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STUDY OF THE SYNTHESIS AND ENVIRONMENTAL REMOVAL OF 4,4'-DIPYRIDINE DERIVATIVES

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Abstract

Dipyridine derivatives are used on large scale and pose significant environmental problems. We have synthesized dipyridine derivatives with: 5-chlorovaleric acid, α -dichlorohidrin, iodoacetamide and 11-bromoundecanoic acid. The synthesized substituted compounds were investigated by LC-MS. The adsorptive removal of dipyridine derivatives from aqueous solution has been studied using medicinal activated carbon. The adsorption rate has been investigated under the controlled process parameters including adsorption time, carbon and organic compound concentration. The results from this study demonstrated that the activated carbon can be used as a low-cost adsorbent for the removal of environmental cationic dipyridine derivatives from the water environment.

Key words: 4,4'-dipyridine derivatives synthesis, activated carbon adsorption, LC-MS analysis

Received: November, 2014; Revised final: February, 2015; Accepted: February, 2015

1. Introduction

Dipyridine and various dipyridine derivatives are currently synthesized and used on a large scale (Howard et al., 1997). Methylviologen, also named paraquat is a very toxic herbicide to aquatic organisms and may cause long-term adverse effects in the aquatic environment (Chemwatch, 2008). Dipyridine derivatives useful in many applications such as: redox chromophores (Žmija and Małachowski, 2011), electrochromic displays (Cummins et al., 2000), battery half-cells (Michaelis, 1935), sensors (Chira et al., 2014), electron acceptors (Kotani et al., 2006), energy conversion materials (Bocarsly et al., 1980), herbicides (Monk, 1998), neuromuscular agents (Buruiana et al., 1991).

Mono, bi or polymeric dipyridine derivatives compounds may be synthesised from dipyridine and

the desired halogenated reagents. Various symmetrical or asymmetrical, mono or bisubstituted compounds derived from dipyridine are mentioned in literature among which (N-(2-carboxyl-ethyl)-N'-(4-vinylbenzyl)-4,4'-bipyridinium dichloride (Liu et al., 2004), 1-(11-dodecylsulfanyl-undecyl)-[4,4'] bipyridinium bromide (Casillia et al., 2004), alkylthiol-substituted viologen (Tang et al., 1996), polyviologens (Liu et al., 2007). The macrocycle cyclo(paraquat-o-phenylene-paraquat-p-phenylene) was synthesized using an o-xylene bridged bis (4,4'-bipyridinium) salt (Scheytza et al., 1998), cyclobis(paraquat-p-phenylene) ring and methyl viologen radical cation composed triradical tricationic complex (Fahrenbach et al., 2012) or viologen-based cyclophanes was synthesized starting from 1,4-bis-bromomethyl-benzene and 4,4'-dipyridine (Tanabe et al., 2009).

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Dipyridine derivatives are organic pollutants which have attracted much attention due to their slow degradation and potential impact on the environmental.

Among various treatments for the removal of environmental contaminants from an aqueous solution, adsorption is an important retention and purification process eliminating the effluent toxicity (Arsene et al., 2013). Activated carbon is one of the most efficient adsorbents used for removing organic pollutants from industrial waste-waters (Al Duri et al., 1996).

This study reports synthetic strategies to a series of novel derivatives based on the dipyridine. The four syntheses reactions using 5-chlorovaleric acid, α -dichlorhidrin, iodoacetamide and 11-bromoundecanoic acid were studied by refluxing halogenated reagents with 4,4'-dipyridine.

The synthesized substituted compounds were investigated by HPLC-MS and were efficiently removed by adsorption on activated carbon.

2. Material and methods

All of reagents used for synthesis used in this paper 4,4'-dipyridine, 5-chlorovaleric acid, α -dichlorhidrin, iodoacetamide, 11-bromoundecanoic acid were purchased from Sigma-Aldrich. The solutions were analyzed using a UV/Vis-Thermo Evolution 260 Bio (Thermo Fischer Scientific). Adsorption studies were carried out with silica gel 100C8, aminopropyl silicagel (Fluka) and medicinal activated carbon (Carbocit-Biofarm) from a local pharmacy. Acetonitrile (ACN for HPLC) was produced by Biosolve. Aqueous solutions were prepared with purified water (18 M Ω cm⁻¹, Millipore).

HPLC analyses were performed using an Agilent 1260 series LC system (Agilent, Waldbronn, Germany) consisting of: binary pump, micro-degasser, thermostatted autosampler, thermostatted column compartment. The LC instrument was coupled with an Agilent 6410B triple-quadrupole mass analyzer fitted with an electrospray ionization source. Data acquisition and analysis were performed using Mass Hunter software, revision B.05.00. All chromatographic runs were carried out on a Zorbax Eclipse Plus C18 150 x 4.6 mm, 5 μ m column from Agilent Technologies. Column was thermostatted at 27°C.

3. Experimental

3.1. Syntheses of dipyridine derivatives

The reactions used to obtain dipyridine derivatives are shown in Fig. 1. It involves treating the 4,4'-dipyridine with reactive halogenated derivatives. It is interesting to note that reagent II has two chlorine moieties and thus multiple products can be obtained.

The syntheses were carried out in 45 mL acetonitrile and water [2:1] at reflux for 24 H or longer. A mixture of the 5-chlorovaleric acid (10 mmol L⁻¹) and 4,4'-dipyridine (2.5 mmol L⁻¹) was heated under reflux for the 24 h to obtain the product (I). In the similar method different halogenated reagents (2.5 mmol L⁻¹) were refluxed 24 h in the presence of dipyridine (10 mmol L⁻¹) to yield the products (II-1), (III), (IV). The resultant products (II-1, II-2 and II-3) were prepared by mixing solution of 4,4'-dipyridine (20 mmol L⁻¹) with α -dichlorhidrin (2.5 mmol L⁻¹) for the 68 h. The reaction mixtures were then cooled to room temperature and were stored at +4 °C.

3.2. HPLC-MS analysis

The analysis was carried out in isocratic conditions at a constant flow-rate of 0.3 mL/min. Mobile phase composition was a mixture of aq. 0.1% formic acid and acetonitrile in the ratio 40 / 60 (v/v). Sample injection volume was 1 μ L. Mass-spectrometric detection of analytes was made using Selected Ion Monitoring acquisition mode (SIM). Analyte SIM values, fragmentor voltages, ionization source parameters and other MS parameters are shown in Tables 1 and 2.

3.3. Adsorption procedure

The adsorption of the organic molecules obtained after syntheses reactions was carried out in Eppendorf tubes of 1 mL into which different volumes of reaction solutions and 20 mg milled activated carbon were added. The mixtures were shaken with Multi-Vortex for tubes at a temperature of 25 \pm 1°C for 30 min. After vortexing, the obtained solutions were centrifuged through a 30 micron membrane filters Millipore at 14,000 g for 15 min.

Table 1. MS acquisition parameters for dipyridine and investigated reaction products

Compound Name	Mass	MS2 Res	Dwell	Fragmentor	Polarity
4,4'-dipyridine	157.2	Unit	200	100	Positive
5-(4,4'-dipyridinium)-valeric acid	258.1	Widest	200	100	Positive
acetamide-4,4'-dipyridinium	215.1	Widest	200	100	Positive
11-(4,4'-dipyridinium)-undecanoic acid	342.1	Widest	200	100	Positive
1,3-di(4,4'-dipyridinium)-2-propanol	370.2	Widest	100	100	Positive
4,4'-di(3-chlor-2-propanol)-dipyridinium	342.1	Widest	100	100	Positive
1-(4,4'-dipyridinium)-3-chlor-2-propanol	250.1	Widest	100	100	Positive

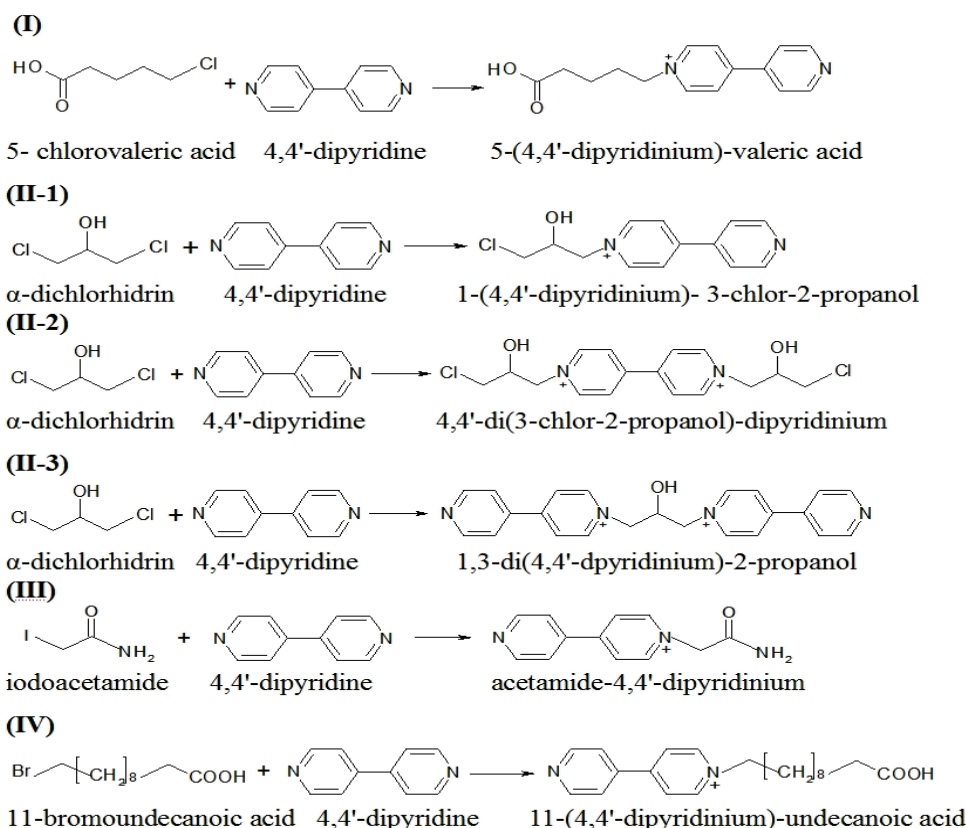


Fig. 1. Synthesis of dipyridine derivatives

Table 2. Electrospray ion source parameters

Drying Gas Flow (L/min)	10
Nebulizer Pressure (psig)	60
Drying Gas Temperature (°C)	300
Capillary Voltage (V)	3000

The all solutions before and after adsorption treatment were analyzed using a UV/Vis by monitoring the absorbance changes at a wavelength of maximum absorbance.

4. Results and discussion

4.1. Synthesis and characterization of dipyridine derivatives

The dipyridine derivatives can be obtained by alkylation with halogenated derivatives that can modify only one or both aromatic nitrogen atoms (mono or bisubstituted derivatives). The reaction yield obtained with different halogenated reagents depends on several factors such as: steric effects, electronic effects and reaction conditions (media, temperature, time). The halogenated reagents used in this work have also other functional moieties (acids, alcohol or amide).

In order to confirm the syntheses and to identify the structure of the obtained resultant products, the reaction mixtures were analyzed by LC-MS. The HPLC-MS analysis results present different peaks with retention time depending on the structure

of synthesized 4,4'-dipyridine derivatives present in the sample. The corresponding peak for 4,4'-dipyridine solution appear at 4.355 min (Fig. 2a).

The chromatograms recorded for a standard solution of 4,4'-dipyridine (277 $\mu\text{g/mL}$) and the refluxing reaction product between 4,4'-dipyridine and 5-chlorovaleric acid (I) are presented below in Fig. 2. For reaction (I) the HPLC-MS data indicated that monoalkylated derivative was obtained by starting 5-chlorovaleric. As it can be observed in Fig. 2b the reaction mixture contains the interest reaction product (5-(4,4'-dipyridinium)-valeric acid). The highest peak found in the sample appears at 3.873 min retention time and the peak area corresponds to 5.7 $\mu\text{g/mL}$ of synthesized compound. From this spectrum, it appears that mass of 258.1 is characteristic for the product of interest. The yield of this reaction was 2.07 %.

The product obtained by refluxing for 24 h of the reaction mixture 4,4'-dipyridine and 1,3-dichloro-2-propanol appears at 3.898 min and has a concentration of 174.1 $\mu\text{g/mL}$ of 1-(4,4'-dipyridinium)-3-chloro-2-propanol (II-1) (Fig. 3a). The reaction yield was 7.73 %. In Fig. 3b different reaction products (II-1, II-2 and II-3) obtained after 68 h refluxing of the same reaction are eluted out at different time intervals (3.898, 3.741 and respectively 3.755 min). These compounds form distinct chromatographic peaks by the mass values: 250.1 (II-1); 342.1 (II-2) and 370.2 (II-3) corresponding to mono and bisubstituted reaction products.

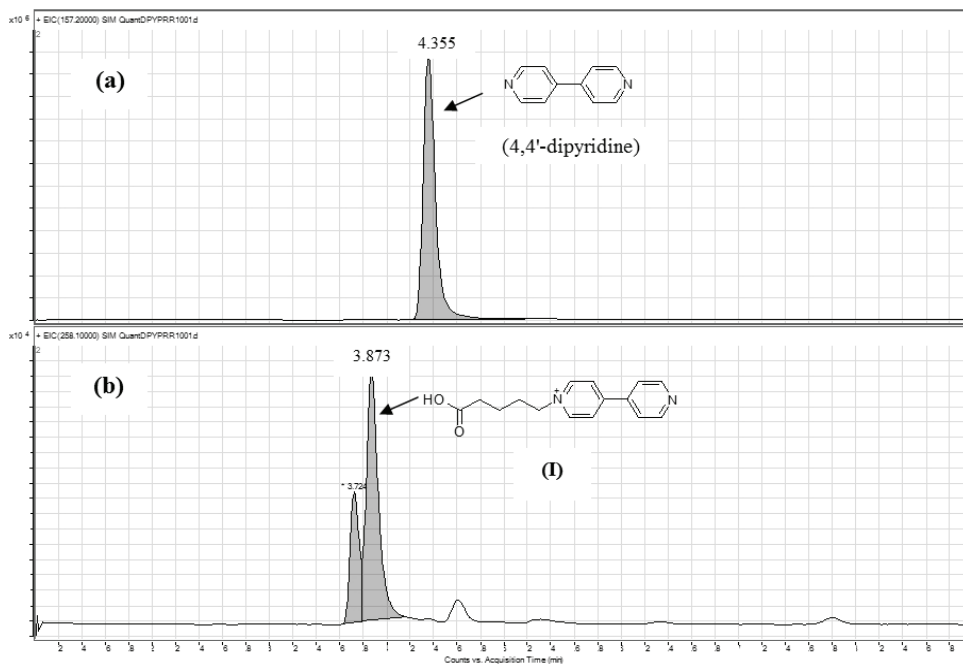


Fig. 2. Chromatograms recorded for the injection of: (a) standard solution of 4,4'-dipyridine (277 $\mu\text{g/mL}$) and (b) product resulted after reaction synthesis: 5-(4,4'-dipyridinium)-valeric acid

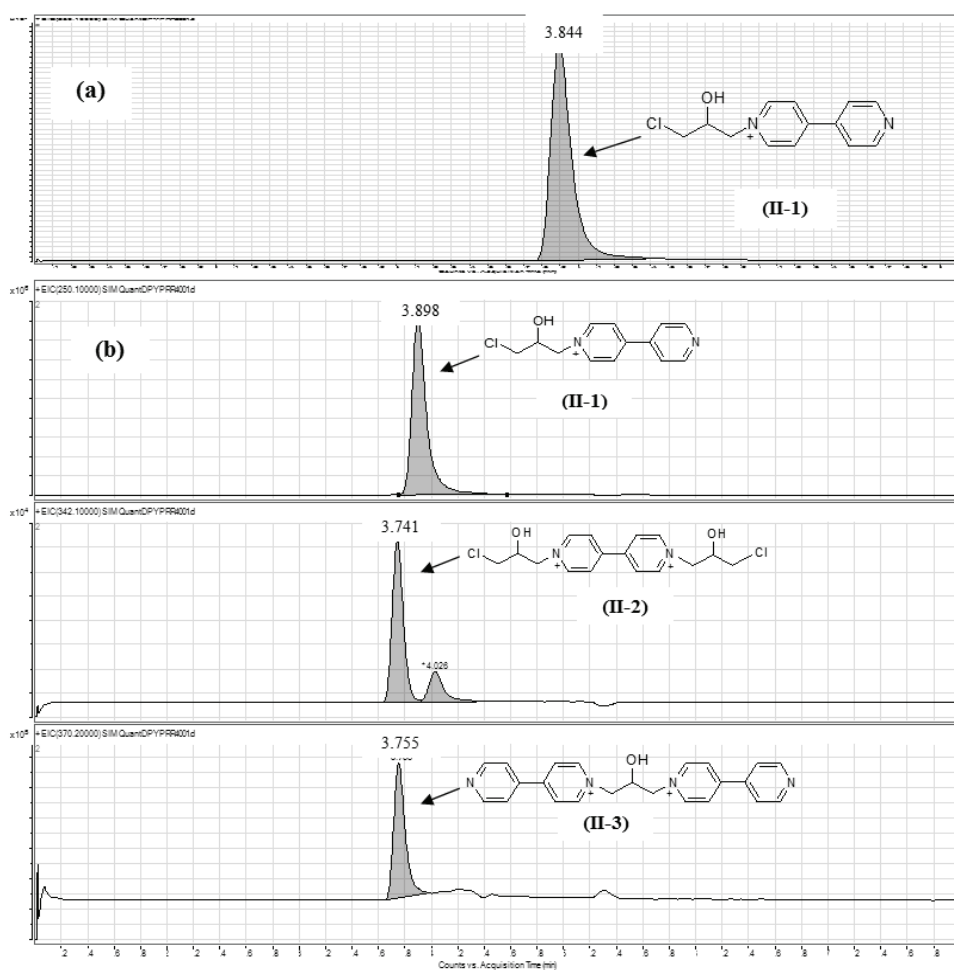


Fig. 3. Chromatograms recorded for the injection of: (a) product mixture resulted after 24 h reaction refluxing: 1-(4,4'-dipyridinium)-3-chlor-2-propanol (II-1) and (b) products mixture resulted after 68 h reaction refluxing: 1-(4,4'-dipyridinium)-3-chlor-2-propanol (II-1), 1,3-di(4,4'-dipyridinium)-2-propanol (II-2) and 4,4'-di(3-chlor-2-propanol)-dipyridinium (II-3)

The reaction compounds 1-(4,4'-dipyridinium)-3-chlor-2-propanol (II-1), 4,4'-di(3-chlor-2-propanol)-dipyridinium (II-2) and trace amount of 1,3-di(4,4'-dipyridinium)-2-propanol (II-3) have reaction yield of 35.82 %, 6.29 %, 0.37 % respectively. The mixture of products contains 710.4 µg/mL of (II-1), 124.7 µg/mL of (II-2) and 7.3 µg/mL of (II-3). The major compound in reaction mixture after 24 h refluxing (II-1) is formed approximately by four times more for the longer reaction time (68 h).

The reaction mixture for reaction (III) was analyzed to characterize the product of interest which is presented in Fig. 4. Excellent yield was obtained for refluxing reaction between 4,4'-dipyridine and iodoacetamide (94.92 %). A significant peak refers to the reaction product that is present in the sample and that is identified with 215.1 mass range and 3.844 min retention time correspond to the formation of acetamide-4,4'-dipyridinium (III). The reaction mixture contain about 1099 µg/mL of acetamide-4,4'-dipyridinium (III).

The structure of synthesis product 11-(4,4'-dipyridinium)-undecanoic acid (IV) obtained by refluxing 4,4'-dipyridine with 11-bromoundecanoic acid was confirmed by recording the chromatogram LC-MS presented in Fig. 5. The chromatogram exhibited a significant peak with m/z 342.1 at 4.021 min. The results indicate about 1036.8 µg/mL. The main reaction product was obtained with a yield of 84.3 %.

The all synthesized 4,4'-dipyridine derivatives (I)-(IV) were successfully obtained in moderate to good yields. It is noteworthy that the syntheses of substituted compounds of 4,4'-dipyridine with halogenated reagents were carried out in a single step

within a reasonable time and the yields were around 2.1-94.9 % (Table 3).

4.2. Adsorption comparison of 4,4'-dipyridine derivatives

In order to investigate the adsorption behavior of synthesized compounds with different functional groups on the activated carbon and silica was quantified by recording the UV-VIS spectra for each reaction mixture before and after adsorption treatment.

The adsorption yield is influenced by structure of the reaction compounds, the concentration of the organic molecules in the analyzed solution and the properties of the absorbent.

The influence of operational parameters such as the mass of activated carbon and the adsorption time were studied for reaction (II for 68 h) because it contained numerous compounds.

In order to investigate the adsorption kinetics of 4,4'-dipyridine derivatives, the stirring time of the solution was investigated between 15 minutes and 1 hour.

The optimum stirring time was chosen 30 minutes as a compromise between a good removal of the organic compounds and a short treatment time. The concentration of activated carbon was studied by varying the carbon mass from 1 to 30 mg/mL and the optimum value was 20 mg/mL.

The reaction products are not absorbed on both silica gel or aminopropyl silicagel even at high quantities (100 mg/mL) and long adsorption time (1 h). The experimental parameters and results are shown in Table 4.

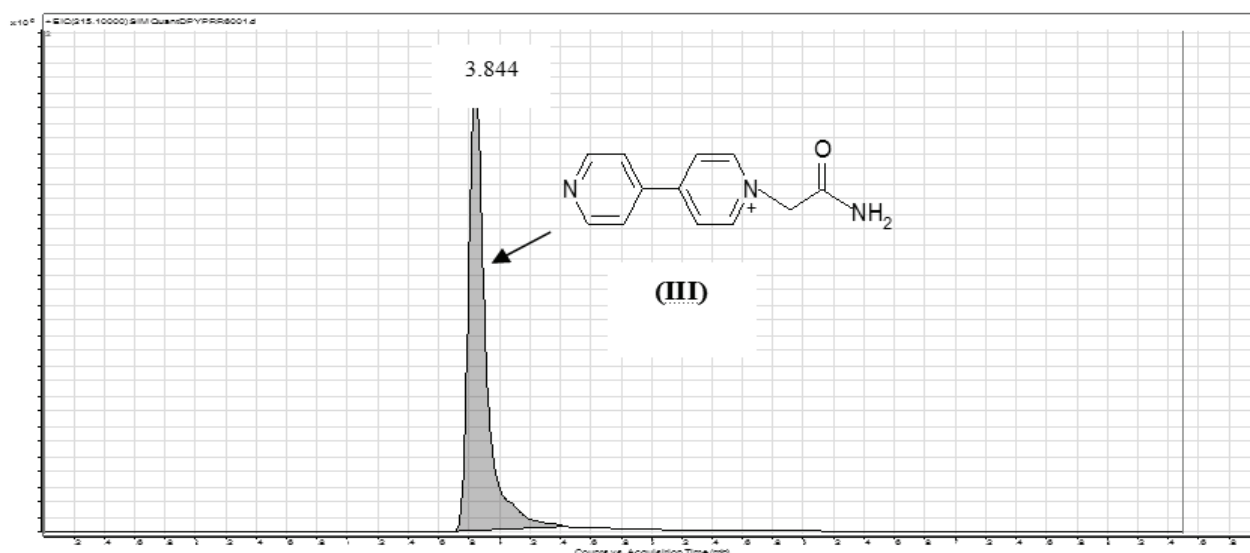


Fig. 4. Chromatogram recorded for the injection of product mixture resulted after 24 h reaction refluxing: acetamide-4,4'-dipyridinium (III)

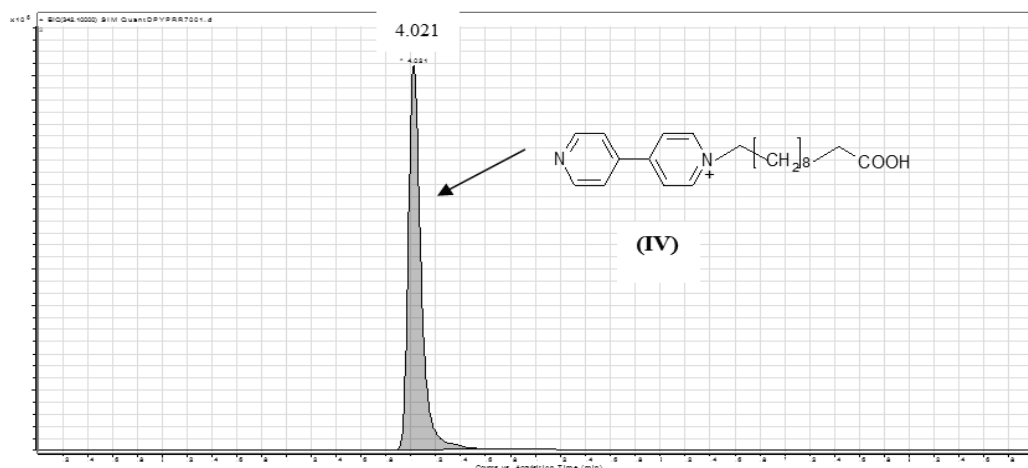


Fig. 5. Chromatogram recorded for the injection of product mixture resulted after 24 h reaction refluxing: 11-(4,4'-dipyridinium)-undecanoic acid (IV)

Table 3. 4,4'-dipyridine derivatives obtained with some halogenated reagents

Compound Name	Molecular mass	Retention time (min)	Solvent	Time (h)	Yield (%)
5-(4,4'-dipyridinium)-valeric acid acetamide-4,4'-dipyridinium	258.1	3.873	CH ₃ CN : H ₂ O [2:1]	24	2.1
11-(4,4'-dipyridinium)-undecanoic acid	215.1	3.844		24	94.9
1-(4,4'-dipyridinium)- 3-chlor-2-propanol	342.1	4.021		24	84.3
	250.1	3.844		24	7.7
		3.898		68	35.8
4,4'-di(3-chlor-2-propanol)-dipyridinium	342.1	3.741		68	6.3
1,3-di(4,4'-dipyridinium)-2-propanol	370.2	3.755		68	0.4

Table 4. Experimental parameters and results for 4,4'-dipyridine derivatives adsorption onto activated carbon

Reaction	Dilution factors	Activated carbon (mg/mL)	λ (nm)	Absorbance	
				initial	after adsorption
(I)	30	20	250	1.184	0.000
(II-24h)-one derivative	200		238	1.290	0.039
(II-68 h)-tree derivatives	200		238	1.412	0.019
(III)	100		232	1.230	0.009
(IV)	70		246	1.334	0.051

It can be observed that the activated carbon has good capabilities to adsorb dipyrindine derivatives from aqueous solution and can be used for treatment of waste waters.

5. Conclusions

We have synthesized six dipyrindine derivatives using four halogenated reagents: 5-chlorovaleric acid, α -dichlorhidrin, iodoacetamide and 11-bromoundecanoic acid. Mono or bisubstituted compounds were obtained depending on the structure of the halogenated compound and reaction time. The synthesized products were investigated by LC-MS and the reaction yields were between 2.1 and 94.9 %.

This study shows that activated carbon can be used as low-cost adsorbent material for the removal of organic pollutants (dipyrindine derivatives) from water. The procedure for dipyrindine derivatives synthesis can be adapted for the obtaining and characterization of different interested compounds.

Acknowledgements

This work was financed by the program Partnership in priority areas - PN II, supported by the Romanian Department of Education and Research (MEN-UEFISCDI) projects no. PN-II-PT-PCCA-2013-4-0203 and PN-II-PT-PCCA-2013-4-0297.

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