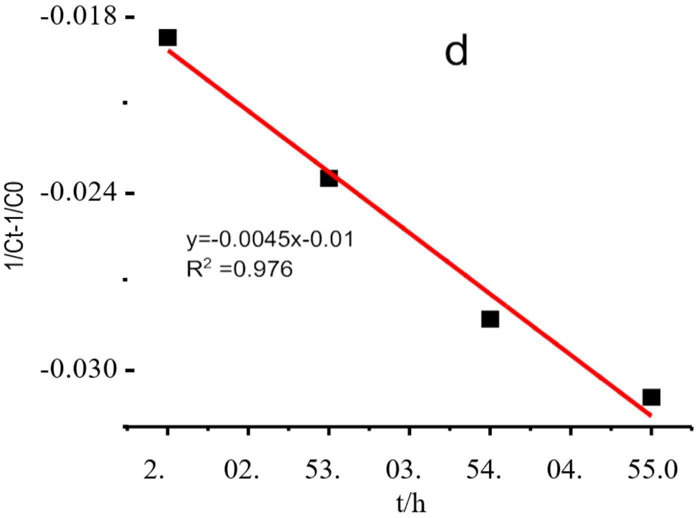

Figure 7: Determination of the second-order rate constant for the adsorption of chromium(III) on to (d) Compound 1a under optimized experimental conditions.

Table 1: Kinetic parameters of adsorbent 1a on chromiumVI.

Adsorbent	R(%)	k2	R2	qe(mg/g)
C2	**16.89**	**0.0008**	**0.998**	**39.63**

Table 2: Kinetic parameters of 1a adsorbents on chromium III.

Adsorbent	R(%)	k2	R2	qe(mg/g)
C2	**0**	**0.0045**	**0.976**	**0**

CONCLUSION

This work is part of the "Environment" theme, and more specifically in the "Pollutant depollution and retention" research area. The aim of the study is to investigate the performance of a first-generation PPI dendrimer (G1) in eliminating chromium from aqueous solutions. In the course of this work, we first synthesized and characterized a new first-generation GI PPI dendrimer and then carried out a kinetic study of chromium adsorption. To do this, we used the immersion adsorption technique under non-optimized conditions. This study demonstrated the ability to eliminate chromium VI or convert it to chromium III. The percentages of chromium elimination found were 16.89% for chromium VI and 00.00% for chromium III. These results led us to conclude that adsorbent 1a eliminates only chromium VI. In order to determine the order of the reaction, the adsorption kinetics of chromium on the adsorbent 1a were studied using the 2nd order Lager Gren model. Comparison of the regression coefficients of the curves showed that the kinetics of the chromium adsorption reaction on 1a is most likely of second order.

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