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Bulgarian Chemical Communications, Volume 44, Number 2 (pp. 113 – 117) 2012

A facile synthesis of calix[4]pyrroles using heteropolyacids as green, eco-friendly, reusable and recyclable catalyst

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A catalytic method was proposed for the synthesis of calix[4]pyrroles and *N*-confused calix[4]pyrroles by reaction of dialkyl or cycloalkyl ketones with pyrrole using heteropolyacids as acidic catalysts with good yields under mild and environmentally friendly conditions.

Keywords: Calix[4]pyrrole; Heteropolyacid; Preyssler; Catalysis; *N*-confused calix[4]pyrrole

1. INTRODUCTION

Heteropolyacids are classified according to their structures. Two classes, the Keggin and the Wells–Dawson structures, have been investigated more extensively than the others [1,2]. The use of heteropolyacids, HPAs, has recently received considerable attention as nontoxic and environmentally benign catalysts for various organic transformations to afford the corresponding products in good yield. Due to the numerous advantages associated with these ecofriendly (green) catalysts, HPAs and their salts have been explored as powerful, efficient and ecofriendly catalysts in organic reactions [3]. An important area of supramolecular chemistry is the design and synthesis of receptors to recognize, sense and bind the anions [4]. Calixarenes are a very important class of macrocyclic compounds which are widely used as ligands in supramolecular chemistry. Modification of the upper rim of calix[4]phenols by means of S_N^H coupling with electron-deficient triazinones is a new approach to change the molecular cavities of these compounds, which opens new possibilities for construction of highly selective ligands [5]. The research and development have been made under milder methods for the synthesis of porphyrins [6], N-C isomerization [7] and higher homologues of porphyrins [8]. The meso-octamethylcalix[4]pyrrole **3a** has been prepared by condensation of pyrrole with acetone in the presence of aqueous hydrochloric acid or methanesulfonic acid in methanol [9]. Calix[4]pyrroles are conformationally flexible macrocycles [10] of significant importance due to their binding under different conditions with anions [11], neutral substrates [9] and metal ions [12]. The complexation behavior of calix[4]pyrroles with anions and cations has been widely studied using fluorescence [13], colorimetric [14] and electrochemical signaling [15] devices. They find interesting applications as raw materials for transformation into novel calix[4]pyridines and calix[4]pyridinopyrroles [16], as new solid supports capable of separating anion mixtures [17], in optical recognition of organic vapors [18] and as biologically active species [19]. Porphyrinogens, bearing hydrogen atoms at meso positions, are key intermediates in biological and chemical synthesis of porphyrins [20].

Synthesis of meso-octamethylcalix[4]pyrrole (**3a**) and *N*-confused octamethylcalix[4]pyrrole (**4b**) has been performed using pyrrole and acetone in the presence of trifluoroacetic acid [21]. The reactions of pyrrole with dialkyl ketones in the presence of protic acids (HCl, H_2SO_4), organic acids (CH_3SO_3H) and Lewis acids (BBr_3 and BF_3) have also been used in the synthesis of calix[4]pyrroles [22]. The reaction of excess of pyrrole with dialkylketones in the presence of acid gave 5,5-dialkyldipyrromethanes which on subsequent reaction with dialkylketones in the presence of borontrifluoride-etherate formed strapped calix[4]pyrroles [23]. These acids are considered hazardous and corrosive and their removal from the reaction mixtures is difficult. Recently, condensations in dichloromethane of pyrrole with dialkyl ketones in the presence of the molecular sieve Al-MCM-41 and the zeolite HY

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afforded dipyrromethane, calix[4]pyrroles and other linear products, but not the *N*-confused calix[4]pyrroles [24]. Heteropolyacids (HPAs) are inexpensive and non-hazardous solid acids, useful as catalysts.

2. EXPERIMENTAL SECTION

Chemicals and apparatus

All chemical compounds were obtained from commercial sources and used as received.

IR spectra were recorded on a Bruker 500 scientific spectrometer. ^{1}H NMR spectra were recorded in $CDCl_3$ with TMS as internal standard on a FT NMR Bruker 100 MHz Aspect 3000 spectrometer. The mass spectra were scanned on a Varian Mat. CH-7 at 70 eV. Melting points were recorded on an Electrothermal type 9100 melting point apparatus and were uncorrected.

Preparation of Catalysts

Preyssler catalyst, $H_{14}[NaP_5W_{30}O_{110}]$ (H_{14}-P_5). H_{14}-P_5 was prepared by passage of an aqueous solution of the potassium salt through a column (50 cm×1 cm) of Dowex50W×8 in the H^+ form and evaporation of the eluate to dryness under vacuum [25].

Wells-Dawson species $H_6[P_2W_{18}O_{62}]$. The Wells-Dawson species $H_6[P_2W_{18}O_{62}]$ was prepared as described elsewhere [26] from an aqueous solution of the α/β $K_6P_2W_{18}O_{62}.10H_2O$ salt, which was treated with ether and concentrated (37%) HCl solution.

General procedure

Preparation of calix[4]pyrroles (3a-g) and N-confused calix[4]pyrroles (4a-4e). Synthesis of meso-octamethylcalix[4]pyrrole (**3a**) and N-confused octamethyl calix[4]-pyrrole (**4a**):

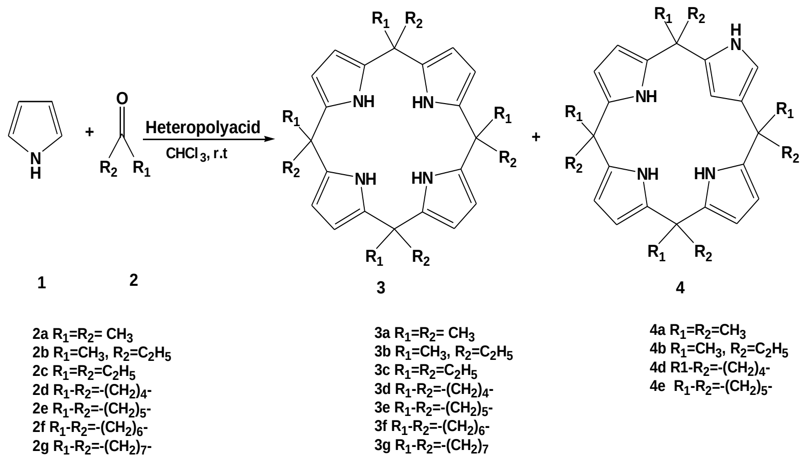
A mixture of pyrrole (8 mmol), acetone (8 mmol), $CHCl_3$ (10 mL) and heteropolyacid catalyst (0.04 mmol) was added to the bottom flask and the mixture was stirred for 6 hours at room temperature. The reaction progress was monitored by thin layer chromatography (TLC). After completion of the reaction, the catalyst was removed by filtration and washed thoroughly with $CHCl_3$ to dissolve all contents. The filtrate was pre-concentrated to give the crude product, which was subjected to column chromatography to afford pure meso-octamethylcalix[4]pyrrole (**3a**). The further elution of the column with petroleum ether-chloroform (2:3, v/v) gave the N-confused isomer of octametylcalix[4]pyrrole (**4a**). The above-described general method was used for the synthesis of different calix[4]pyrroles (**3b**-3**g)** and *N*-confused calix[4]pyrroles (**4b**, **4d** and **4e)**.

Reusability of catalyst

The recycled catalyst could be washed with dichloromethane and subjected to a second run of the reaction process with the same substrate. The results of the first and subsequent experiments were almost consistent in yields (83, 82.5 after three runs).

3. RESULTS AND DISCUSSION

We wish to report the synthesis of calix[4]pyrrole (**3a)** and the *N*-confused calix[4]pyrrole (**4a)** by using heteropolyacids as acid catalysts, and we performed this synthesis in a choroform solution of pyrrole (**1**) with acetone for 6 hrs in the presence of Preyssler catalyst (Scheme 1, Table 1).



Scheme 1. Synthesis of calix[4]pyrroles using Preyssler and Wells-Dawson heteropolyacids

Table 1. Reaction of different ketones (2a-2g) with pyrrole in $CHCl_3$, catalyzed by a Preyssler heteropolyacid catalyst H_{14}-P_5.

Compound	Time (h)	% Conversion of Pyrrole	^{a}Yield(%)/mp°C, (3)	(lit.mp°C,[ref.])(3)	^{a}Yield(%)/mp°C,(4)	(lit. mp °C, [ref.])(4)
2a	6	95	84.5/295	(296 [27])	11.5/185	(184 -185 [41])
2b	8	88	80/144	(146 [42])	10/121	-
2c	18	71.5	74.5/222	-	-	-
2d	5	93	83/235	(236 [42])	11.5/198	-
2e	5	96	85/273	(271-272 [43])	12/224	(223.2-223.6[43])
2f	24	37	32/163	-	-	-
2g	48	25.5	21.5/223	-	-	-

^{a} Isolated yields.

Table 2. Preyssler catalyzed condensation of pyrrole and acetone in different solvents.

Entry	Solvent	^{a}Yield (%) **3a**	^{a}Yield (%) **4a**
1	$CHCl_3$	84.5(83, 82.5)^b	11.5 (11, 10.5)^b
2	CCl_4	56	-
3	Benzene	45	-
4	Toluene	44	-
5	DMF	39	-
6	DMSO	36	-
7	Ethanol	71.5	9.5
8	THF	51	-
9	Acetonitril	68	8

^{a} Isolated yields. ^{b} Catalyst was reused over three runs.

Table 3. Reaction of different ketones (2a-2g) with pyrrole in $CHCl_3$, catalyzed by Wells-Dawson and Keggin (12-tungestophosphoric acid).

Compound	Reaction time (min)	^{a}Yield (%) using $H_6P_2W_{18}O_{62}$ (3)	^{a}Yield (%) using $H_3PW_{12}O_{40}$ (3)	^{a}Yield (%) using $H_6P_2W_{18}O_{62}$ (4)	^{a}Yield (%) using $H_3PW_{12}O_{40}$ (4)
2a	6	81	77	8.5	7
2b	8	76.5	75	8	-
2c	18	70	68	-	-
2d	5	79	74.5	8	-
2e	5	82.5	79	7.5	-
2f	24	26	20	-	-
2g	48	16.5	11.5	-	-

^{a} Isolated yields.

We carried out the synthesis of calix[4]pyrrole (**3a**) using various heteropolyacids (Table 2). The results showed that the yield of this synthesis is excellent using Preyssler and Wells–Dawson type tungstophosphoric heteropolyacid, $H_6P_2W_{18}O_{62}$, catalysts. The synthesis reaction (Scheme 1) was tested using different solvents and the best yields were obtained in chloroform (Table 2).

We performed this synthesis with other ketones (**3b-3g**) and pyrrole in chloroform as a solvent and used the Preyssler and Wells–Dawson type tungstophosphoric heteropolyacid, $H_6P_2W_{18}O_{62}$, catalyst (Table 3).

The reactions of cycloheptanone (**2f**) and cyclooctanone (**2g**) with pyrrole in presence of the Preyssler catalyst gave the corresponding calix[4]pyrroles (**3f**) and (**3g**) in 32% and 21.5% yields at ambient temperature, but the time required for the conversions was considered too long. In the reactions of pyrrole with **2c**, **2f** and **2g**, the corresponding *N*-confused calix[4]pyrroles could not be isolated. This could be attributed to the steric hindrance encountered with these higher acyclic and cyclic ketones. The atoms at C-2 and C-5 positions in pyrrole are more reactive than those at C-3 and C-4 positions, hence the electrophilic reaction at the C-2 and C-5 positions of pyrrole

Table 4. ^{1}HNMR spectral data for meso-octaalkyl and cycloalkyl calix[4]pyrroles (3a-3g).

Compound	^{1}HNMR δ (ppm)[a]
3a	7.01 (4H, br s, NH), 5.89 (8H, d, *J*=2.5 Hz, β-pyrrole), 1.50 (24 H, s)
3b	6.97 (4H, br s, NH), 5.80 (8H, d, *J*=2.5 Hz, β-pyrrole), 1.79-1.76 (8H, q, -CH2), 1.45-1.18 (12H, br s, CH_3), 0.80-0.63 (12 H, t, CH_3)
3c	7.05 (4H, br s, NH), 5.89 (8H, d, *J*=2.3 Hz, β-pyrrole), 1.79-1.57 (16H, q, -CH2), 0.71-0.58 (24 H, t, CH_3)
3d	7.03 (4H, br s, NH), 5.85 (8H, d, *J*=2.3 Hz, β-pyrrole), 2.21-2.00 (16H, m), 1.68-1.44 (16H, m)
3e	7.25 (4H, br s, NH), 5.89 (8H, d, *J*=2.5 Hz, β-pyrrole), 1.91-1.90 (16H, m), 1.50-1.41 (24H, m)
3f	6.88 (4H, br s, NH), 5.83 (8H, d, *J*=2.5 Hz, β-pyrrole), 2.01-1.94 (16H, m), 1.72-1.52 (32H, m)
3g	6.99 (4H, br s, NH), 5.93 (8H, d, *J*=2.4 Hz, β-pyrrole), 1.97-1.95 (16H, m), 1.52-1.34 (32H, m), 1.23-1.21 (8H, m)

[a] All products are known, characterized by ^{1}H-NMR and compared with authentic samples [24].

Table 5. ^{1}HNMR spectral data for meso-octaalkyl and cycloalkyl *N*-confused calix[4]pyrroles (4a, 4b, 4d, 4e).

Compound	^{1}HNMR δ (ppm)
[a] 4a	NH: 7.75 (1H, br), 7.41 (1H, br), 7.26 (2H, br); α-pyrrole: 6.30 (1H, d, J= 2 Hz), β-pyrrole: 6.04 (2H, br), 5.97 (2H, br), 5.93 (2H, m), 5.50 (1H, br); 1.56-1.48 (24H, m)
4b	NH: 7.63 (1H, br), 7.53 (1H, br), 7.35 (2H, br); α-pyrrole: 6.40 (1H, d, J= 2 Hz) ; β-pyrrole: 6.03 (2H, br), 5.88 (2H, br), 5.78 (2H, m), 5.53 (1H, br); 1.92 (3H, s, CH3), 1.83-1.12 (29H, m)
4d	NH: 7.48 (1H, br), 7.29 (1H, br), 7.00 (2H, br); α-pyrrole: 6.42 (1H, d, J=1.97 Hz); β-pyrrole: 6.00 (2H, br), 5.90 (2H, br), 5.88 (2H, m), 5.58 (1H, br); 2.25-1.98 (16H, m), 1.50-1.20 (16H, m)
[a]4e	NH: 7.63 (1H, br), 7.44 (1H, br), 7.10 (2H, br); α-pyrrole: 6.42 (1H, d, J= 1.98 Hz); β-pyrrole: 6.03 (2H, br), 5.97 (2H, br), 5.82 (2H, m), 5.50 (1H, br); 2.70-2.10 (16H, m), 1.60-1.20 (24H, m)

[a] Products N-confused calix[4]pyrroles (4a, 4e) are known, characterized by ^{1}H-NMR and compared with authentic samples [27].

with acetone in the presence of acid gave calix[4]pyrrole in preference to *N*-confused calix[4]pyrrole [27]. The recovered catalyst was recycled twice with a modest loss in product yield (Table 1). The catalytic activity of the heteropolyacid catalysts is remarkable. Heteropolyacid catalysts are environmentally benign and commercially available. The spectral data for the compounds (**3a-3g** and **4a, 4b, 4d, 4e)** are shown in Tables 4, 5.

4. CONCLUSIONS

We reported a catalytic method for the synthesis of calix[4]pyrrole using a Preyssler heteropolyacid catalyst as an efficient, reusable and ecofriendly heterogeneous inorganic catalyst. It is noteworthy that the catalyst is reusable. Even after three runs for the calix[4]pyrrole reaction, the catalytic activity of $H_{14}[NaP_5W_{30}O_{110}]$ was almost the same as that of a fresh catalyst. $H_{14}[NaP_5W_{30}O_{110}]$ is non-corrosive, environmentally benign and presents fewer disposal problems. Furthermore it was confirmed that a heteropolyacid with Preyssler structure displays higher activity and leads to higher yields due to the higher number of acidic protons.

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ЛЕСНА СИНТЕЗА НА КАЛИКС[4]ПИРОЛИ, ИЗПОЛЗВАЙКИ “ЗЕЛЕНИ”, ЕКОЛОГИЧНО СЪВМЕСТИМИ И РЕЦИКЛИРУЕМИ КАТАЛИЗАТОРИ

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(Резюме)

Предложен е каталитичен метод за синтезата на каликс[4]пироли и техни конформационни изомери с високи добиви чрез реакции на диалкил- и циклоалкил-кетони с пирол използвайки хетеро-поли-киселини като киселинни катализатори при меки и екологично съвместими условия.

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The synthesis of cyclotriveratrylene using heteropolyacids ($H_{3+x}PMo_{12-x}V_xO_{40}$) as recyclable heterogeneous catalysts

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The synthesis of cyclotriveratrylene (CV) using formaldehyde (37%) in the presence of heteropolyacids, $H_{3+x}PMo_{12-x}V_xO_{40}$ (x = 1–3) was studied in different solvents. In all cases the heteropolyacid with $x = 3$ gave the highest yield using ethanol as solvent. The effects of the catalyst and the solvent on the reaction were studied.

Key words: cyclotriveratrylene (CV), formaldehyde, heteropolyacid, catalyst.

1. INTRODUCTION

The facile condensation reaction between formaldehyde and phenols or their derivatives provides a major route to obtain rigid macrocycles used in supramolecular chemistry. Calixarenes, the best-known class of phenol-derived macrocycles, are prepared in this way, as are spherands and their relatives. Cyclotriveratrylene (CV), however, is an excellent exemplar of the ‘molecular basket’ type of ligands and has been known for the best part of a century. Many derivatives have been prepared and some exhibit useful inclusion properties such as that in Figure 1.

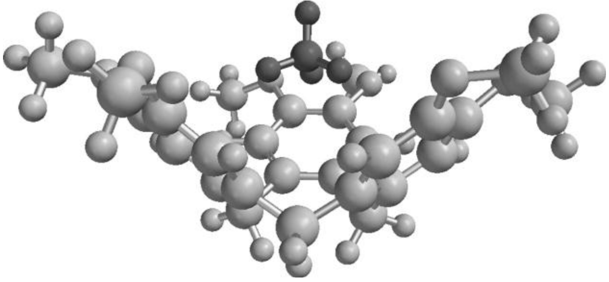

Fig. 1. Structure of a cyclotriveratrylene inclusion complex.

The synthesis included here is based on that reported by Robinson. In her paper the structure of the colourless crystalline precipitate resulting from the condensation of veratrole with formaldehyde in sulphuric acid was given a dimeric, rather than trimeric, configuration. At the time the product was believed to be 2,3,6,7-tetramethoxy-9,10-dihydroxyanthracene; however, as this was determined by the percentage of carbon and hydrogen in the compound, it is an understandable error as the composition would be the same for any higher homologue. The procedure is a result of much trial and error together with careful observation: as will be seen from the literature surrounding acid-catalysed reactions between aldehydes and phenols (or their derivatives such as resorcinol, pyrogallol and veratrole), yields are highly variable [1-6]. The structure of cyclotriveratrylene (CV) is (10,15-dihydro-2,3,7,8,12,13-hexamethoxy-5*H*-tribenzo[a,d,g]cyclononene).

The application of heteropolyacids, HPAs, as catalytic materials is growing continuously in the catalytic field. These compounds possess unique properties such as: well-defined structure, Brønsted acidity, possibility to modify their acid–base and redox properties by changing their chemical composition (substituted HPAs), ability to accept and

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release electrons, high proton mobility, being environmentally benign and presenting fewer disposal problems [7]. Because of their stronger acidity, they generally exhibit higher catalytic activity than conventional catalysts such as mineral acids, ion exchange resins, mixed oxides, zeolites, etc [8].

2. EXPERIMENTAL

Chemicals and apparatus

All compounds were purchased from Merck Company and all of the catalysts were prepared in accordance with the literature data [9-12]. The Wells–Dawson, $H_6[P_2W_{18}O_{62}]$ was prepared as described elsewhere [13] from an aqueous solution of α/β $K_6P_2W_{18}O_{62}.{}_{10}H_2O$ salt, which was treated with ether and concentrated (37%) HCl solution. All products were identified and their physical and spectroscopic data were compared with those of authentic samples. Melting points were measured using Barnstead Electro thermal. IR spectra were recorded on Bruker 4000–400 cm^{-1}. ^1H NMR spectra were recorded on a FT-NMR Bruker 90 MHz. The yields are based on GC/mass analysis using Agilent 6890 GC system Hp-5 capillary 30m×530μm×1.5μm nominal.

General preparation of cyclotriveratrylene (CTV)

Add cold 1,2-dimethoxybenzene (10 mL, 78.5 mmol) to heteropolyacid (0.04 mmol) in a 150 mL round-bottomed flask and stir vigorously. Add dropwise aqueous formaldehyde (12.5 mL, 37 %) and then add the indicated solvent (75 mL) using a syringe at indicated times, again with vigorous stirring. The syringe needle should be pushed through a septum that has a second needle inserted to release the pressure. Again, it is vital that stirring is vigorous otherwise the formaldehyde will fail to mix properly. By the end of the addition, about 45 min, the reaction mixture becomes a paste. Leave the paste for indicated times, then add indicated solvent (75 mL), stir and warm the mixture briefly with a heat gun to break up any large solid lumps. The progress of the reaction was monitored by TLC using petroleum ether:ethyl acetate as eluent. After completion, the reaction mixture was cooled to room temperature. Then the mixture was filtered, washed with ethanol (3×50 mL) and with diethyl ether (50 mL), then the solid residue was isolated and dissolved in dichloromethane. The catalyst was filtered off and the solvent was evaporated from the reaction mixture. The solid product was purified by recrystallization from aqueous dichloromethane. The crude product was obtained in quantitative yield as off-white powder. The yields were determined by GC-MS.

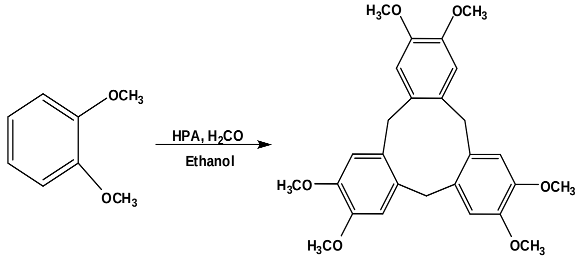
m.p.: 225–228 ^oC; IR (ν, cm^{-1}): 1518, 1269, 1094; ^1H NMR (δ, ppm; $CDCl_3$),: 6.7 (s, 6 H, ArH), 4.9, 3.5 (dd, 6 H, CH_2), 3.7 (s, 18 H, CH_3).

Reusability of the catalyst

The catalyst was recovered after the reaction and was reused in these reactions. Several subsequent recoveries had only slightly decreased the catalytic activity, pointing to the stability and retention capability of this polyanion. At the end of the reaction, the catalyst was filtered, washed with diethyl ether, dried at 130 ^oC for 1 h, and reused in another run. The recycled catalyst was used in three consecutive runs without appreciable loss in catalytic activity.

3. RESULTS AND DISCUSSION

Synthesis of cyclotriveratrylene (CV) with formaldehyde (37%) in different solvents was explored using vanadium (V)-substituted polyoxomolybdates, $H_{3+x}PMo_{12-x}V_xO_{40}$ (x = 1–3) and Wells-Dawson, $H_6[P_2W_{18}O_{62}]$, (Scheme 1). Heteropolyacids with x = 1–3 catalyze the synthesis of cyclotriveratrylene leading to a major product depending on the solvent of the reaction. In a systematic study in the presence of all catalysts, the reaction was examined with different solvents and then in the solvent of choice. In the latter, the effects of the reaction time were studied. Recrystallization often results in the formation of a fine white solid.

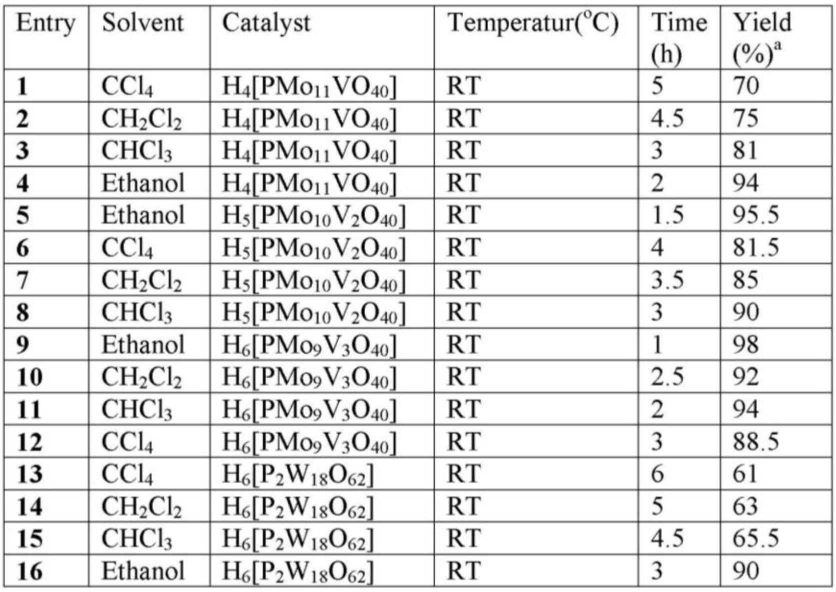


Scheme 1. Synthesis of cyclotriveratrylene

Effect of the solvent

The synthesis of cyclotriveratrylene (CV) at reflux temperature was carried out using various common solvents such as carbon tetrachloride, dichloromethane, and chloroform. The results are shown in Table 1. With all catalysts, the highest yield of cyclotriveratrylene and the shortest time required for completion of the reaction was obtained with ethanol as solvent. The highest yield of 98% for cyclotriveratrylene in ethanol indicates the influence of the solvent on the reaction yield (Table 1).

Table 1. Catalytic synthesis of cyclotriveratrylene with formaldehyde (37%) in the presence of different solvents and catalysts



Entry	Solvent	Catalyst	Temperatur(°C)	Time (h)	Yield (%)[a]
1	CCl_4	$H_4[PMo_{11}VO_{40}]$	RT	5	70
2	CH_2Cl_2	$H_4[PMo_{11}VO_{40}]$	RT	4.5	75
3	$CHCl_3$	$H_4[PMo_{11}VO_{40}]$	RT	3	81
4	Ethanol	$H_4[PMo_{11}VO_{40}]$	RT	2	94
5	Ethanol	$H_5[PMo_{10}V_2O_{40}]$	RT	1.5	95.5
6	CCl_4	$H_5[PMo_{10}V_2O_{40}]$	RT	4	81.5
7	CH_2Cl_2	$H_5[PMo_{10}V_2O_{40}]$	RT	3.5	85
8	$CHCl_3$	$H_5[PMo_{10}V_2O_{40}]$	RT	3	90
9	Ethanol	$H_6[PMo_9V_3O_{40}]$	RT	1	98
10	CH_2Cl_2	$H_6[PMo_9V_3O_{40}]$	RT	2.5	92
11	$CHCl_3$	$H_6[PMo_9V_3O_{40}]$	RT	2	94
12	CCl_4	$H_6[PMo_9V_3O_{40}]$	RT	3	88.5
13	CCl_4	$H_6[P_2W_{18}O_{62}]$	RT	6	61
14	CH_2Cl_2	$H_6[P_2W_{18}O_{62}]$	RT	5	63
15	$CHCl_3$	$H_6[P_2W_{18}O_{62}]$	RT	4.5	65.5
16	Ethanol	$H_6[P_2W_{18}O_{62}]$	RT	3	90

Effect of the catalyst

The hetropolyacids of the series $H_{3+x}PMo_{12-x}V_xO_{40}$ (x = 1–3) showed good to excellent catalytic behaviour in the synthesis of cyclotriveratrylene in ethanol, carbon tetrachloride, dichloromethane and chloroform. The results are shown in Table 1. $H_6[PMo_9V_3O_{40}]$ catalyzes efficiently the formation of cyclotriveratrylene giving a total yield of 98% in ethanol. The yield with this catalyst was found to decrease from 98% to 88.5% when the solvent was changed from ethanol to carbon tetrachloride (Table 1, entries 9-12). In addition, $H_4[PMo_{11}VO_{40}]$ and $H_5[PMo_{10}V_2O_{40}]$ gave a total yield of 70% and 81.5% in carbon tetrachloride, respectively (entries 1 and 6). In other words, the activities of the $H_{3+x}PMo_{12-x}V_xO_{40}$ (x = 1–3) catalysts in the synthesis of cyclotriveratrylene in carbon tetrachloride, were found to decrease in the following order: $H_6[PMo_9V_3O_{40}]$>$H_5[PMo_{10}V_2O_{40}]$ >$H_4[PMo_{11}VO_{40}]$ >$H_6[P_2W_{18}O_{62}]$. Many properties of the heteropoly compounds in solution depend on the reaction time, the solvent type, the structure of the catalyst, the pH value of the solution, and other factors. The Keggin anion has an assembly of 12 corner-shared octahedral MoO_6 from trimetallic groups $[Mo_3O_{13}]$ around a heteroatom tetrahedron PO_4 [14]. The introduction of vanadium (V) into the Keggin framework of $[PMo_{12}O_{40}]^{3-}$ is beneficial for catalytic reactions [15]. Usually positional isomers coexist when two or more vanadium atoms are incorporated into the Keggin structure (for example 5 and 13 isomers for x=2 and 3, respectively) [16]. Studies on these isomers in catalytic reactions indicated that different isomers displayed different reactivities [17-19]. The efficiency of the catalysts is related to the mol percentage of metal atoms. The Wells–Dawson HPA has 18 tungsten atoms, so the relative efficiency of the systems is: Keggin>Wells–Dawson. Considering the mass catalytic ratio (Mo = 96, V = 51), it is clear that Keggin HPAs are more efficient than others.

4. CONCLUSIONS

Recyclable, eco-friendly, easily prepared and inexpensive vanadium (V)-substituted poly-oxomolybdates were used as catalysts for the synthesis of cyclotriveratrylene. Important features of this protocol are: simplicity and versatility of process engineering and environmentally safe disposal. The catalyst can be easily recovered, regenerated and reused without appreciable loss of structure and activity, thus providing economic and environmentally friendly method for preparation of cyclotriveratrylene.

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СИНТЕЗА НА ЦИКЛОВЕРАТРИЛЕН С ПОМОЩТА НА ХЕТЕРО-ПОЛИКИСЕЛИНИ ($H_{3+X}PMO_{12-X}V_XO_{40}$) КАТО РЕЦИКЛИРУЕМИ ХЕТЕРОГЕННИ КАТАЛИЗАТОРИ

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(Резюме)

Изследвана е синтезата на цикловератрилен (CV) от формалдехид (37%) в присиствие на хетеро-поликиселини ($H_{3+x}PMo_{12-x}V_xO_{40}$, x = 1–3) в различни разтворители. Изучен е ефектът на катализатора и на разтворителя върху хода на реакцията. Във всички случаи хетеро-поликиселините с x = 3 дават най-висок добив при етанол като разтворител.

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Copper nitrate catalyzed synthesis and biological activity evaluation of some naphtho[2,3-d]imidazoles

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A series of naphtho[2,3-d]imidazoles **(2a-l)** were synthesized in good yields by the reaction of 2,3-diaminonaphthalene with aromatic aldehydes in the presence of catalytic amounts of copper nitrate, $Cu(NO_3)_2.6H_2O$. Some features of this practical protocol are: use of catalyst, short reaction times and easy workup. The antibacterial activity of these naphtho[2,3-d]imidazoles was tested against *Staphylococcus aureus* (mm) and *Escherichia coli* (mm) bacterial strains.

Key words: aromatic aldehydes, imidazole, 2,3-diaminonaphthalene, catalyst.

1. INTRODUCTION

Naphtho[2,3-d]imidazoles have received substantial attention because of their broad application for the preparation of biologically active molecules and for the Chichibabin reaction [1,2].

Several methods have been reported for the preparation of benzimidazoles. The general procedure for the synthesis of simple benzimidazoles usually involves the reaction of carboxylic acids or their derivatives (nitriles, orthoesters, imidates) with *o*-phenylenediamines, and the reaction of *o*-phenylenediamines with aldehydes in the presence of an acid catalyst under various reaction conditions [3-11]. In each case, the cyclization involves coupling at the *o*-phenylene nitrogen. However, due to the low basicity of 2,3-diaminonaphthalene compared to 1,2-phenylenediamine, synthesis of simple naphtho[2,3-d]imidazoles is difficult under similar conditions and most of the references in the literature report the synthesis of substituted naphtho[2,3-d]imidazoles under different conditions [12,13]. Because of the increasing importance of naphtho[2,3-d]imidazoles, a simple procedure for the synthesis of these heterocyclic compounds would be of great value.

In view of these points and as a part of our research work on the development of new methods for the synthesis of condensed imidazoles [4,6,11] we are going to report a clean and practical synthetic method for the preparation of naphtho[2,3-d]imidazoles using $Cu(NO_3)_2.6H_2O$ as an efficient catalyst.

2. EXPERIMENTAL

Reagents and methods

All used chemicals were purchased from Merck or Fluka Company. Melting points were determined on an Electrothermal digital melting point apparatus. The IR spectra were recorded on a Unicom Galaxy series FT-IR 5000 spectrometer. NMR spectra were recorded on a Bruker (300 MHz) spectrometer. Chemical shifts (ppm) were referred to the internal standard tetramethylsilane (TMS). Microanalyses were performed by the Elemental Analyzer (Elemental, Vario EL III). The microanalyses results agreed with the calculated values. Reactions were monitored by thin layer chromatography using silica gel F_{254} aluminum sheets (ethyl acetate/ n-nexane, 3:1). The microbial strains were identified and obtained from the Pasteur Institute of Iran: *Staphylococcus aureus* (RTCC, 1885), and *Escherichia Coli* (ATCC, 35922).

General procedure for the preparation of naphtho[2,3-d]imidazoles

To a solution of 2,3-diaminonapthalene (1 mmol) and the corresponding aromatic aldehyde (1 mmol) in ethanol (15-20 mL) $Cu(NO_3)_2.6H_2O$ (15 mol%) was added. The reaction mixture was stirred at 50°C for desired time (Table 1). The reaction progress was monitored by TLC. After completion of the reaction, water (20-25 mL) was added. The precipitated crystals were filtered, washed with cold water and air dried.

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Table 1. Reaction of 2,3-diaminonaphthalene with aromatic aldehydes catalyzed by 15 mol% $Cu(NO_3)_2.6H_2O$ at 50 °C

Product (**2**)	Ar	Time (min)	Yield (%)	M.P. (°C)
a	$2\text{-}NO_2C_6H_4$	20	68	270 (dec)
b	$4\text{-}NO_2C_6H_4$	40	78	180 (dec)
c	$4\text{-}CH_3C_6H_4$	50	65	241 (dec)
d	$3\text{-}BrC_6H_4$	30	58	240-242
e	$4\text{-}BrC_6H_4$	35	67	270 (dec)
f	$2\text{-}ClC_6H_4$	40	78	274-278
g	$3\text{-}ClC_6H_4$	35	60	212 (dec)
h	$4\text{-}ClC_6H_4$	38	89	220 (dec)
i	$4\text{-}CH_3OC_6H_4$	55	60	320 (dec)
j	C_6H_5	45	40	260 (dec)
k	$2\text{-}Cl\text{-}6\text{-}F\text{-}C_6H_3$	30	67	267-268
l	$2\text{-}OH\text{-}5\text{-}Br\ C_6H_3$	40	63	312-314

Table 2. Zone inhabitation of naphtho[2,3-d]imidazoles **(2a-l)**

Entry	Compound	*Staphylococcus aureus* (mm)	*Escherichia coli* (mm)
1	2a	9 ± 0.1	18 ± 0.2
2	2b	36 ± 0.1	—
3	2c	6 ± 0.2	—
4	2d	30 ± 0.1	—
5	2e	9 ± 0.1	—
6	2f	24 ± 0.2	—
7	2g	30 ± 0.1	—
8	2h	27 ± 0.2	—
9	2i	39 ± 0.2	—
10	2j	42 ± 0.2	—
11	2k	27 ± 0.1	—
12	2l	15 ± 0.2	—
13	DMSO	—	—
	Standard drugs	Penicillin 33 mm	Gentamicin 18 mm

— indicates resistance of bacteria to compounds

Antibacterial study

The agar disk diffusion technique was used for evaluation of the biological activity. In each test 5 mg of the synthesized naphtho[2,3-d]imidazole **(2a-l)** were dissolved in 250 μl of DMSO and 100 μl of the test compounds of known concentration were introduced onto the disks (0.7 cm) and then allowed to dry. The disk was completely saturated with the test compounds. Then the disk was introduced onto the upper layer of the medium with the bacteria. 100 μl of solvent (DMSO) were added to the blank disk, which was used as a negative control on each plate along with the standard drugs. The plates were incubated overnight at 37°C. The inhibition zones were measured and compared with the controls. The results are given in Table 2.

2-(2-Nitrophenyl)-1-*H*-naphtho[2,3-*d*]imidazole (2a)

IR (KBr): ν= 3055 ($CH_{aromatic}$), 1525, 1477 cm^{-1}. ^{1}HNMR (300 MHz, DMSO): δ= 7.47-8.24 (m, 10H, $CH_{aromatic}$), 13.51 (bs, 1H, NH). Anal. calcd. for $C_{17}H_{11}N_3O_2$: C, 70.58; H, 3.83; N, 14.53%. Found: C, 70.68; H, 3.56.; N, 14.45%.

2-(4-Nitrophenyl)-1-*H*-naphtho[2,3-*d*]imidazole (2b)

IR (KBr): ν= 3387 (NH), 3079 ($CH_{aromatic}$), 1606 (C=N), 1518 cm^{-1}. ^{1}HNMR (300 MHz, DMSO): δ= 8.05-8.55 (m, 10H, $CH_{aromatic}$), 13.34 (bs, 1H, NH). Anal. calcd. for $C_{17}H_{11}N_2O_3$: C, 70.56; H, 3.83; N, 14.53%. Found: C, 70.44; H, 3.98; N, 14.61%.

2-*p*-Tolyl-1-*H*-naphtho[2,3-*d*]imidazole (2c)

IR (KBr): ν= 3448 (NH), 3049 ($CH_{aromatic}$), 1612 (C=N), 1491 cm^{-1}. ^{1}HNMR (300 MHz, DMSO): δ=

7.39-8.20 (m, 10H, $CH_{aromatic}$), 13.10 (bs, 1H, NH). Anal. calcd. for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.84%. Found: C, 83.49; H, 5.59; N, 10.98%.

2-(3-Bromophenyl)-1-*H*-naphtho[2,3-*d*]imidazole (2d)

IR (KBr): ν= 3049 ($CH_{aromatic}$), 1541 (C=N), 1471 cm^{-1}. ^{1}HNMR (300 MHz, DMSO): δ= 7.30-8.53 (m, 10H, $CH_{aromatic}$), 13.40 (bs, 1H, NH). Anal. calcd. for $C_{17}H_{11}BrN_2$: C, 63.18; H, 3.43; N, 8.67%. Found: C, 62.91; H, 3.25; N, 8.96%.

2-(4-Bromophenyl)-1-*H*-naphtho[2,3-*d*]imidazole (2e)

IR (KBr): ν= 3049 ($CH_{aromatic}$), 1599 (C=N), 1483 cm^{-1}. ^{1}HNMR (300 MHz, DMSO): δ= 7.40-8.23 (m, 10H, $CH_{aromatic}$), 13.20 (bs, 1H, NH). Anal. calcd. for $C_{17}H_{11}BrN_2$: C, 63.18; H, 3.43; N, 8.67%. Found: C, 63.01; H, 3.56; N, 8.77%.

2-(2-Chlorophenyl)-1-*H*-naphtho[2,3-*d*]imidazole (2f)

IR (KBr): ν= 3047 ($CH_{aromatic}$), 1473 cm^{-1}. ^{1}HNMR (300 MHz, DMSO): δ= 7.49-8.21 (m, 10H, $CH_{aromatic}$), 13.70 (bs, 1H, NH). Anal. calcd. for $C_{17}H_{11}ClN_2$: C, 73.25; H, 3.98; N, 10.05%. Found: C, 73.32; H, 4.10; N, 10.21%.

2-(3-Chlorophenyl)-1-*H*-naphtho[2,3-*d*]imidazole (2g)

IR (KBr): ν= 3474 (NH), 3049 ($CH_{aromatic}$), 1543 (C=N), 1473 cm^{-1}. ^{1}HNMR (300 MHz, DMSO): δ= 7.45-8.41 (m, 10H, $CH_{aromatic}$), 13.40 (bs, 1H, NH). Anal. calcd. for $C_{17}H_{11}ClN_2$: C, 73.25; H, 3.98; N, 10.05%. Found: C, 73.41; H, 3.84; N, 10.12%.

2-(4-Chlorophenyl)-1-*H*-naphtho[2,3-*d*]imidazole (2h)

IR (KBr): ν= 3036 ($CH_{aromatic}$), 1618 (C=N), 1483 cm^{-1}. ^{1}HNMR (300 MHz, DMSO): δ= 7.40-8.32 (m, 10H, $CH_{aromatic}$), 12.90 (bs, 1H, NH). Anal. calcd. for $C_{17}H_{11}ClN_2$: C, 73.25; H, 3.98; N, 10.05%. Found: C, 73.10; H, 4.23; N, 9.92%.

2-(4-Methoxyphenyl)-1-*H*-naphtho[2,3-*d*]imidazole (2i)

IR (KBr): ν= 3053 ($CH_{aromatic}$), 2939 ($CH_{aliphatic}$), 1608 (C=N), 1499, 1450 cm^{-1}. ^{1}HNMR (300 MHz, DMSO): δ= 3.86 (s, 3H CH_3), 7.16-8.29 (m, 10H, $CH_{aromatic}$), 13.00 (bs, 1H, NH). Anal. calcd. for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21%. Found: C, 78.58; H, 5.21, N, 10.29%.

2-Phenyl-1-*H*-naphtho[2,3-*d*]imidazole (2j)

IR (KBr): ν= 3300 (NH), 3047 ($CH_{aromatic}$), 1545 (C=N), 1471 cm^{-1}. ^{1}HNMR (300 MHz, DMSO): δ= 7.46-8.35 (m, 11H, $CH_{aromatic}$), 13.40 (bs, 1H, NH). Anal. calcd. for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.47%. Found: C, 83.69; H, 5.09 N, 11.69%.

2-(2-Chloro-6-fluorophenyl)-1-*H*-naphtho[2,3-*d*]imidazole (2k)

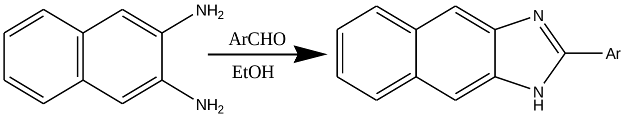
IR (KBr): ν= 3148 (NH), 3051 ($CH_{aromatic}$) 1525, 1475 cm^{-1}. ^{1}HNMR (300 MHz, DMSO): δ= 7.55-8.28 (m, 9H, $CH_{aromatic}$) 13.80 (bs, 1H, NH). Anal. calcd. for $C_{17}H_{10}$ $ClFN_2$: C, 68.81; H, 3.40; N, 9.44%. Found: C, 68.56; H, 3.53, N, 9.62%.

4-Bromo-2-(1H-naphtho[2,3-d]imidazol-2-yl)phenol (2l)

IR (KBr): ν= 3284 (NH), 3045 ($CH_{aromatic}$), 1606 (C=N), 1510, 1456 cm^{-1}. ^{1}HNMR (300 MHz, DMSO): δ= 6.81-8.41 (m, 9H, $CH_{aromatic}$), 13.43 (bs, 1H, NH). Anal. calcd. for $C_{17}H_{11}BrN_2O$: C, 60.20; H, 3.72; N, 8.26%. Found: C, 60.28; H, 3.55; N, 8.39%.

3. RESULTS AND DISCUSSION

During our recent research directed toward the development of simple and practical procedures for the synthesis of some condensed imidazoles,[4,6,11] we have succeeded in preparing the naphtho[2,3-d]imidazoles **(2a-l)**, by condensation reaction of the appropriate aromatic aldehyde with 2,3-diaminonaphthalene in the presence of $Cu(NO_3)_2.6H_2O$ in good yields. No byproducts were observed in this reaction (Scheme 1).



1 **Scheme 1** 2

For the primary study and optimization of the reaction conditions, we investigated the reaction of equimolar amounts of *p*-nitrobenzaldehyde and 2,3-diaminonaphthalene in the presence of copper nitrate. After many examinations, we found that the best conditions for this reaction were: 15 mol% of catalyst at 50 °C using ethanol as a solvent. The results are presented in Table 3.

To explore the validity of this procedure, we extended our study using 15 mol% copper nitrate as a catalyst at 50 °C with different aromatic aldehydes to prepare a series of naphtho[2,3-d]imidazoles.

Table 3. Optimization of the reaction conditions of *p*-nitrobenzaldehyde with 2,3-diaminonaphthalene in the presence of copper nitrate

Entry	Solvent	$Cu(NO_3)_2.6H_2O$ (mol%)	Temperature (°C)	Time (min)	Yield (%)[a]
1	CH_3CN	15	50	40	74
2	DMF	15	50	40	62
3	DMSO	15	50	40	58
4	CH_3OH	15	50	40	67
5	C_2H_5OH	15	50	40	78
6	C_2H_5OH	5	50	70	65
7	C_2H_5OH	10	50	55	70
8	C_2H_5OH	20	50	40	77
9	C_2H_5OH	-	Reflux	45	<5

[a] Isolated yields

The results are summarized in Table 1. Various aromatic aldehydes bearing electron-withdrawing groups (such as nitro, halide) and electron-releasing groups (such as methyl and methoxy) show almost equal ability of product formation in reasonable yields. Aliphatic aldehydes such as formaldehyde or acetaldehyde were also examined under the same conditions, but the corresponding products were isolated in low yields (< 5%). The procedure is simple and more convenient than other reported methods in the literature, which were carried out under forced reaction conditions or using special starting materials [12,13].

The structure of the synthesized compounds was confirmed by IR and NMR spectral data. The chemical shifts in the ^1H NMR spectra of the compounds were related to the substituted Ar group. The Ar group with an electron donor substituent (e. g. CH_3, OCH_3) produces a lower shift. The ^1H NMR spectra of (**2a-h)** display a multiplet at 7.30-8.55 ppm and a broad singlet at 12.90-13.70 ppm attributed to the resonance of 10 aromatic protons and the NH group, respectively. The ^1H NMR spectra of (**2k-l)** are very similar to those of (**2a-h)** and have a multiplet with integration of 9 due to the resonance of 9 aromatic protons. The broad singlet of the NH group appeared at 13.40-13.80 ppm. The appearance of one NH proton signal in the ^1H NMR spectra of **2a-l** in high field compared to the spectra of the starting materials is a good support of the observed reactions**.** This broad signal for compounds **2a** and **2f** appeared at a lower shift compared to that of other compounds containing an electron withdrawing group, probably due to the interaction between the NH group and the Cl or NO_2 group at the ortho position. The IR spectra of the compounds revealed the presence of absorption bands in the range from 3284 to 3448 cm^{-1} for the NH group, from 3036 to 3079 cm^{-1} for C-H and from 1450 to 1518 cm^{-1} for C=C aromatic stretching vibrations.

The antibacterial study (Table 2) shows that all naphtho[2,3-d]imidazoles **(2a-l)** exert antibacterial activity against *Staphylococcus aureus* as gram positive and only compound **2a** has antibacterial activity against *Escherichia coli* as gram negative bacteria. The maximum and minimum antibacterial activities against *Staphylococcus aureus* were related to compounds **2j** and **2c**, respectively**.** The biological activity did not give a reasonable relationship with the electronic effects of the substituents and was comparable with that of imidazole or benzimidazole derivatives [14,15].

6. CONCLUSIONS

In summary, we have developed a simple and efficient methodology for the synthesis of various biologically active naphtho[2,3-d]imidazoles in the presence of copper nitrate as a catalyst without using drastic conditions. In addition to the efficiency and simplicity provided by this procedure, ease of workup and short reaction time make the method advantageous**.** Further investigations with appropriate structural modifications of title compounds may improve their biological activities.

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СИНТЕЗА НА НЯКОИ НАФТО[2,3-d] ИМИДАЗОЛИ ПРИ КАТАЛИЗАТОР ОТ МЕДЕН НИТРАТ И ОЦЕНЯВАНЕ НА БИОЛОГИЧНАТА ИМ АКТИВНОСТ

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(Резюме)

Синтезирани са група от нафто[2,3-d] имидазоли с добър добив чрез реакцията между 2,3-диаминонафтален и ароматни алдехиди в присъствие на $Cu(NO_3)_2.6H_2O$ като катализатор. Следствия от протокола на изследванията е кратки времена на реакцията в присъствие на катализатор и лесно изолиране на продукта. Изследвана е антибактериалната активност върху *Staphylococcus aureus* и *Escherichia coli*.

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Computing Padmakar-Ivan index of four classes of dendrimers

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Suppose G is a connected graph, $e = uv$ is an edge of G, $n_u(e)$ is the number of edges lying closer to u than v *and* $n_v(e)$ is defined analogously. The Padmakar–Ivan index of G is a graph invariant defined as the summation of $[n_u + n_v]$ over all edges of G. General formulas are given for the Padmakar–Ivan index of dendrimers.

Key words: Dendrimer, PI index.

1. INTRODUCTION

A topological index or graph invariant for a molecular graph G is a number reflecting certain structural features of molecules that are obtained from the molecular graph. Here, a molecular graph is a labeled graph whose vertices correspond to the atoms and the edges correspond to chemical bonds**.** Suppose x and y are vertices of G. Then $d(x,y)$ denotes the length of the shortest path connecting x and y. A topological index defined by the distance function $d(–,–)$ is called a distance–based topological index. One of the oldest topological index is the Wiener index, introduced by Harold Wiener [1]. It is defined as the summation of distances between all pairs of vertices in G.

Another molecular graph invariant, referred to as the PI index, and denoted by *PI* is put forward by Padmakar V. Khadikar based on distances on edges of the molecular graph under consideration. The PI index is the first topological index considering the distance between edges as those of vertices. It is defined as $PI(G) = \Sigma[n_u(e) + n_v(e)]$, where $n_u(e)$ is the number of edges of G lying closer to u than v, $n_v(e)$ is the number of edges of G lying closer to v than u and summation goes over all edges of G[2].

Many topological indices have been defined and several of them have found applications as means to model physical, chemical, pharmaceutical and other properties of molecules. Khadikar and his team [3–9] investigated the behavior of some physico–chemical quantities under PI index. Diudea and his co–workers [10–17] considered the problem of computing distance–based topological indices of nanostructured materials. After proposing the PI index, one of us (ARA) [18–28] computed the PI index of some classes of nanotubes, nanotori, nanocones and also of dendrimers. The motivation of this study is taken from the leading works of Diudea and his team on the problem of computing Wiener index of nanostructured materials. For the mathematical properties of the PI index we encourage the interested readers to consult papers [29–39] and references therein for background material as well as basic computational techniques.

3. MAIN RESULTS AND DISCUSSION

The dendrimer is part of a new group of macromolecules that appear to be photon funnels just like artificial antennas. This is built by a starting atom, such as nitrogen, to which carbon and other elements are added by a repeating series of chemical reactions that produce a spherical branching structure. In a divergent synthesis of a dendrimer, one starts from the core and grows out to the periphery. In each repeated step, a number of monomers are added to the core or actual structure in a radial manner, resulting in quasi concentric shells, called generations. In a convergent synthesis, the periphery is first built up and next the branches (called dendrons) are connected to the core. The stepwise growth of a dendrimer follows a mathematical progression and its size is in the nanometer scale.

In this section, we consider four classes of dendrimers are shown in Figures 1–4. These dendrimers are denoted by $D_1[k]$, $D_2[k]$, $D_3[k]$ and $D_4[k]$, where $k \geq 1$ is a positive integer denoting the stepwise growth of the dendrimers. The set of edges of these dendrimers is denoted by $E(D_i[k])$, where i = 1, 2, 3, 4. To compute the PI index of these dendrimers we apply the following theorem.

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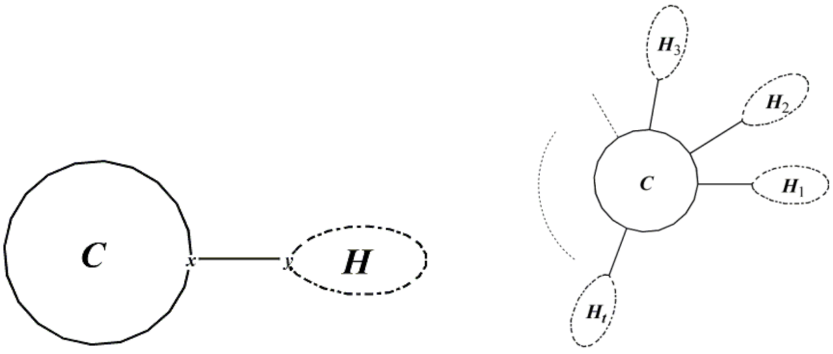

(a) (b)

Fig. 1. a) The Graph F; b) The Graph J.

Theorem. Let G be a graph constructed from cycles of even lengths C_1, C_2, … ,C_k joined by paths P_1, P_2, … ,P_s such that for every $i \neq j$, C_i and C_j do not have a common vertex. Then the PI index of G is computed as follows:

$$PI(G)=\left(\sum_{i=1}^{s}|V(P_i)|-s\right)\left(\sum_{i=1}^{k}|V(C_i)|+\sum_{i=1}^{s}|V(P_i)|-s-1\right)$$
$$+\left(\sum_{i=1}^{k}|V(C_i)|\right)\left(\sum_{i=1}^{k}|V(C_i)|+\sum_{i=1}^{s}|V(P_i)|-s-2\right)$$

Proof. Suppose G is a graph with exactly m edges. If $e = uv$ is a cut edge of G, then $n_u(e) + n_v(e) = m - 1$. On the other hand, suppose H is an arbitrary graph, C is an even cycle, $x \in V(H)$, $y \in V(C)$ and F is a graph constructed from H and C joined by an edge xy, Figure 1(a). Then for each edge $f = uv \in E(C)$, $n_u(e) + n_v(e) = |V(C)| + |E(H)| - 1$. Similarly, if H_1, H_2, …, H_t are arbitrary graphs, C is an even cycle, x_1, x_2, …, x_t are different vertices of C, $y_i \in H_i$, $1 \leq i \leq t$, and J is the graph such that $V(J) = V(C) \cup V(H_1) \cup V(H_2) \cup \ldots \cup V(H_t)$ and $E(J) = E(C) \cup E(H_1) \cup E(H_2) \cup \ldots \cup E(H_t) \cup \{x_1y_1, x_2y_2, \ldots, x_ty_t\}$ then $n_u(e) + n_v(e) = |V(C)| + |E(H_1)| + |E(H_2)| + \ldots + |E(H_t)| - 1$, Figure 1(b). Therefore,

$$PI(G)=\left(\sum_{i=1}^{s}|V(P_i)|-s\right)\left(\sum_{i=1}^{k}|V(C_i)|+\sum_{i=1}^{s}|V(P_i)|-s-1\right)$$
$$+\left(\sum_{i=1}^{k}|V(C_i)|\right)\left(\sum_{i=1}^{k}|V(C_i)|+\sum_{i=1}^{s}|V(P_i)|-s-2\right)$$

Corollary. Suppose G is a connected graph constructed from h hexagons such that hexagons do not have a common edge. Then $PI(G) = |E(G)|^2 - |E(G)| - 6h$.

In what follows, four classes of nanostars with above conditions are presented. In each case the PI index of the dendrimer molecule is computed by our main theorem.

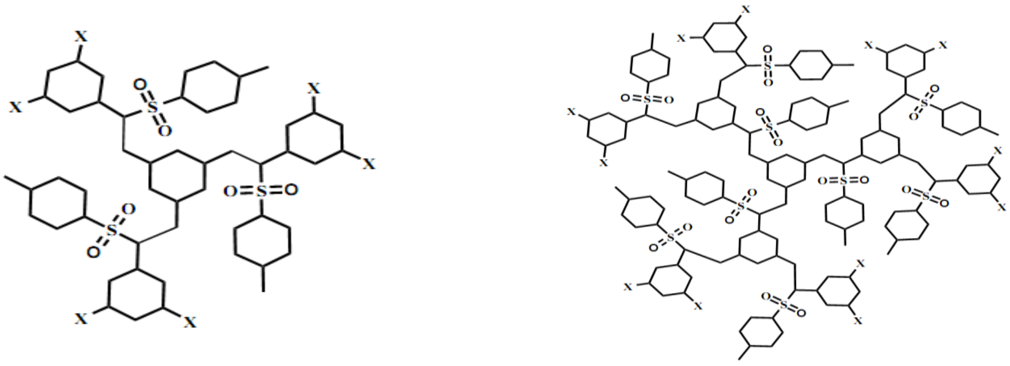

Fig. 2. The bulky dendrimers $D_1[1]$ and $D_1[2]$.

$|E(D_1[k])| = 63 \times 2^k - 54$; $h(D_1[k]) = 6 \times 2^k - 5$; $\mathrm{PI}(D_1[k]) = 3969 \times 4^k - 6903 \times 2^k + 3000$.

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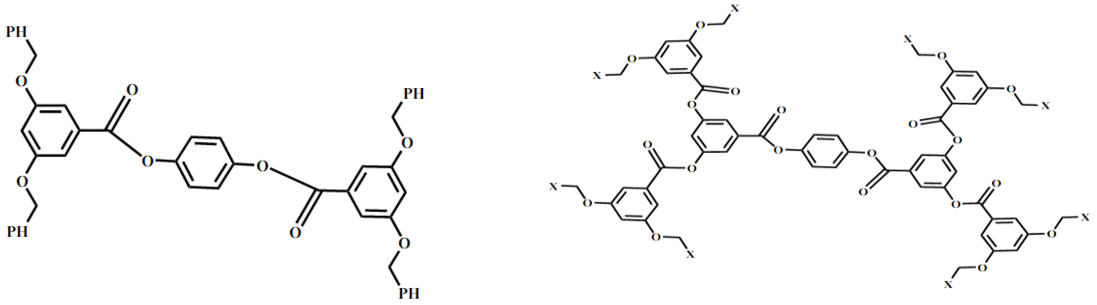

Fig. 3. The Dendrimers $D_2[1]$ and $D_2[2]$.

$|E(DNS_2[k])| = 26 \times 2^k - 14$, $h(DNS_2[k]) = 2^{k+1} - 1$; $\mathrm{PI}(DNS_2[k]) = 676 \times 4^k - 766 \times 2^k + 216$.

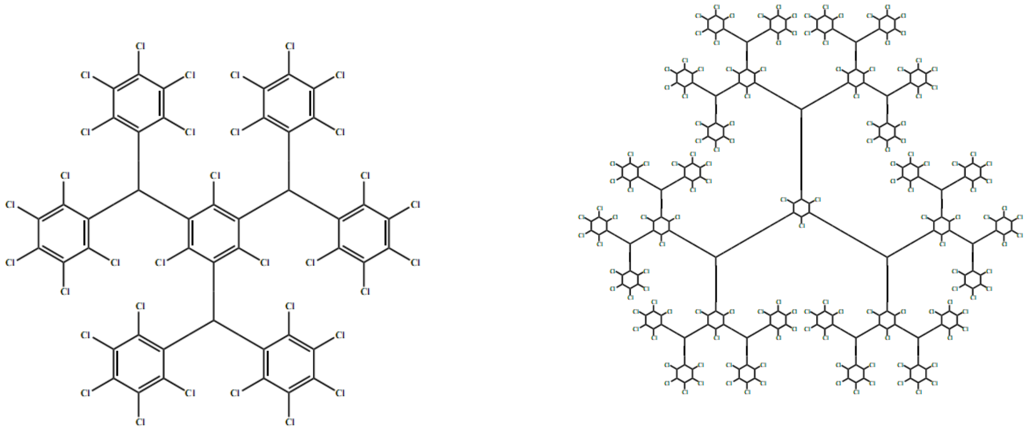

Fig. 4. The dendrimers $D_3[1]$ and $D_3[2]$.

$|E(DNS_3[k])| = 72 \times 2^k - 60$, $h(DNS_3[k]) = 6 \times 2^k - 5$, $\mathrm{PI}(DNS_3[k]) = 5184 \times 4^k - 8748 \times 2^k + 3690$.

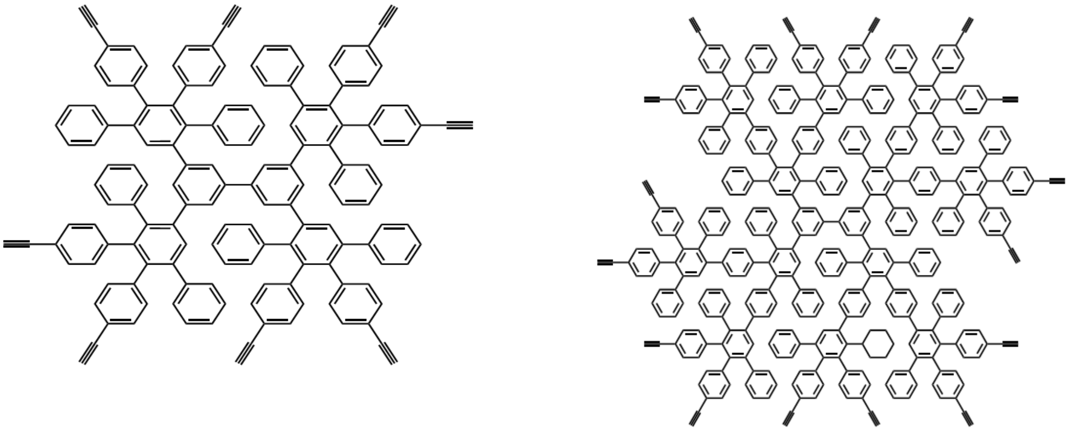

Fig. 5. The dendrimers $D_4[1]$ and $D_4[2]$.

$|E(DNS_4[k])| = 144 \times 2^k - 127$, $h(DNS_4[k]) = 20 \times 2^k - 18$, $\mathrm{PI}(DNS_4[k]) = 20736 \times 4^k - 36840 \times 2^k + 16364$

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ПРЕСМЯТАНЕ НА ИНДЕКСА PADMAKAR-IVAN ЗА ЧЕТИРИ КЛАСА ДЕНДРИМЕРИ

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(Резюме)

Приема се, че *G* е свързан граф, $e = uv$ е ръба на *G*, $n_u(e)$ е броя на ръбовете, разположени по-близо до *u* отколкото *v*, а $n_v(e)$ се дефинира аналогично. Индексът Padmakar–Ivan на G е инвариант на графа, дефиниран като сумиране на $[n_u + n_v]$ по всички ръбове на *G*. Получении са общи формули на индевксите Padmakar–Ivan за дендримери.

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Binary mixture sorption of basic dyes onto wheat straw

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Simultaneous adsorption of Basic Blue 3 (BB 3) and Basic Red 18 (BR 18) onto wheat straw (WS) from a binary system was studied and compared with a single dye system in a batch mode. The single-component Langmuir and Freundlich isotherm models were applied to the adsorption equilibrium data for single-component and binary-component systems. The equilibrium adsorption for the binary system was also analyzed by using multi-component modified Langmuir and Sheindorf–Rebuhn–Sheintuch (SRS) models. Equilibrium data of BB 3 in single and binary systems fitted more adequately to the Freundlich adsorption isotherm. For BR 18, the Langmuir model was the best one for fitting the adsorption equilibrium in single and binary systems. The pseudo-first order and pseudo-second order models were employed to fit the experimental data for the adsorption kinetics of BB 3 and BR 18 on WS from single- and binary-component systems. The pseudo-second-order model provided better correlation for the adsorption process in single- and binary-component systems. Adsorption results from the binary system indicated the competitive adsorption between dyes. The maximum adsorption capacities of WS for BB 3 and BR 18 dyes in single solution system were found as 90.91 mg g^{-1} and 142.86 mg g^{-1}, respectively, while in binary mixture they decreased to 76.92 mg g^{-1} and 111.11 mg g^{-1}, respectively, as a result of their antagonistic behavior.

Key words: adsorption, basic dyes, binary mixture, wheat straw, equilibrium, kinetics.

1. INTRODUCTION

Agriculture is an important sector in the world economy. However, wastes are generated as part of the cycle of harvest, preparation of crops for use and preparation of land for a subsequent crop. Although some of the crop residues are reutilized, the inadequate management of the remaining residues has been identified as a source of significant environmental threats and has contributed to serious disposal problems.

Agricultural wastes, particularly those containing cellulose, show potential sorption capacity for various pollutants. The basic components of the agricultural waste materials include cellulose, hemicellulose, lignin, lipids, proteins, simple sugars, hydrocarbons, and starch, containing a variety of functional groups. Agricultural waste materials being economic and eco-friendly due to their unique chemical composition, availability in abundance, renewable nature and low cost are a viable option for water and wastewater remediation.

There has been much interest in the use of agricultural wastes as adsorbents to prevent and remediate environmental contamination by dyes (Ahmad and Kumar [1]; Allen et al. [2]; Amin [3]; Annadurai et al. [4]; Arami et al. [5]; Franca et al. [6]; Hameed et al. [7]; Ho and McKay [8]; Garg et al. [9]; Gupta et al. [10]; Khattri and Singh [11]; Nasuha et al. [12]; Namasivayam and Kavitha [13]; Senturk et al. [14]; Sulak et al. [15].

Much of the work on the adsorption of dyes by various kinds of adsorbents has been focused on the uptake of single dyes. Since industrial effluents may contain several dyes, it is necessary to study the simultaneous sorption of two or more dyes and to quantify the interference of one dye with the sorption of the other. Thus, the studies on the equilibrium and kinetics of dyes adsorption from multi-component systems are very important. The equilibrium adsorption isotherm equations proposed for single-component adsorption have been extended and modified to represent the multi-component adsorption equilibria. However, no information is available in the literature for the simultaneous removal of BB 3 and BR 18 by WS.

The aim of the present paper was: (i) to study the feasibility of using the agricultural waste wheat straw (WS) as an adsorbent for the individual and simultaneous removal of BB 3 and BR 18 dyes from aqueous solutions, (ii) to determine the

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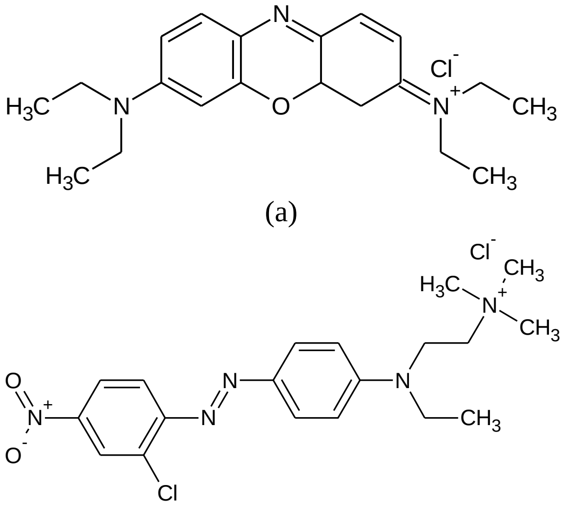
applicability of non-competitive adsorption isotherm models (i.e., Langmuir and Freundlich) for single and binary component systems, (iii) to examine the applicability of the multi-component adsorption isotherm equations to the competitive adsorption equilibria of the dyes in a binary system, and (iv) to establish which kinetic model is most suitable for describing the adsorption of BB 3 and BR 18 on WS.

2 MATERIALS AND METHODS

2.1 Adsorbates

The dyes used as adsorbates were Basic Blue 3 (BB 3) and Basic Red 18 (BR 18), whose chemical structures and general characteristics are depicted in Fig. 1 and Table 1, respectively. Experimental solutions of desired dye concentration were obtained by dissolving accurately weighed quantities in distilled water. For binary mixture studies, desired combinations of BB 3 and BR 18 were prepared by mixing them in the test medium before adding the adsorbent.


(a)

(b)

Fig.1. Chemical structures of (a) BB 3 and (b) BR 18.

2.2 Adsorbent

Wheat straw (WS) used in this study as an adsorbent was harvested from Egyptian fields. WS was used as received without grinding or further treatment. The following chemical characteristics of WS: ash content, cellulose, hemicellulose, lignin and organic extractives were analyzed by TAPPI standard methods (Kouris [16]). The chemical composition of WS presented in Table 2 indicates that WS is composed mainly of cellulose, hemicellulose and lignin, which provides binding sites for the dyes due to the presence of functional groups such as hydroxyl, carboxyl, methoxy, phenolic, etc.

Table 1. General characteristics of BB 3 and BR 18.

Characteristics	Dye	
	BB 3	BR 18
C.I. name	Basic Blue 3	Basic Red 18
Chemical class	Monoxazine	Mono-azo
MW (g mol^{-1})	359.89	390.89
λ_{max} (nm)	610	488

Table 2. Chemical composition of WS

Constituents	%
α-Cellulose	56.2
Hemicellulose	16
Lignin	23
Extractives	3.2
Ash	1.6
Moisture	9.81

2.3 Isotherms of single and binary dye systems

The sorption studies were conducted by the batch technique. A number of stoppered 100 cm^3 Erlenmeyer flasks containing a definite volume (50 cm^3) of solutions with a desired concentration of each component were placed in a shaker at 20 °C.

For isotherm studies, 0.5 g of WS was treated with 50 cm^3 of a solution of a single or binary dye mixture with pre-determined initial dye concentrations (100-700 mg dm^{-3}). The flasks were shaken at 150 rpm for 2 days to ensure that equilibrium was reached. The supernatant solution was separated from the adsorbent by filtration using a syringe 0.2 μm filter unit (Minisart) and then the equilibrium concentrations of the dyes were measured on the spectrophotometer (Spekol 11, Carl Zeiss JENA). For the binary systems, all solutions were prepared with equimolar solutions of the two basic dyes.

The amount of dye adsorbed at the equilibrium (q_e, mg g^{-1}) was calculated according to the expression:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 and C_e are the initial and equilibrium dye concentrations (mg dm^{-3}), respectively, V is the solution volume (dm^3), and m is the mass of WS (g).

2.4 Kinetics of single and binary dye systems

The kinetics of BB 3 and BR 18 adsorption in single and binary adsorption systems onto FS and WS were studied at 20 °C. Experiments were carried out in a standard agitated reactor experimental setup (a 2 dm^3 glass beaker) with a two-blade impeller to stir the dye solution using a Heidolph RZR 2100 motor.

In all adsorption experiments, a pre-selected amount of adsorbent (17 g) was dispersed in 1.7 dm^3 of dye solution of 400 mg dm^{-3} concentration (in single and binary systems) while being constantly stirred by a mechanical stirrer at a speed of 60 rpm. Samples (3-5 cm^3) were withdrawn from the mixture at regular time intervals (from 1 min up to 540 min) using a syringe, immediately filtered using a syringe filter unit (0.2 µm) and analyzed spectrophotometrically.

2.5 Analysis of dye concentration

2.5.1 Analysis in single-component systems. The concentrations of dyes in single-component systems were measured spectrophotometrically prior to (initial concentration) and following the adsorption test (residual concentration) by monitoring the absorbance changes at the wavelengths of maximum absorbance (λ_{max}) of 610 and 488 nm for BB 3 and BR 18, respectively, using standard calibration curves.

2.5.2 Analysis in binary-component systems. Suppose that there is no interaction between the two dyes in binary-component systems, the total absorbance for a mixed dye solution is equal to the sum of the absorbances of each dye (Skoog et al. [17]). This is represented in Eq. (2).

To determine whether the presence of one dye affected the adsorption of another dye, the adsorption capacities of each dye in mixed solutions are computed using Eqs. (3) and (4).

$$A_\lambda = A_{BB} + A_{BR} \tag{2}$$

$$A_{\lambda 1} = \varepsilon_{1BB} l C_{BB} + \varepsilon_{1BR} l C_{BR} \tag{3}$$

$$A_{\lambda 2} = \varepsilon_{2BB} l C_{BB} + \varepsilon_{2BR} l C_{BR} \tag{4}$$

where: A_λ, $A_{\lambda 1}$ and $A_{\lambda 2}$ are the absorbances at wavelengths λ, λ_1 and λ_2, respectively; A_{BB} and A_{BR} are the absorbances of BB 3 and BR 18 at a wavelength λ, respectively; ε_{1BB} and ε_{2BB} are the molar absorptivities of pure BB 3 at wavelengths λ_1 and λ_2, respectively; ε_{1BR} and ε_{2BR} are the molar absorptivities of pure BR 18 at wavelengths λ_1 and λ_2, respectively; C_{BB} and C_{BR} are the concentrations of BB 3 and BR 18 in the mixed solutions; l is the cell width (1 cm); λ_1 (610 nm) is the wavelength of maximum absorbance for BB 3; and λ_2 (488 nm) is the wavelength of maximum absorbance for BR 18. The concentrations C_{BB} and C_{BR} are determined from Eqs. (3) and (4) and then used to obtain the adsorption capacity for each dye in the mixed solutions.

3. ADSORPTION ISOTHERM MODELS

3.1 Single-component models

Isotherm models such as Langmuir [18] and Freundlich [19] were often used to fit the data with a view to understand the adsorption process and to obtain the information needed for scaling up to a larger system.

3.1.1 Langmuir isotherm. The Langmuir model assumes monolayer coverage of adsorbate on an energetically identical homogeneous adsorbent surface. The Langmuir equation and its linearized form may be written as:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{5}$$

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{6}$$

where: q_e is the dye uptake at equilibrium (mg g^{-1}), C_e is the concentration of the solution at equilibrium (mg dm^{-3}), while b (dm^3 g^{-1}) and q_m (mg g^{-1}) are related to the affinity and maximum sorption capacity, respectively.

3.1.2 Freundlich isotherm. The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface.

The Freundlich adsorption isotherm equation and its linear form can be written as follows:

$$q_e = K_F C_e^{1/n} \tag{7}$$

$$\log q_e = \log K_F + {}^1\!/_n \log C_e \tag{8}$$

where: K_F is the Freundlich constant representing the adsorption capacity (dm^3 g^{-1}), and n is the Freundlich exponent depicting the adsorption intensity.

3.2 Multi-component models

When several components are present, there is interference and competition between the different components for the adsorption sites. The isotherm models for a single-component system are thus inapplicable. A multi-component system requires a more complex mathematical isotherm model.

3.2.1 Modified Langmuir model. The modified Langmuir model assumes that all adsorbate ions or molecules compete for energetically identical adsorption sites and it can be written for N components in the mixture as follows (McKay and Al Duri [20]):

$$q_{e,i} = \frac{q_{m,i} b_i C_i}{1 + \sum_{j=1}^{N} b_j C_j} \qquad (9)$$

where: C_i and C_j are the concentrations of the adsorbates *i* and *j* remaining in liquid at equilibrium (mg dm^{-3}), $q_{e,i}$ is the equilibrium uptake of the adsorbate *i* in the multi-component system (mg g^{-1}). b_i and b_j are the Langmuir adsorption constants of the adsorbates (dm^3 g^{-1}) and $q_{m,i}$ is the Langmuir adsorption capacity of the adsorbate *i* (mg g^{-1}) that can be estimated from the fitting of the experimental data by the corresponding individual Langmuir isotherm equation.

For a binary system, the modified Langmuir isotherms can be written as:

$$q_{e,1} = \frac{q_{m,1} b_1 C_1}{1 + b_1 C_1 + b_2 C_2} \qquad (10)$$

$$q_{e,2} = \frac{q_{m,2} b_2 C_2}{1 + b_1 C_1 + b_2 C_2} \qquad (11)$$

where: the subscripts 1, 2 represent the two solutes (BB 3 and BR 18) in the binary system used in the present study.

3.2.2 Sheindorf–Rebuhn–Sheintuch (SRS) model. Sheindorf et al. [21] derived a Freundlich-type multi-component adsorption isotherm, the Sheindorf–Rebuhn–Sheintuch (SRS) equation, to represent experimental data. The assumptions incorporated in the derivation are: (i) each component individually obeys the Freundlich isotherm; and (ii) for each component in a multi-component adsorption system, there exists an exponential distribution of site adsorption energies.

The general SRS equation for a component *i* in an *N*-component system is given as:

$$q_i = K_i C_i \left(\sum a_{ij} C_j \right)^{n_i - 1} \qquad (12)$$

where: q_i is the adsorption capacity of component *i* (mg g^{-1}); C_i and C_j are the concentrations of *i* and *j* in the equilibrium solution (mg dm^{-3}); K_i (dm^3 g^{-1}) and n_i are the Freundlich constants obtained for *i* in a single-component system; and a_{ij} is the competition coefficient for the adsorption of component *i* in the presence of component *j*.

The bicomponent isotherm can be written as:

$$\frac{C_1}{C_2} = \frac{\beta_1}{C_2} - a_{12} \qquad (13)$$

and

$$\frac{C_2}{C_1} = \frac{\beta_2}{C_1} - a_{21} \qquad (14)$$

with

$$\beta_1 = \left(\frac{K_1 C_1}{q_1} \right)^{1/(1-n_1)} \qquad (15)$$

and

$$\beta_2 = \left(\frac{K_2 C_2}{q_2} \right)^{1/(1-n_2)} \qquad (16)$$

If both concentrations vary during the experiment, then plotting C_1/C_2 vs β_1/C_2 yields a straight line of unity slope and the competition coefficient could be determined from the intercept.

4. ADSORPTION KINETICS MODELS

The applicability of the pseudo-first-order kinetics (Lagergen [22]) and the pseudo-second order kinetics (Ho&McKay [23]) was tested for the adsorption kinetics of BB 3 and BR 18 on WS from single- and binary-component systems.

4.1 The Pseudo-first order kinetic model

Assuming pseudo-first order kinetics, the rate of the adsorptive interactions can be evaluated using the simple Lagergren equation:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \qquad (17)$$

Integrating Eq. (17) for the boundary conditions, $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the linear form of the equation becomes:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (18)$$

where: q_e and q_t are the values of amount adsorbed per unit mass at equilibrium and at any time *t*, respectively, and k_1 is the pseudo-first order rate constant (min^{-1}).

The values of k_1 and calculated equilibrium adsorption capacity, q_e, can be obtained from the slope and intercept, respectively, of the linear plot of $\ln(q_e - q_t)$ versus *t*.

4.2 The Pseudo-second order kinetic model

If the rate of adsorption follows a second order mechanism, the pseudo-second order kinetic rate equation is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{19}$$

where: k_2 is the second order rate constant (g mg $^{-1}$ min^{-1}).

For the boundary conditions, $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated linear form of the equation is written as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \tag{20}$$

The plot of t/q_t versus t gives a linear relationship, which allows computation of k_2 and predicted q_e.

5. RESULTS AND DISCUSSION

5.1 Adsorption of dyes in single and binary systems

Single-component models of Langmuir and Freundlich were each applied to adsorption data from single and binary systems. In adsorption in binary solutions, these models were applied to each dye neglecting the possible interference by the other dye. The possible reduction in dye adsorption capacity onto WS in binary mixtures was evaluated by comparing the maximum adsorption capacity from single dye solutions to that of binary dye solutions for each particular dye. Such comparisons should only be made if the initial conditions are identical in single and binary dye solution systems. As illustrated in section 2.3, the adsorption isotherms data in this study were determined under identical experimental conditions.

It should be noted that equilibrium adsorption for a binary system was also analyzed by using multi-component modified Langmuir and Sheindorf–Rebuhn–Sheintuch (SRS) models which describe competitive adsorption. Moreover, single-component models have been used to simulate competitive adsorption systems (Allen and Brown [24]; Allen et al. [25]; Martin and Al-Bahrani [26]).

The results of fitting Eqs. (6) and (8) to the adsorption data of single and binary systems are presented in Table 3.

Table 3 shows the maximum adsorption capacity (q_m) of WS for basic dyes from single and binary solutions. The maximum adsorption capacities of WS for BB 3 and BR 18 dyes in a single solution system were found as 90.91 mg g^{-1} and 142.86 mg g^{-1}, respectively, while in a binary mixture they decreased to 76.92 mg g^{-1} and 111.11 mg g^{-1}, respectively, as a result of their competitive behavior. Although the maximum adsorption capacities of WS for BB 3 and BR 18 dyes decreased in binary mixture, simultaneous removal of these dyes is still possible owing to the high adsorption capacities obtained in the binary system.

Table 3. Parameters of Langmuir and Freundlich isotherms for single (S) and binary (B) systems for WS.

System	Langmuir		Freundlich	
	q_m(mg g^{-1})	b(dm^3 g^{-1})	K_F (dm^3 g^{-1})	n
BB 3 (S)	90.91	0.054	7.89	0.579
BB 3 (B)	76.92	0.115	11.75	0.482
BR 18 (S)	142.86	0.010	2.01	0.816
BR 18 (B)	111.11	0.038	5.71	0.700

In the application of adsorption for purification of wastewater the solution will normally be a mixture of many compounds rather than a single one. The interactions of these compounds may mutually enhance or mutually inhibit adsorption capacity (Ho and McKay [27]). In general, a mixture of different adsorbates may exhibit three possible types of behavior: synergism, antagonism and non-interaction (Srivastava et al. [28]). In this study, the binary solution exhibited inhibitory (antagonistic) adsorption for each dye, thereby resulting in a lower q_m.

Generally, the adsorption capacities of each individual dye proportionally decrease in the presence of another solute. This can be attributed mainly to the competitive interaction between the dyes on the solid surface. Other factors may include the electrical repulsion of a dye from the adsorbent surface by the other adsorbed dye of similar charge. In addition, the dye with the higher saturation value may effectively occupy most of the active sites hindering further adsorption of the other dye possessing a lower affinity (Porter [29]).

Allen et al. [25] considered the competitive adsorption of three basic dyes. Their results showed that the adsorption capacity of an individual dye decreased in the presence of a second or a third dye. They reported that reduced capacities could be attributed to a combination of a number of factors. These include: (i) interaction between dyes in solution; (ii) change in the adsorbent surface charge due to adsorption; (iii) competitive adsorption between dyes for active sites on the adsorbent surface where displacement effects replace the other dyes from the adsorption sites.

5.2 Fitting adsorption data to adsorption models

The single-component Langmuir and Freundlich isotherm models were applied to the adsorption equilibrium data for a single-component and a binary mixture. Equilibrium adsorption for the binary system was also analyzed by using multi-component modified Langmuir and Sheindorf–Rebuhn–Sheintuch (SRS) models.

The sum of the squares of the errors (*SSE*) function was used to test the adequacy and accuracy of the fit of the four isotherm models with the experimental data:

$$SSE = \sum_{i=1}^{N} \left(q_{e,cal} - q_{e,exp}\right)_i^2 \qquad (21)$$

where: the subscripts '*exp*' and '*cal*' indicate the experimental and calculated values, respectively and *N* is the number of measurements.

The best fitting model is determined on the basis of the lowest *SSE* values. Table 4 summarizes the values of *SSE* for single-component and multi-component isotherms models. Equilibrium data of BB 3 in single and binary systems fitted more adequately to the Freundlich adsorption isotherm. For BR 18, Langmuir model was the best one for fitting the adsorption equilibrium in single and binary systems.

Table 4. *SSE* values for single-component and multi-component isotherms models for WS**.**

System	Langmuir	Freundlich	Modified Langmuir	SRS model
BB 3 (S)	296.07	219.35		
BB 3 (B)	187.47	97.23	642.11	6E+13
BR 18 (S)	184.12	450.02		
BR 18 (B)	76.67	169.54	4109.35	4.6E+11

Table 5. Kinetic parameters for the adsorption of BB 3 and BR 18 on WS in single and binary systems.

			Pseudo-first order kinetic model			Pseudo-Second order kinetic model		
Dyes	Adsorption system	q_e, exp. (mg g^{-1})	q_e, cal. (mg g^{-1})	K_1 (min^{-1})	R^2	q_e, cal. (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	R^2
BB 3	BB 3-S	39.33	7.34	0.012	0.961	40	0.009	0.999
	BB 3-B	38.07	12.9	0.010	0.961	38.46	0.004	0.999
BR 18	BR 18-S	40.66	6.64	0.016	0.881	41.67	0.014	1
	BR 18-B	39.02	8.46	0.008	0.925	40	0.005	0.999

5.3 Kinetics modeling

The study of adsorption kinetics in wastewater treatment is important since it provides valuable insights into reaction pathways and mechanism of adsorption process.

Figs. 2 and 3 show the effect of the contact time on the amounts of dyes adsorbed in single and binary dye systems for BB 3 and BR 18, respectively. As contact time increases, dye uptake initially increases and then becomes almost stable, denoting attainment of equilibrium. These changes in dye uptake may be due to the fact that, initially, all adsorbent sites were vacant and the solute concentration was high. After that period, only a very low increase in the dye uptake was observed because there are few free surface active sites on WS.

As can also be seen from the figures, the adsorption capacities decreased for both dyes after adsorption in binary systems, indicating their competitive behavior. The pseudo-first order and pseudo-second order models were employed to fit the experimental data for the adsorption kinetics of BB 3 and BR 18 on WS from single- and binary-component systems.

Plots of pseudo-first order and pseudo-second order models are demonstrated in Figs. 4 and 5, respectively. Modeling of kinetics models and parameters obtained from the pseudo-first-order and pseudo-second-order models are given in Table 5. It can be seen that the correlation coefficients,

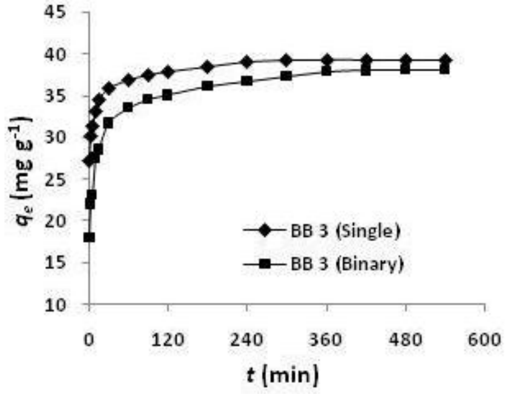


Fig. 2. Effect of contact time on the amounts of BB 3 adsorbed on WS in single and binary systems.

R^2, of the pseudo-second order model are close to 1 while correlation coefficients for the pseudo-first order kinetics model range from 0.881 to 0.961.

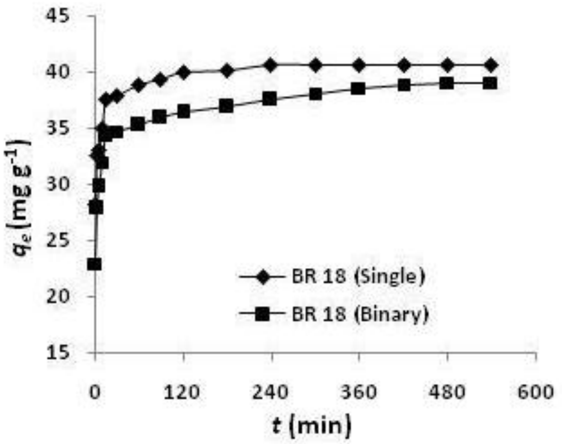


Fig. 3. Effect of contact time on the amounts of BR 18 adsorbed on WS in single and binary systems.

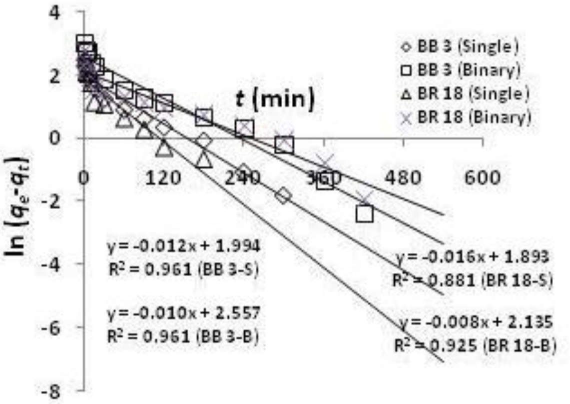


Fig.4 Pseudo-first order kinetics for adsorption of BB 3 and BR 18 on WS in single and binary systems.

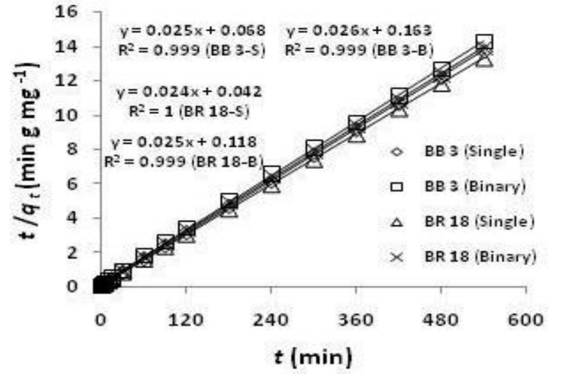


Fig.5. Pseudo-second order kinetics for adsorption of BB 3 and BR 18 on WS in single and binary systems.

Adsorption capacities calculated (q_e, cal.) by the pseudo-second order were also close to those obtained from experiments (q_e, exp.). Hence, the pseudo-second-order model provides better correlation for the adsorption process of BB 3 and BR 18 on WS in single- and binary component systems.

6. CONCLUSIONS

The agricultural waste, wheat straw, displayed a high adsorption capacity for basic dyes (BB 3 and BR 18) from single and binary solutions. It was found that the maximum adsorption capacities decreased in a binary system as compared to single dye systems.

Although the maximum adsorption capacities of WS for BB 3 and BR 18 dyes decreased in a binary mixture, simultaneous removal of these dyes is still possible due to the high adsorption capacities obtained in the binary system (76.92 mg g^{-1} and 111.11 mg g^{-1} for BB 3 and BR 18, respectively).

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ДВУКОМПОНЕНТНА АДСОРБЦИЯ НА ОСНОВНИ БАГРИЛА ВЪРХУ ПШЕНИЧЕНА СЛАМА

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(Резюме)

Изследвана е едновременната адсорбция на основно синьо 3 (BB 3) и основно червено 18 (BR 18) върху пшеничена слама (WS) и е сравнена с еднокомпонентните им системи. Приложени са моделите на Лангмюир и Фройндлих за описание на равновесието на едно- и двукомпонентните системи. Адсорбционното равновесие на двукомпонентната система е анализирано чрез използването на модифицирания за многокомпонентни системи модел на Лангмюир и този на Sheindorf-Rebuhn-Sheintuch. Равновесните данни за BB 3 в моно- и двукомпонентна системи се описва адекватно с адсорбционната изотерма на Фройндлих. За BR 18 моделът на Лангмюир е по-подходящ за моно- и двукомпонентна смес. За описание на адсорбционната кинетика на BB 3 и BR 18 върху WS за моно- и двукомпонентни системи са използвани моделите от псевдо-първи и псевдо-втори порядък. По-добра корелация предоставя моделът от псевдо-втори порядък. Резултатите при двукомпонентната система показват конкурираща се адсорбция на багрилата. Максималните адсорбционни капацитети на WS за еднокомпонентни системи на BB 3 и BR 18 са съответно 90.91 mg g^{-1} и 142.86 mg g^{-1}, докато за двукомпонентните смеси те намаляват съответно до 76.92 mg g^{-1} и 111.11 mg g^{-1} в резултат на антагонистичното поведение на багрилата.

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Synthesis and design of a progesterone-alkyne derivative

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In this work a progesterone-alkyne derivative was synthesized. The first stage involves preparation of a progesterone-ethylenediamine derivative (**2**) by the reaction of progesterone with ethylenediamine using Mannich reaction. The second stage involves the formation of ethylenediamine-progesterone oxime (**4**) by the reaction of **2** with hydroxylamine hydrochloride (Method A). Additionally, **4** was also synthesized by the reaction of pregn-4-ene-3E,20E-dioxime (**3**) with ethylenediamine using Mannich reaction (method B). Finally, the route for synthesis of progesterone-alkyne derivative (**5**) was followed using a three-component system (compound **4,** benzaldehyde and 1-hexyne) in the presence of anhydrous cupric chloride.

Key words: Progesterone, oxime, three-component system.

1. INTRODUCTION

There are several reports of multi-component reactions for the synthesis of several compounds [1-3]; for example, some studies [4] described the preparation of propargylamines using a three-component system (aldehyde, amine, and alkyne) in water or copper iodide [5] as catalyst. In other studies an enantioselective, copper(I)-catalyzed three-component reaction is used for the preparation of propargylamines [6]. In ref. [7] the diastereoselective synthesis of α-oxyamines using a three-component system (α-oxyaldehyde, amine and alkyne) in presence of gold, silver and copper in water is used. In other studies [8] the synthesis of tertiary propargylamine using a three-component system which involves aldehyde, alkyne and 4-piperidone hydrochloride in presence of cupric bromide is developed. In the report of Yadav and coworkers [9] the synthesis of propargylamines by reaction of aldehydes, amines and alkyne derivatives using copper (I) bromide as catalyst in ionic liquids is described. Recently a carbamazepine-alkyne derivative was synthesized using a three-component system (carbamazepine, benzaldehyde and 1-hexyne) in presence of cupric chloride as catalyst [10]. All these studies report the synthesis of several compounds using a three-component system; nevertheless, various protocols and special conditions are required for its development. In this study, our initial design included a facile synthesis of a new steroid-alkyne derivative; the route involves preparation of progesterone-alkyne derivative using a three-component system such as 4-[(2-amino-ethylamino)-methyl]-pregnen-4-en-3E,20E-dioxime, benzaldehyde and 1-alkyne in the presence of cupric chloride as catalyst.

2 EXPERIMENTAL

General methods

Pregn-4-ene-3E,20E-dioxime was prepared according to a previously reported method [11]. Progesterone and the other compounds used in this study were purchased from Sigma-Aldrich Co., Ltd. The melting points of the compounds were determined on an Electrothermal (900 model) apparatus. Infrared (IR) spectra were recorded in KBr pellets on a Perkin Elmer Lambda 40 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-300/5 FT NMR spectrometer at 300 and 75.4 MHz in DMSO-d_6 using TMS as internal standard. EIMS spectra were obtained on a Finnigan Trace GCPolaris Q. spectrometer. Elemental analysis data were acquired from a Perkin Elmer Ser. II CHNS/0 2400 elemental analyzer.

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4-[(2-Amino-ethylamino)-methyl]-17-(1-hydroxyimino-ethyl)-10,13-dimethyl-1,2,6,7,8, 9,10,11,12,13,14,15,16,17-tetradecahydro-cyclopenta[a]phenanthren-3-one oxime (2).

A solution of pregn-4-en-3,20-dione (100 mg, 0.32 mmol), ethylenediamine (35 μL, 0.52 mmol), and methanol (3 mL) in formaldehyde (10 mL) was gently refluxed for 24 h and then cooled to room temperature. The reaction mixture was evaporated to a smaller volume, diluted with water and extracted with chloroform. The organic phase was evaporated to dryness under reduced pressure; the residue was purified by crystallization from methanol:water (4:1) yielding 75 % of product, m.p. 92-94°C; IR (V_{max}, cm^{-1}): 3384, 3354, 1716; ^{1}HNMR (300 HMz, DMSO-d_6) δ_H: 0.65 (s, 3H), 0.89-0.98 (m, 2H), 1.08 (s, 3H), 1.17-1.44 (m, 3H), 1.46-1.64 (m, 4H), 1.67-1.78 (m, 3H), 2.03-2.11 (m, 4H), 2.14 (s, 3H), 2.18 (m, 1H), 2.52 (broad , 3H), 2.54-2.60 (m, 3H), 2.66 (t, 2H, J = 6 Hz), 2.82 (t, 2H, J = 6 Hz), 3.36 (m, 2H) ppm. ^{13}C NMR (74.5 MHz, DMSO-d_6) δ_C: 13.26 (**C**-18), 17.20 (**C**-27), 20.78 (**C**-5), 23.30 (**C**-11), 23.80 (**C**-9), 26.64 (**C**-8), 29.90 (**C**-28), 30.97 (**C**-10), 34.88 (**C**-3), 35.02 (**C**-15), 35.58 (**C**-16), 38.10 (**C**-6), 38.88 (**C**-17), 41.17 (**C**-24), 43.80 (**C**-1), 44.60 (**C**-21), 52.10 (**C**-23), 56.12 (**C**-2), 57.64 (**C**-4), 63.40 (**C**-7), 132.70 (**C**-13), 159.44 (**C**-12), 196.76 (**C**-14), 206.60 (**C**-19) ppm. MS (70 ev): *m/z* 386.20 [M$^+$]; Anal. calcd. for $C_{24}H_{38}N_2O_2$: C, 74.57; H, 9.91; N, 7.25; 0, 8.28. Found: C, 74.50; H, 9.90.

4-[(2-Amino-ethylamino)-methyl]-17-(1-hydroxyimino-ethyl)-10,13-dimethyl-1,2,6,7,8, 9,10,11,12,13,14,15,16,17-tetradecahydro-cyclopenta[a]phenanthren-3-one oxime (4).

Method A. A solution of **2** (100 mg, 0.29 mmol), ethylenediamine (35 μL, 0.52 mmol) and ethanol (3 mL) in formaldehyde (10 mL) was gently refluxed for 24 h and then cooled to room temperature. The reaction mixture was evaporated to a smaller volume, diluted with water and extracted with chloroform. The organic phase was evaporated to dryness under reduced pressure; the residue was purified by crystallization from methanol:water (3:1) yielding 60 % of product, m.p. 118-120 ºC; IR (V_{max}, cm^{-1}): 3380, 3352, 3300;^{1}HNMR (300 HMz, DMSO-d_6) δ_H: 0.87 (s, 3H), 0.89-0.98 (m, 2H), 1.01 (s, 3H), 1.23-1.44 (m, 3H), 1.46-1.64 (m, 3H), 1.67-1.69 (m, 2H), 1.74 (s, 3H), 1.78-2.16 (m, 6H), 2.28-2.45 (m, 2H), 2.62 (m, 1H), 2.68 (t, 2H, J = 6 Hz), 2.82 (t, 2H, J = 6 Hz), 2.83 (m, 1H), 3.50 (s, 2H), 4.40 (broad, 5H) ppm. ^{13}CNMR (74.5 MHz, DMSO-d_6) δ_C: 12.70 (**C**-30), 13.25 (**C**-18), 19.25 (**C**-29), 21.17 (**C**-5), 21.31(**C**-15), 22.53 (**C**-11), 25.84 (**C**-9), 26.64 (**C**-8), 30.81 (**C**-16), 30.97 (**C**-10), 34.88 (**C**-3), 37.88 (**C**-17), 37.95 (**C**-6), 41.17 (**C**-25), 44.06 (**C**-22), 44.89 (**C**-1), 52.10 (**C**-24), 54.91 (**C**-4), 56.70 (**C**-2), 57.14 (**C**-7), 137.70 (**C**-13), 152.06 (**C**-12), 156.76 (**C**-14), 161.12 (**C**-19) ppm. MS (70 ev): *m/z* 416.40 [M$^+$]; Anal. calcd. for $C_{24}H_{40}N_4O_2$: C, 69.19; H, 9.68; N, 13.45; 0, 7.68. Found: C, 69.15; H, 9.71.

Method B. A solution of **2** (100 mg, 0.26 mmol), hydroxylamine hydrochloride (54 mg, 0.77 mmol) and sodium hydroxide (5%) in 10 mL of ethanol was refluxed for 24 h. The reaction mixture was evaporated to a smaller volume. The residue was dissolved in 10 mL of distilled water. The solution was adjusted to pH 2 with conc. hydrochloric acid and extracted with 20 mL of ethyl acetate: chloroform (2:1). The organic solution was dried with Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was extracted with chloroform and chromatographed on a silica gel column (10 × 75 mm). The product was purified by crystallization from methanol:water yielding 25 % of product. The ^{1}H NMR and ^{13}C NMR data were similar to those of the product obtained by Method A.

4-{[2-(Hex-1-ynil-phenyl-amino)-ethylamino]-methyl}-17-(1-hydro-xyimino-ethyl)-10,13-dimethyl-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-cipenta[a]phenan-thren-3one oxime (5).

A solution of **4** (100 mg, 0.29 mmol), benzaldehyde (60 μL, 0.59 mmol) 1-hexyne (50 μL, 0.43 mmol) and ethanol (10 mL) was stirred for 10 min at room temperature. Then anhydrous cupric chloride (113 mg, 0.84 mmol) was added and the mixture was stirred for 48 h at room temperature. The reaction mixture was evaporated to a smaller volume, diluted with water and extracted with chloroform. The organic phase was evaporated to dryness under reduced pressure; the residue was purified by crystallization from methanol:water (3:1) yielding 70 % of product, m.p. 162-164 ºC; IR (Vmax, cm^{-1}) 3350, 3304 2140 cm^{-1}: ^{1}HNMR (300 HMz, DMSO-d_6) δ_H: 0.87 (s, 3H), 0.89 (m, 1H), 0.91 (t, 3H, J = 7.0 Hz), 0.94 (m, 1H),1.05 (s, 3H), 1.20-1.40 (m, 3H), 1.44-1.48 (m, 4H), 1.49-1.70 (m, 5H), 1.74 (s, 3H), 1.78-2.28 (m, 7H), 2.35 (m, 2H), 2.42-2.85 (m, 3H), 2.94 (t, 2H, J = 7.0 Hz), 3.19 (t, 2H, J = 7.0 Hz), 3.50 (s, 2H), 6.08 (broad, 3H), 6.58-7.16 (m, 5H) ppm. ^{13}CNMR (74.5 MHz, DMSO-d_6) δ_C: 12.71 (**C**-36), 13.24 (**C**-18), 15.63 (**C**-42), 16.95 (**C**-39), 19.55 (**C**-35), 21.17 (**C**-5), 21.31 (**C**-15), 21.98 (**C**-41), 22.51 (**C**-11), 25.84 (**C**-5), 26.62 (**C**-8), 30.67 (**C**-16), 30.96 (**C**-10), 32.01 (**C**-40), 34.88 (**C**-3), 37.68 (**C**-17), 37.95 (**C**-6), 44.06 (**C**-22), 44.89 (**C**-1), 49.18 (**C**-24), 52.73 (**C**-4), 54.91 (**C**-2), 57.73 (**C**-7), 58.02 (**C**-25), 59.25 (**C**-38), 82.56 (**C**-37), 114.67 (**C**-32, **C**-28), 120.72 (**C**-30), 129.63 (**C**-31, **C**-29), 137.77 (**C**-13), 146.23 (**C**-27), 151.40 (**C**-12), 156.96 (**C**-14), 161.29 (**C**-19) ppm. MS (70 ev): *m/z* 572.70 [M^+]; Anal. calcd. for $C_{36}H_{52}N_4O_2$: C, 75.48; H, 9.15; N, 9.78; 0, 5.59. Found: C, 75.44; H, 9.17.

5. RESULTS AND DISCUSSION

In this study, a straightforward route is reported for the synthesis of a progesterone-alkyne derivative (**5**). The first stage was carried out by reacting pregnen-4-en-3,20-dione (**1**) with ethylenediamine and formaldehyde to form an amino-progesterone derivative (**2**) using the Mannich method (Figure 1).

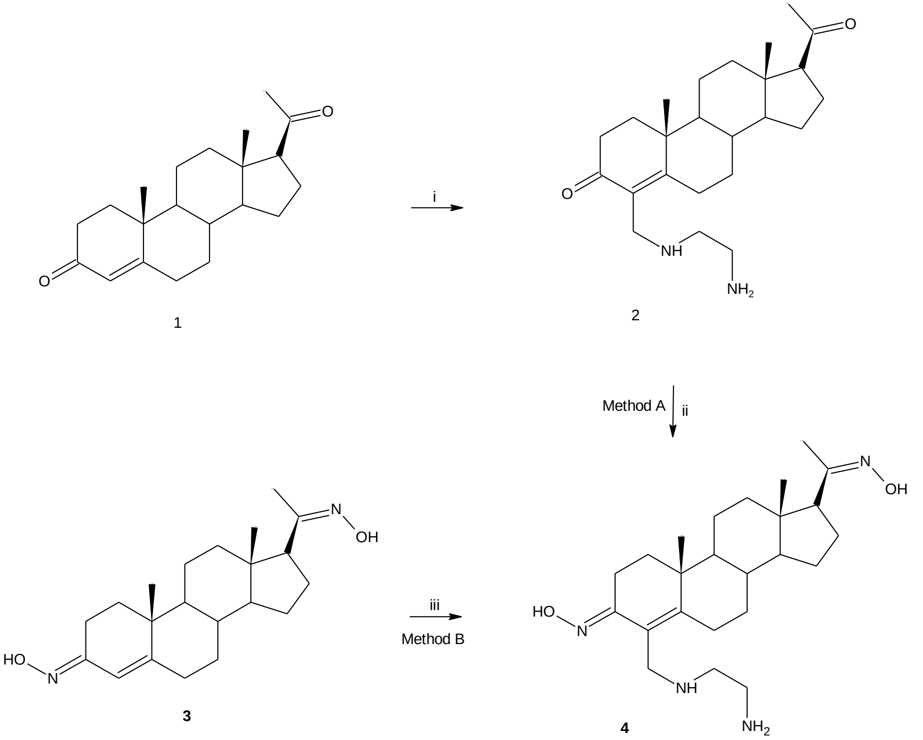

Fig. 1. Synthesis of an ethylenediamine-progesterone oxime derivative (**4**). The first stage involves the preparation of a progesterone-ethylenediamine derivative (**2**) by the reaction of progesterone with ethylenediamine, followed by formation of the compound (**4**) by oximation of (**2**) (method A). The second stage (method B) involves the synthesis of (**4**) by the reaction of progesterone-oxime (**3**) with ethylenediamine. i = formaldehyde/methanol; ii = hydroxylamine hydrochloride; iii = formaldehyde/methanol.

It is important to mention that several amino-steroid derivatives have been obtained using the Mannich reaction; the structural chemistry of these compounds [12] involves an activated methyl group in ring A. Therefore, in this work a study of the reactivity of the hydrogen atom involved in ring A of compound 1 was undertaken by means of Mannich reaction. The ^1H NMR spectrum of 2 showed several signals at 0.65, 1.08 and 2.14 ppm corresponding to methyls presents in the steroid nucleus and at 0.89-0.98 and 1.17-2.60 ppm for protons involved in the steroid nucleus. Several signals at 2.52 ppm for protons of amino groups; at 2.66-3.36 ppm for methylene groups involved in the arm bound to A-ring of steroid nucleus were found. The ^{13}C NMR spectra displayed chemical shifts at 13.26, 17.20 and 29.90 ppm for the carbons of methyl groups present in the steroid nucleus. The chemical shifts of the methylenes involved in the steroid nucleus were found at 20.78-26.64, 30.97-38.78, 43.80 and 56.12-196.76 ppm. Additionally, several chemical shifts at 41.17, 44.60 and 52.10 ppm for methylenes present in the arm bound to the A-ring of the steroid nucleus were displayed. A signal at 206.60 ppm for a ketone group was found. The presence of the compound 2 was further confirmed by the mass spectrum which showed a molecular ion at m/z 386.20.

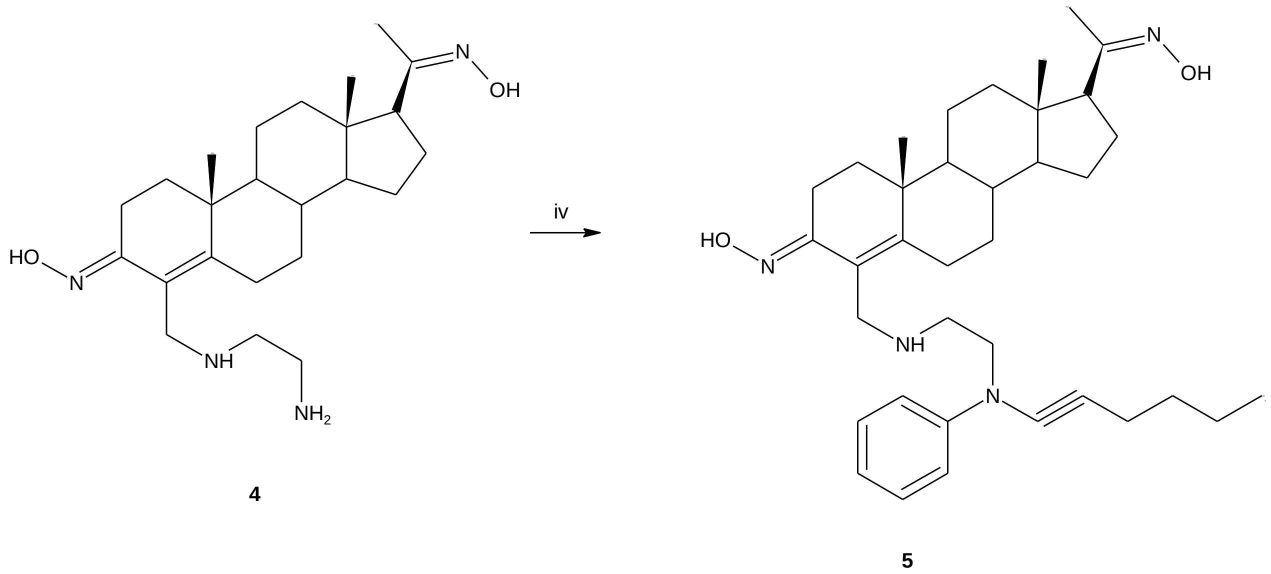

Fig. 2. Synthesis of a progesterone-alkyne derivative (**5**) using a three-component system (compound (**4**), benzaldhehyde and 1-hexyne). iv = anhydrous cupric chloride /ethanol

The second stage was performed by the synthesis of 4 using two different methods; in method A, the pregnen-4-en-3E,20E-dioxime (3) was reacted with ethylenediamine to form 4 using the Mannich reaction. The ^{1}H NMR spectrum of 4 showed several signals at 0.87, 1.01 and 1.74 ppm corresponding to methyls present in the steroid nucleus; at 0.89-0.98, 1.23-1.69, 1.78-2.62 and 2.83 ppm for protons involved in the steroid nucleus were found. In addition, signals at 2.68, 2.82 and 3.50 ppm for hydrogens involved in the arm bound to the A-ring of the steroid nucleus were registered. A signal at 4.40 ppm for both hydroxyl and amino groups was found as well. The ^{13}C NMR spectra displayed chemical shifts at 12.72, 13.25 and 19.45 ppm for the carbons of methyl groups present in the steroid nucleus. The chemical shifts of the methylenes involved in the steroid nucleus were found at 21.17-37.95, 44.89, 54.91-151.40 ppm. In addition, several chemical shifts at 41.17, 44.06 and 52.12 ppm for the arm bound to the A-ring of the steroid nucleus were displayed. Signals at 156.96 and 161.29 ppm carbons bound to hydroxyl amino group were found as well. The presence of compound 4 was further confirmed by the mass spectrum which showed a molecular ion at m/z 416.40. In the method B the compound 2 was reacted with hydroxylamine hydrochloride to form 4. The ^{1}H NMR and ^{13}C NMR data were similar to those of the product obtained by method A. It is important to mention that method A gives higher yields of compound 4 than method B.

The third stage was performed using the three-component system for the synthesis of 5 (see Figure 2). There are many procedures which use a three component system for the synthesis of several compounds. The most widely practiced method employs boric acid [13], silica sulfuric acid [14], poly(4-vinylpyridine-codivynylbenzene)-Cu(II) complex [15], H_2SO_4[16], silica triflate [17] and phosphorus pentoxide [18]. Nevertheless, despite their wide scope, the protocols mentioned suffer from several drawbacks owing to the limited stability of some reagents. Analyzing these data and the reports which indicate that the copper (I) reagent has been found to be an efficient catalyst for an enantioselective one-pot three-component synthesis using aldehydes, amines, and alkynes [19,20], in this study we report a straightforward route for the synthesis of 5 using a three-component system consisting of compound 4, benzaldehyde and 1-alkyne in presence of cupric chloride as catalyst (see Figure 2). The ^{1}H NMR spectrum of 5 showed several signals at 0.87, 1.05 and 1.74 ppm for methyl groups present in the steroid nucleus; at 0.91 ppm for a methyl group involved in the arm of alkyne; at 0.89-0.94, 1.20-1.40, 1.49-1.70, 1.78-2.28 and 2.43-2.85 ppm for protons involved in the steroid nucleus. Several chemical shifts at 1.44-1.48 and 2.35 ppm for methylenes involved in the arm of alkyne; at 2.94, 3.19 and 3.50 ppm for an arm bound to the A-ring of the steroid nucleus were displayed. Signals at 6.08 ppm for both hydroxyl and amino groups and at 6.58-7.16 ppm for protons involved in the phenyl group were found. The presence of the compound 5 was further confirmed by the mass spectrum which showed a molecular ion at m/z 572.70.

6. CONCLUSIONS

In this study, we report an easy methodology to synthesize a progesterone-alkyne derivative (**5**).

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СИНТЕЗ И ДИЗАЙН НА ПРОГЕСТЕРОН-АЛКИНОВИ ПРОИЗВОДНИ

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(Резюме)

В настоящата работа се съобщава за синтезирането на прогестерон-алкинови производни. Първият етап включва проготвяне на прогестерон-етилендиаминово производно (**2**) изпозлвайки реакцията на Mannich. Вторият етап включва получаването на оксима на етилендиамина-прогестерона (**4**) чрез реакцията на **2** с хидроксиламин-хидрохлорид (метод А). Освен това **4** е също синтезирано чрез реакцията на прегно-4-ен-3Е,20Е-диоксим (**3**) с етиленсиамин по реакцията на Маних (метод В). Накрая се следва маршрута за синтезата на прогестерон-алкиновите производни (**5**) в три

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Some physicochemical properties of silver loaded clinoptilolite from Beli plast, East Rhodopes by spray pyrolysis method

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Silver loaded zeolite was obtained by the spray pyrolysis method. The material was characterized by DC arc atomic emission spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), IR spectroscopy and scanning electron microscopy (SEM). The concentration of Ag in the final samples, calculated from the XPS spectra, corresponds to that in the precursor solution. The SEM photographs reveal both separate silver particles and agglomerates located on the zeolite surface and inside the channels.

Keywords: Ag coated, HEU, Spray pyrolysis, zeolite, SEM

1. INTRODUCTION

The Bulgarian clinoptilolite (CAS No:12173-10-3) is a natural zeolite with HEU–type framework. Its structure and properties are widely investigated and discussed in the literature [1-7]. As a representative of the zeolite class, clinoptilolite can be used as a catalyst support, adsorbent and ion exchanger. Our interest in silver loaded clinoptilolite was provoked by these facts: clinoptilolite is a natural mineral and is cheaper than synthetic zeolites; Ag loaded zeolites can be used as catalysts for several types of reactions (e.g., oxidation with ozone [6]) or as materials with antibacterial properties [8].

Over the last decades spray pyrolysis has been one of the mainstream chemical methods applied for the formation of thin layers and particles (powders) of different compounds [9-11]. The method is cheap and requires simple equipment in comparison with the physical methods (vacuum evaporation, magnetron sputtering, etc.). Spray pyrolysis allows mixing of the initial components at a molecular level. It allows doping with any chemical element in various proportions; a distinctive feature of sprayed catalysts is the homogeneous distribution of the ingredients throughout the entire particle since all ingredients are formed in a homogeneous solution [12-15].

The aim of this article was to prepare Ag loaded natural clinoptilolite (Ag/CL) via spray pyrolysis method and to investigate the physicochemical properties of the samples.

2. EXPERIMENTAL PROCEDURES

General methods

An aqueous $AgNO_3$ precursor solution was used to obtain a final product with 7.5 wt % silver. Clinoptilolite (CL) 10 g (fraction 3-5 mm), obtained from Beli Plast deposit by Bentonit AD, was put in a ceramic crucible and was heated in a hot furnace at 250-300^{o}C. The temperature was sufficient to decompose the precursor.

The aerosol of the precursor solution was generated by a pneumatic glass nebulizer and was transported to the substrate. The spray coating was repeated 5 times in 10-second intervals. The sample was mechanically stirred in order to obtain homogeneous distribution of the drops over the whole surface of zeolite particles. The final treatment at 350^{o}C was carried out for 60 min.

The silver content of the Ag/CL sample was analyzed by a D.C. arc - AES method on a spectrograph PGS-2 (Carl Zeiss - Jena), equipped with a ruled grating 650 grooves mm^{-1} and λ blaze 570 nm. D.C. power generator was used for spectra excitation in electrodes RW–0, Ringsdorff. The electrode spacing was 4.0 mm, and the amount of sample - 10 mg.

The crystalline phase composition of the samples was studied on a X-ray diffractometer Philips PW 1050 with CuK_{α}-radiation.

The chemical composition was determined on a VG ESCALAB II electron spectrometer using AlK_{α} radiation with energy of 1486.6 eV. The binding energies were determined with an accuracy of

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±0.1 eV utilizing the C1s line at 285.0 eV (from an adventitious carbon) as a reference. The chemical composition of the samples was investigated on the basis of areas and binding energies of C1s, O1s, Ag3d photoelectron peaks (after linear subtraction of the background) and Scofield's photoionization cross-sections.

The morphology of the samples was investigated by SEM (JSM-5510 of JEOL).

3. RESULTS AND DISCUSSION

The D.C. arc - AES method proved the presence of Ag in the samples. The photographic plate is shown on Fig. 1. The characteristic Ag lines at 328.068 pm and 338.289 pm can be seen. Two characteristic lines of Al (308.215 and 309.271 pm) and of Si (288.157 pm) are also seen. This method indicated that the silver was successfully coated on the zeolite, but gave no information on the distribution of the Ag particles.

Fig. 1. Ag/CL spectral plate from D.C. arc – AES analysis.

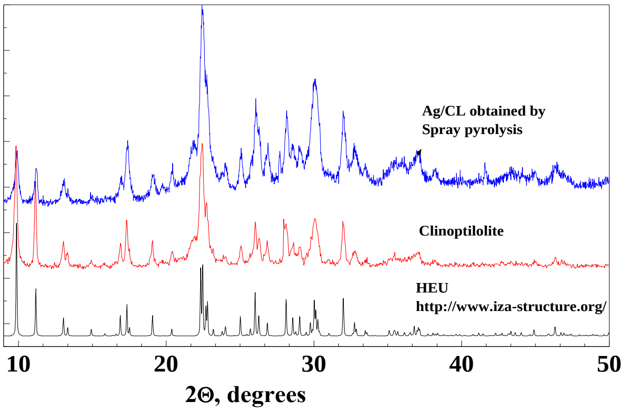

Fig 2. XRD diffractogram of CL, Ag loaded CL and HEU type structure according to zeolite data base atlas.

XRD analysis (Fig. 2) revealed that the natural Bulgarian clinoptilolite contains less than 17 % impurities of cristobalite, quartz, albite and microcline. The increased intensity of the diffraction peak at $2\Theta = 30$ is a result of the presence of silver. XRD analysis did not detect any Ag phases, although the samples contain over 5 wt % silver. Probably, some of the silver particles are incorporated inside the zeolite channels, due to the porous structure of the zeolite.

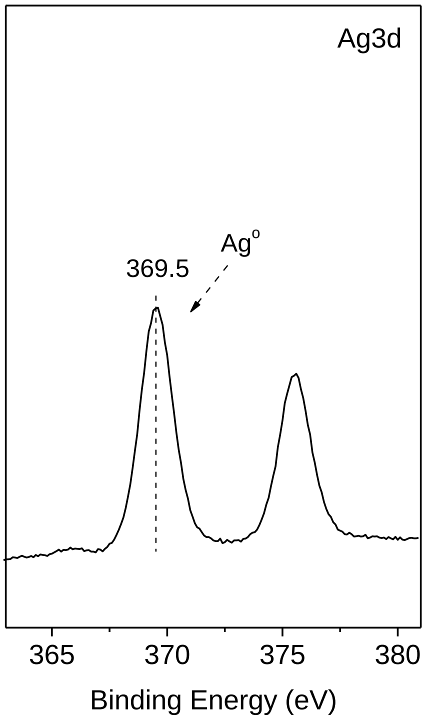

Fig 3. Ag 3d photoelectron spectra of the Ag loaded CL.

The chemical composition of CL and Ag/CL was investigated on the basis of areas and binding energies of C1s, O1s, Si2s, Si2p, Al2s, Al2p and Ag3d photoelectron peaks. The surface atomic concentrations of O, Al, Si, Ag, Na, K and Ca were estimated as well and are shown in Table 1. It can also be seen that the concentration of silver in the zeolite (Fig. 3, Table 1) corresponds to that in the spray precursor solution.

Fig. 4 presents the morphology of the Ag loaded zeolite. It can be seen that single Ag particles (indicated by black arrows) and aggregate heaps of Ag particles (indicated by white arrows) are situated on its surface. A thin silver layer is probably formed in some sections of the (010) zeolite plane. The IR spectrum of the Ag/CL sample is presented on Fig. 5. The main vibrational absorbance peaks are presented in Table 2. They correspond to Si-O-Si or Si-O-Al vibrations. The typical silanol vibrations (950 and 570 cm^{-1}) can not be observed because natural clinoptilolite is not in H form. The possible ~O-H vibrations were shifted to higher wavelenghts at 465, 604 and 3453 cm^{-1} , due to the presence of

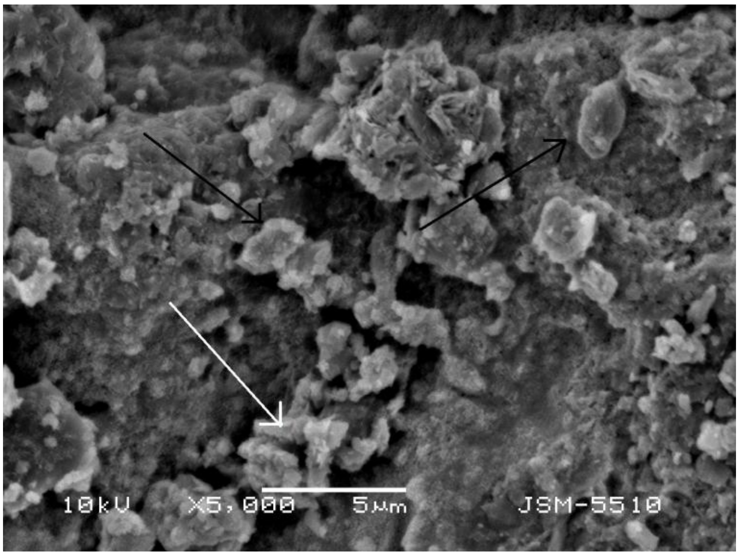

Fig.4. SEM image of Ag loaded CL.

Table 1. Chemical composition of the samples according to the data of the XPS analysis

Chemical composition	O [at.%]	**SI [AT.%]**	Al [at.%]	Na [at.%]	K [at.%]	Ca [at.%]	Ag [at.%]
clinoptilolite	60.5	31.6	4.2	<0.5	1.9	1.5	-
Ag/clinoptilolite	55.5	27.0	8.8	<0.5	0.5	0.8	7.3

Table 2. Key infrared bands of the samples according to values, given in [6].

Wavelength, cm^{-1}	Assignment
1200, 1070	ν_{as} (Si-O-Si)
950	ν (Si-OH)
798	ν_s (Si-O-Si)
570	ν (Si-OH)
450	δ (Si-O-Si)

silver, as has been found before [16]. The band at 1390 cm^{-1} was attributed to NO_3^- ions which should decompose after annealing at a temperature of 350°C. This peak can also be assigned to polluted air.

4. CONCLUSIONS

Spray pyrolysis is a faster and more flexible way for coating metals on alumino-silicate media in comparison with ion-exchange or wet impregnation methods. We have successfully applied the spray pyrolysis to produce Ag loaded clinoptilolite. Silver ions or particles located inside the channels, as well as on the outer zeolite fragments were found. The samples may find application as catalysts, antibacterial substances, etc., due to their high surface area and low price.

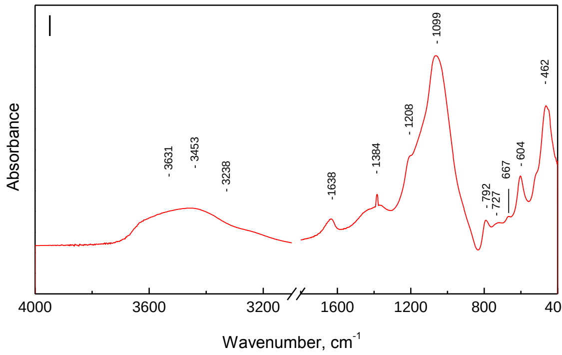

Fig.5. IR absorbance spectra of Ag loaded CL.

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НЯКОИ ФИЗИКО-ХИМИЧНИ СВОЙСТВА НА КЛИНОПТИЛОЛИТ ОТ БЕЛИ ПЛАСТ, ИЗТОЧНИ РОДОПИ, ПОКРИТ СЪС СРЕБРО ЧРЕЗ СПРЕЙ ПИРОЛИЗА

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(Резюме)

Получен е нанесен със сребро зеолит чрез спрей пиролиза. Материалът е охарактеризиран с атомно-емисионна спектроскопия (AES), рентгенова фотоелектронна спектроскопия (XPS), рентгенова дифракция (XRD) и сканираща електронна микроскопия (SEM). Концентрацията на сребро в образците, изчислена от XPS спектрите, отговаря на тази в изходния разтвор. На SEM фотографията се наблюдават както отделни сребърни частици, така и агломерати от тях, разположени върху повърхността и вътре в каналите на зеолита.

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Assessment of urea residues in agricultural soil samples around Mysore, Karnataka, India

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The present study comprises the analysis of 12 soil samples from rainfed, irrigated and garden lands of agricultural areas around Mysore. The soil samples were analyzed for urea residues, texture, moisture content, bulk density, particle density, water holding capacity, pH, EC, chloride, organic carbon, calcium, magnesium, total nitrogen, ammoniacal nitrogen, nitrate, sodium, potassium and phosphorus. The study reveals that the application of urea fertilizer has a great influence on the physico - chemical properties of the soil. The soil samples S4 and S7 were found to be acidic in nature. Decline in the levels of basic cations like calcium and magnesium was reported compared to the normal levels in the majority of the sampling areas. Higher phosphorus levels were found in all sampling areas, which is due to over-use of phosphate fertilizers. From the study it was concluded that judicious application of urea fertilizers may help maintaining soil quality and productivity. However, it is necessary to apply a liming material to reduce the acidifying effect on agricultural lands in order to maintain basic cation levels in soil.

Key words: urea residues, soil properties, rainfed, irrigated, garden lands, judicious application

1. INTRODUCTION

Urea is one of the nitrogenous fertilizers which has received widespread attention in agriculture, because of its potential capacity of alleviating seedling damage, nitrate toxicity, ammonia volatilization, air and water pollution problems [1-2]. When urea is applied to soil, it is rapidly hydrolyzed to ammonia and carbon dioxide by soil urease enzyme. The rate at which urea gets hydrolyzed is closely related to soil physico-chemical characteristics such as soil pH, moisture content, organic carbon and temperature [3]. Generally inorganic fertilizers are applied to maintain or improve crop yield but their application causes directly or indirectly changes in the physical and chemical properties of the soil. Some of the studies have shown that continued use of inorganic fertilizers may result in lowering soil quality and productive capacity [4]. Studies of urea residues in soil extracts were reported by very few researchers [5,6]. Studies of the physico-chemical characteristics of agricultural soils were reported by several researchers [7-17]. However, not much work is reported on determination of urea residues along with the physico-chemical characteristics of agricultural soils. Therefore, the present study was undertaken to investigate the physico-chemical characteristics of soils along with urea residues, particularly in the agricultural lands around Mysore, with a view to understand the role of urea residues on soil quality.

2 MATERIALS AND METHODS

Study area: Agriculture is the predominant occupation in Mysore. The total geographical area of Mysore is 81740 hectares, out of which, 38600 hectares corresponds to cultivable lands. The study area, lying on 12^0 30' N latitude and 76^0 65' E longitudes, receives annual rainfalls of about 798 mm. During the past 15 years, the consumption rate of chemical fertilizers in Mysore has been about 83,353 metric tons per year, out of which 50% contribution was for nitrogenous fertilizers, particularly urea. The description of the sampling place, cropping pattern, fertilizer type and quantity applied is presented in Table 1.

Collection of the soil samples: The sampling area was divided into rainfed, irrigated and garden lands. From each of the farm lands, four composite soil samples were collected. The soil samples were collected at a 0-15 cm depth. The soil samples were air-dried, ground, sieved through a 2 mm sieve and stored in polythene bags until analysis.

Analysis of soil: The soil samples were analyzed for texture, moisture content, bulk density, particle density, pH, electrical conductivity, organic

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carbon, total nitrogen, phosphorus, sodium, potassium, calcium, magnesium, ammoniacal nitrogen, nitrate and urea residues.

Experimental work: The textural analysis was carried out by the international pipette method and the soil moisture content was assessed by a gravimetric method. The bulk density and particle density were determined using the Core sampler method and the volumetric flask method. The urea residues were quantified spectrophotometrically by the reaction of urea with diacetylmonoxime under acidic conditions. The soil pH was measured in 1:5 soil/water suspensions using a pH meter with a glass electrode. The electrical conductivity of the soil extracts was determined using a conductivity meter. The organic carbon was determined by the potassium dichromate wet oxidation method. The total nitrogen was determined by the Kjeldahl distillation method, while the available phosphorus was determined by Trough's method. Sodium and potassium were determined by flame photometry. Calcium and magnesium were determined by EDTA titration and the ammoniacal nitrogen - by Nessler's reagent method.

3. RESULTS AND DISCUSSION

The results for the physico-chemical characteristics and the content of urea residues in the soil samples are presented in Table 2.

The ordinary examination of the soil in the studied area reveals that the soil samples are of sandy, clay, clay-loam, and sandy-clay texture. The water holding capacity is the amount of water retained in the soil pores. Generally, in medium-textured soils, the amount of water retained is very low when compared to clay-textured soil. In the present study the water holding capacity ranged from 46.8 to 90.3 %. Except for the samples S4 and S12, all soil samples were found to have a high water holding capacity, which is due to the large pore space present in-between the soil particles, helping to retain a larger amount of water.

Bulk density is defined as the mass of soil material per unit volume of moist soil in natural undisturbed conditions. The bulk density of clay and clay-loam soils normally ranges from 1 to 1.65 mg/m^3. Variation of the bulk density from 1.20 to 1.80 mg/m^3 could be found in sandy and sandy-loam soils. In the present studied area, the bulk density ranges from 0.94 to1.3 mg/m^3. In some of the soil samples lower bulk densities were reported, which may due to the high organic carbon content in the soil.

The particle density is the density of solid particles in the soil sample. In the studied area, the particle density of soil samples ranged from 2 to 5 mg/m^3. Normally the particle density ranges from 2 to 2.65 mg/m^3, which indicates the presence of clay and quartz minerals in the soil matrix. High particle density indicates the presence of iron-rich soils, e.g., the density of ferromagnesian minerals ranges from 2.9 to 3.5 mg/m^3 and the density of iron oxides and other heavy minerals can reach up to 5 mg/m^3.

Porosity or pore space of a soil is that portion of the total soil volume, which is not occupied by solid particles, but occupied by air or water. The pore space of a soil varies depending on soil texture, shape of individual soil particles, organic carbon content, and nature of crop soil management. In the present study, the porosity values ranged from 45 to 77.6 %. Lower porosity is reported for S12 and higher one - for S1. The soils are of sandy and clay texture. Generally, the pore space in sandy soils is very low when compared to clay soils, while the compactness between soil particles is higher in clay soils rather than in sandy soils.

The urea residues are found to range from 1.12 to 8.73 kg/ha. Generally, when urea is applied to the soil, it is rapidly hydrolyzed to ammonia and carbon dioxide by the urease enzyme present in the soil. The rate of degradation depends on soil pH, temperature, moisture content, organic carbon and quantity of urea applied. In the present study, high urea residues were reported in S7, which is due to the acidic nature of this sampling area. Acidic conditions reduce the urease enzymatic activity in the soil.

The present study on, irrigated and garden lands shows a pH range from 5.81 to 8.31. Soils with pH values from 5.5 to 6.5 are lime free and are satisfactory for most of the crops. pH values from 6.5 to 7.5 are most favorable for the crops and plants.

Electrical conductivity values from zero to 2 dS/m are safe for all crops. The EC values of the studied area varied from 0.11 to 1.04 dS/m, which reveals that most of the soil samples have a safe range of electrical conductivity.

Organic carbon is an index of soil productivity and reflects the amount of carbon broken down from plants and animals, which is stored in the soil. In the present study the organic carbon content in the soil samples of the studied area ranged from 0.57 to 7.23 %. The organic carbon in all soil samples was found to be high, which may due to decomposition of crop residues on the soil surface.

The ammonia and nitrate concentrations in the soil samples of the studied area were 3.13 – 12.54 kg/ha and 2.68-18.86 kg/ha, respectively. These values mainly depend on the moisture content and the enzymatic activity in the soil (which may vary from one place to another).

The total nitrogen content values for all soil samples were found to be in the range from 784 to 1784.8 kg/ha. The high nitrogen values are due to both the excessive application of nitrogenous fertilizers and the leguminous crop rotation.

The calcium and magnesium ions were found to range from 1.8 to 12.7 meq/l and from 1.0 to 11.4 meq/l, respectively, except for the sample S3. Sodium and potassium concentrations were found to be between 100.8 to 257.6 kg/ha and 44.8 to 188.16 kg/ha, respectively. For urea-applied soils, the hydrolysis of urea yields nitrate ions which are not strongly adsorbed by the soil particles and will move down through the soil profile. The negatively charged nitrate ions carry positively charged basic cations, such as calcium, magnesium, sodium, and potassium in order to compensate for the electrical charge on the soil particles. The depletion of these basic cations will accelerate the acidification process of the soil which is another reason for the decrease in soil pH.

Phosphorus levels in the studied area varied from 62.72 to 288.96 kg/ha. The available phosphorus levels in all sampling areas were found to be higher than the normal range, which is due to excessive application of phosphate fertilizers [18].

These results are demonstrated in Figs. 1-3.

Table 1. Sampling points with sampling codes, crop types and types of fertilizers applied to the agricultural field

No	Sampling location	Types of crops cultivated	Types of fertilizer	Land type	Quantity of urea applied, kg/ha
S1	Marballi	Ragi, Vegetables	Urea	Rainfed area	100
S2	Arasinakere	Cotton	Urea	Rainfed area	100
S3	Jayapura	Maize, Cabbage, Cauliflower, Tomato	Urea	Rainfed area	100
S4	Doora	Banana, Papaya, Pomegranate, Lemon	Urea	Rainfed area	100
S5	Varakodu	Areca nut, Banana plantation	Urea	Irrigated land	100
S6	Mosaimbayanahalli	Ragi, Paddy, Maize	Urea	Irrigated land	100
S7	Duddgere	Ragi, Paddy	Urea,	Irrigated land	100
S8	Varuna	Paddy	Urea	Irrigated land	100
S9	Koppalure	Coconut, Areca nut	Urea	Garden land	100
S10	Gejjagalli	Sugar cane, Green leafy vegetables	Urea	Garden land	100
S11	Mandakalli	Turmeric, Banana plantation, Green leafy vegetables	Urea	Garden land	100
S12	Bandipalya	Coconut, Green leafy vegetables, Banana	Urea	Garden land	100

.

Table 2. Physico-chemical characteristics of agricultural soil samples of Mysore.

Parameters	Normal range	Rainfed area				Irrigated land				Garden land			
		S-1	**S-2**	**S-3**	**S-4**	**S-5**	**S-6**	**S-7**	**S-8**	**S-9**	**S-10**	**S-11**	**S-12**
Texture	-	Clay	Sandy loam	Sandy Clay loam	Sandy	Clay sand	Sandy clay loam	Sandy clay loam	Sandy clay loam	Sandy clay loam	Sandy loam	Sandy loam	Sandy soil
Moisture content %	-	37.5	32.5	43.33	10.2	13.04	13.63	18.18	19.04	22.5	37.03	20	14.13
WHC %	-	90.3	78.3	87.6	47.9	69.8	66.92	52.8	71.8	73.8	54.6	52.9	46.8
Bulk density mg/m^3	1-1.65	1.12	1.2	1.12	1.3	0.98	1.18	0.98	1.06	0.94	1.1	1.16	1.1
Particle density mg/m^3	2-2.65	5	2.5	3.33	2.5	2.5	3.33	2.5	3.33	3.33	2.5	2.5	2
Porosity %	30-55	77.6	52	66.4	48	63.2	64.6	60.8	68.2	71.5	56	53.6	45
UREA Residues 100 kg/ha	-	**1.12**	-	**2.68**	**7.16**	**6.27**	**4.48**	**8.73**	**3.80**	**2.68**	**1.56**	**2.01**	**3..58**
pH	6.5-7.5	7.81	6.94	8.16	6.51	8.12	7.02	5.81	7.94	7.78	7.39	8.31	8.09
Conductivity ds/m	0-2	0.31	0.36	0.39	0.11	0.23	0.18	1.04	0.62	0.41	0.48	0.29	0.48
Calcium meq/lit	10-30	8.7	1.9	12.7	8.2	3.9	2.6	3.9	1.8	7.4	9.1	4.6	5.6
Magnesium meq/lit	5-10	3.2	1.8	11.4	6.4	2.9	3.9	4.1	1.0	3.4	7.1	5.2	4.1
OC %	0.50-0.75	0.57	1.32	1.98	0.69	2.29	2.61	1.89	2.7	7.23	1.23	0.62	1.8
Chloride %	0.020-0.120	0.0923	1.597	0.0639	0.0852	0.0639	0.0142	0.113	0.0497	0.0994	0.149	0.0568	0.0284
TN Kg/ha	200-500	1254.4	784	1254.4	1724.8	705.6	1077.6	940.8	627.2	1411.2	1176	1960	1411.2
Ammonia kg/ha	-	7.39	5.82	9.40	4.25	6.72	7.84	3.36	4.92	12.54	5.82	7.39	3.13
Nitrate kg/ha	-	6.72	5.37	7.61	5.6	7.16	4.48	3.13	2.68	8.08	3.58	4.92	18.86
Sodium kg/ha	-	219.52	257.6	208.32	244.18	129.92	100.8	194.88	159.04	150.08	217.28	132.16	145.6
Potassium kg/ha	50-125	168	188.16	165.76	170.24	53.76	58.24	76.16	44.8	76.16	96.32	51.52	64.96
Phosphorus kg/ha	11.2-22.4	194.88	134.4	134.4	235.2	170.24	132.16	288.96	62.72	125.44	105.28	125.44	210.56

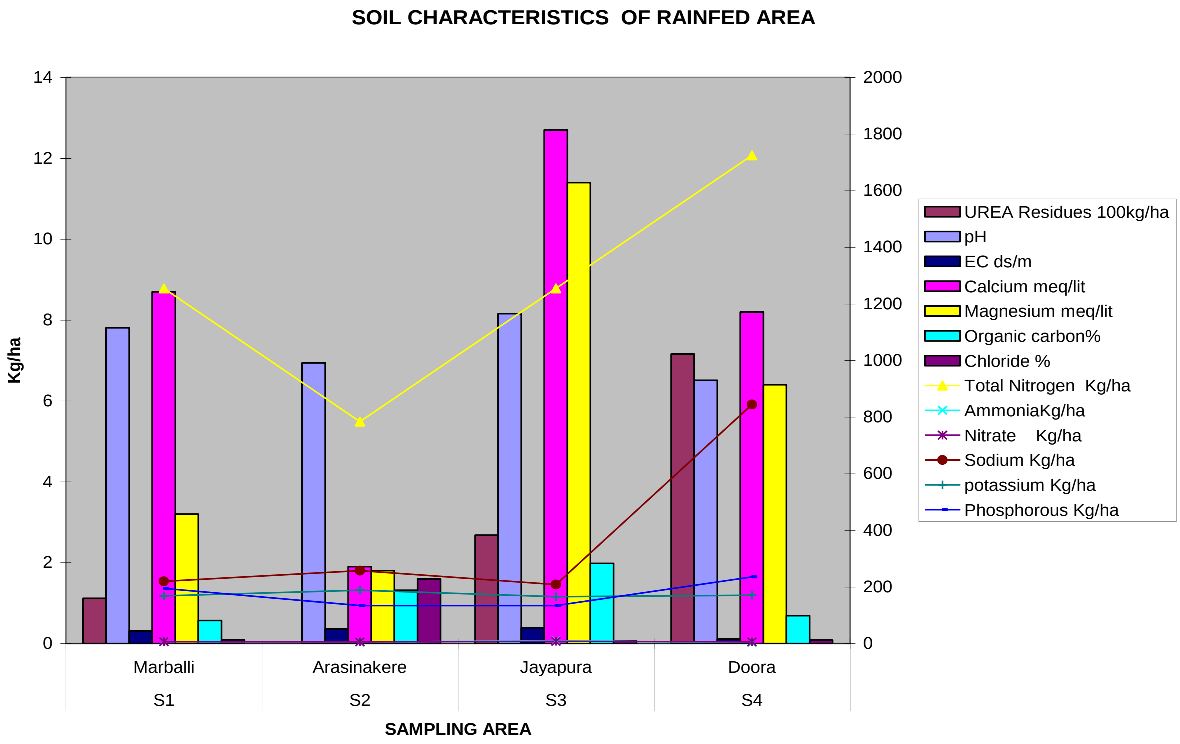

Fig.1. Soil characteristics of rainfed area.

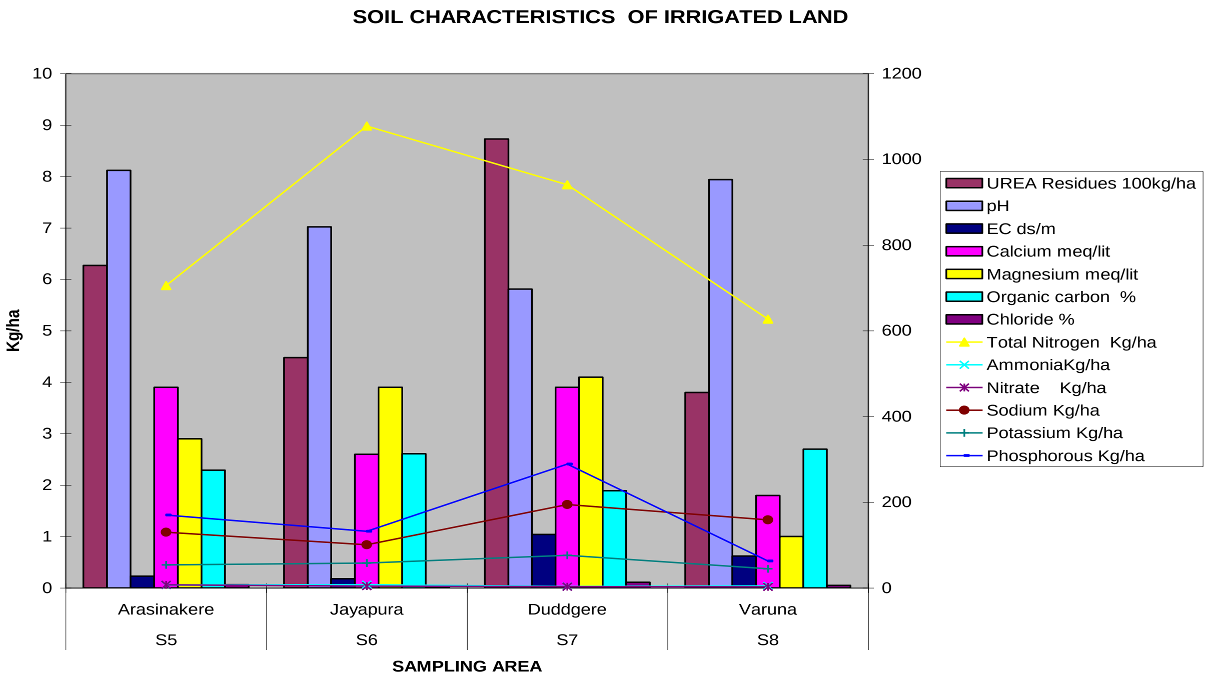

Fig.2. Soil characteristics of irrigated land.

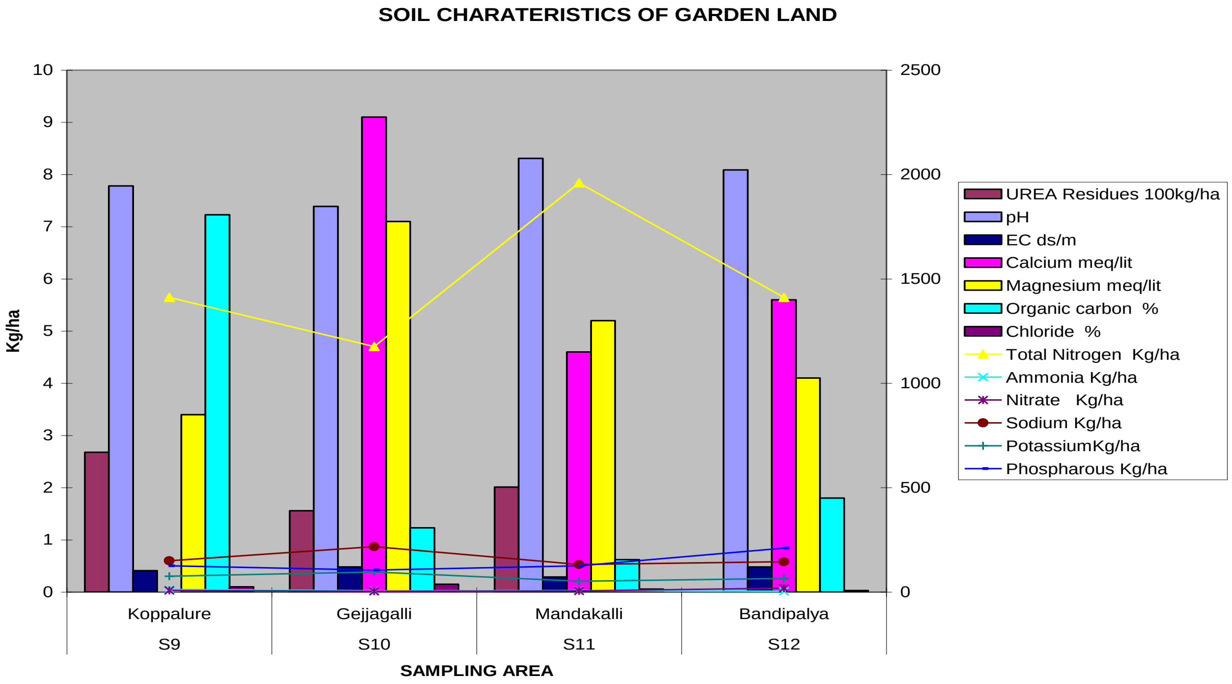

Fig.3. Soil characteristics of garden land.

4. CONCLUSIONS

The present study indicates that the application of urea fertilizers has a great influence on the physico-chemical properties of the soil. The pH values of soil samples S4 and S7 were found to be acidic and declining in basic cations. In all sampling areas the phosphorus levels were found to be higher, which is due to over-use of phosphate fertilizers. It follows from the study that judicious application of inorganic fertilizers must be kept in order to preserve soil quality and productivity. It is necessary to apply liming material to reduce the acidification of agricultural lands and to maintain basic cation levels in soil.

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ОПРЕДЕЛЯНЕ НА ОСТАТЪЧЕН КАРБАМИД В ПРОБИ ОТ ЗЕМЕДЕЛСКИ ПОЧВИ ОКОЛО ГР. МАЙСОР, ЩАТ КАРНАТАКА В ИНДИЯ

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(Резюме)

Настоящето изследване съдържа анализи на 12 почвени проби от естествено напоявани, напоявани и градински земи в земеделската област около гр. Майсор. Пробите са анализирани за остатъчен карбамид, влага, текстура, обемна плътност, плътност на частиците, влагозадържащ капацитет, pH, електропроводимост, хлориди, органичен въглерод, калций, магнезий, общ азот, амонячен азот, нитрати, натрий, калий и фосфор. Изследването разкрива, че употребата на карбамида като тор има голямо влияние върху физико-химичните свойства на почвите. Установено е,ч е почвени проби S4 и S7 са естествено кисели. Намерени са отклонения от нивата на основни катиони, като калций и магнезий за мнозинството на пробовзиманията. Установени са повишени нива на фосфора за всички изследвани места, което се дължи на прекомерно торене с форфорни торове. Направено е заключението, че разумната употреба на карбамид може да спомогне за поддържането на качеството на почвите и плодородието им. Необходимо е обаче да се следи за киселинния ефект върху земеделските земи, за да се поддържа основното основното ниво на катионите в тях.

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A Novel Route for the Synthesis of Six- and Seven- Membered 6-Trimethylsilylspiro[4,n]alk-6-enes

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A novel route for the synthesis of 6-trimethylsilylspiro[4,5]dec-6-ene and 6-trimethylsilylspiro[4,6]undec-6-ene by the Wurtz-Fittig type coupling reaction of 6-iodospiro[4,5]dec-6-ene and 6-iodospiro[4,6]undec-6-ene with alkali metals and chlorotrimethylsilane in good yields is reported. The compounds serve as a new class of spiranyl cyclic vinylanionic synthons.

Key words: spiranes, cyclic vinylsilanes, anionic synthons, Wurtz-Fittig reaction.

1. INTRODUCTION

Cyclic vinylsilanes are an important class of compounds in organic synthesis [1]. The compounds serve as masked vinylanionic synthons [2]. Spirocyclics on the other hand, are important compounds with diverse properties, which are found to occur as subunits in many natural products [3]. To our knowledge, there is only one report on the preparation of spiranyl cyclic vinylsilanes in the literature by Paquette [4]. Substitution of the trimethylsilyl group in simple spirocyclic compounds alters the electronic properties of the molecules, thereby providing a route for easy functionalization with diverse functional groups [5].

We had earlier prepared a wide variety of simple and substituted cyclic vinylsilanes by the Wurtz-Fittig coupling reaction of the corresponding cyclic vinyl bromides/chlorides with sodium and chlorotrimethylsilane in different anhydrous solvents [6].

The most recent of the substituted cyclic vinylsilanes synthesized by us are the 2-trimethylsilylcycloalkenones [7]. The compounds are α-acylvinyl anionic synthons [8].

During our study on the synthesis of the 2-trimethylsilylcycloalkenones, we found 6-trimethylsilyl-7-methyl-1,4-dioxaspiro[4,5]dec-6-ene to be highly unstable even in the mildest acidic medium [9]. The 6-trimethylsilyl-7-methyl-1,4-dioxaspiro[4,5]dec-6-ene could not be isolated under the conditions of our work, even though the compound has been isolated by Yus [10]. Therefore, we chose to prepare the corresponding carbon equivalents, which are the spiranyl-compounds. These novel spiranyl cyclic vinyl silanes are expected to be very stable.

2. EXPERIMENTAL

IR spectra were recorded on a Shimadzu FT-IR 8400S spectrometer. NMR spectra were recorded on a Bruker AMX 400 MHz spectrometer. GC was run on a Shimadzu 14-B/Mayura 9800 Gas Chromatograph using a SE-30 SS 2m × 1/8” column. Yields refer to the isolated yields of the products. GC-MS spectra were obtained using a Shimadzu GC-MS QP 5050A.

General procedure for the preparation of spiro[4, n]alkanones

Spiro[4,n]alkanones (3 and 4): To a magnetically stirred suspension of potassium *tert*-butoxide (2.2 mol equivalents) in 100 mL refluxing anhydrous benzene was added a mixture of cycloalkanone (10 g) and 1,4- dibromobutane (1.2 mol equivalents) over a period of 40 min. After completion of the addition, the mixture was further refluxed for 10 hrs. The reaction mixture was cooled, diluted with 50 mL ether and added to 100 mL of ice cold water. The organic layer was separated, and the aqueous layer was extracted with ether (3×50 mL). The combined organic extracts were washed with water (2×50 mL), brine (2×30 mL) and dried over anhydrous potassium carbonate. The solvent was removed on a rotary evaporator and distilled *in vacuo* to isolate spirocyclic ketones **3** and **4** in yields as reported in the literature.

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Spiro[4,5]decan-6-one (3) [13]: IR (Neat); 2937, 2864, 1708, 1448, 1342, 1311, 1236, 1193, 1126, 1060, 954, 904, 852, 800 ; **^{1}H NMR (**CDCl$_3$)**: δ** 1.27-1.28 **(** m, 2H), 1.30-1.31 (m, 4H), 1.46-1.49 (m, 4H), 1.70-1.71 (m, 2H), 1.91-1.96 (m, 2H), 2.21-2.31 (m, 2H). **GC-MS:** m/e (rel. intensity**):** 152 (36), 123 (11), 111 (100), 95 (35), 81 (22), 67 (93), 55 (29), 41 (44).

Spiro[4,6]undecan-6-one (4) [12]: IR (Neat) ; 2931, 2858, 1703, 1446, 1346, 1313, 1141, 1076, 1029, 979, 937, 840 ; **^{1}H NMR (**CDCl$_3$)**: δ** 1.27-1.33 (m, 2H), 1.39-1.41 (m, 2H), 1.51-1.57 (m, 10H), 1.69-1.72 (m, 2H), 1.82-1.91 (m, 2H). **^{13}C NMR** (DMSO)**: δ** 25.4, 26.0, 26.3, 30.1, 36.5, 37.9, 59.0, 216.4. **GC-MS:** m/e (rel. intensity**);** 166 (10), 148 (3), 125 (26), 95 (37), 81 (29), 67 (100), 55 (38), 41 (68).

6-Iodospiro[4,n]alk-6-enes (5 and 6): Triethylamine (1.5 mol equivalents) and hydrazine monohydrate (18 mol equivalents) were added to a solution of spiro[4,n]alkanones in absolute ethanol (25 mL) and the mixture was refluxed for 12 hours. Ethanol was evaporated *in vacuo*. The residue was extracted with ether (3×20 mL), the organic layers were combined, dried over anhydrous sodium sulfate, and evaporated *in vacuo* to get the hydrazones of **3** and **4.**

A solution of iodine (2.2 mol equivalents) in dry ether (50 mL) was added dropwise to a solution of spiro[4,n]alkanone hydrazones (4 g) and 1,5–diazabicyclo[4.3.0]non-5-ene (6 mol equivalents) in dry ether (50 mL). After the reaction mixture was stirred for 3.5 hours, it was quenched with saturated sodium bicarbonate solution (20 mL). The layers were separated and the aqueous layer was extracted with ether (3×40 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and evaporated *in vacuo.* The residue was chromatographed using silica gel to isolate **5** and 6**.** Further distillation gave the pure compounds.

6-Iodospiro[4,5]dec-6-ene (5): B.p. 80-82°C/1 mm **IR (Neat) ;** 2933, 2864, 1618, 1444, 1319, 1180, 1085, 1024, 954, 877,804,738,688 cm^{-1}; **^{1}H NMR (**CDCl$_3$)**: δ** 1.47 (m, 2H), 1.67 (m,4H), 1.75 (m, 4H), 1.83 (m, 2H), 2.07 (m,2H), 6.43 (1H, t, *J*=4 MHz), **^{13}C NMR** (CDCl$_3$)**: δ** 19.8, 25.2, 29.9, 36.5, 40.8, 49.7, 117.9, 138.9 ; **GC-MS:** m/e (rel. intensity**):** 262 (36), 135 (83), 107 (26), 93 (81), 79 (72), 66 (100), 54 (20), 40 (42).

6-Iodospiro[4,6]undec-6-ene (6) B.p. 80-82°C/0.6mm **IR**(Neat)**:** 2929, 2862,1699, 1608, 1446, 1359, 1330, 1220, 1101, 1024, 995, 937, 844, 815, 715, 676 cm^{-1}; **^{1}H NMR (**CDCl$_3$)**: δ** 1.57-1.58 (m, 4H), 1.64-1.65 (m, 4H), 1.73-1.74 (m, 4H), 1.83-1.85 (m, 2H), 2.03-2.07 (m, 2H), 6.54 (t, 1H, *J*=6.8 Hz); **^{13}C NMR** (CDCl$_3$)**: δ** 23.6, 25.0, 26.3, 29.4, 33.1, 41.6, 55.6, 123.0, 142.9. **GC-MS:** m/e (rel. intensity**):** 276 (0.9), 149 (8), 126 (16), 107 (10), 91 (31), 79 (31), 67 (33), 41 (100); Anal. calcd. for $C_{11}H_{17}I$: C, 47.84%; H, 6.20%. Found: C, 48.13%; H, 6.34%.

Synthesis of 6-trimethylsilylspiro[4,n]alkenes (7 and 8):

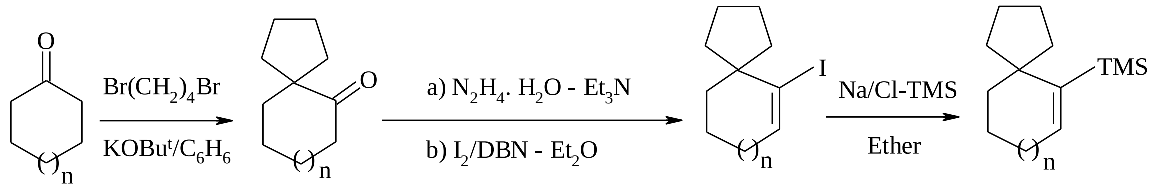
To a suspension of finely cut metal pieces (5 mol equivalents) and chlorotrimethylsilane (3 mol equivalents) in 10 mL of anhydrous ether, 6-iodospiro[4,n]alkene (1g) in 5 mL of dry ether was added. The mixture was refluxed with efficient stirring on an oil bath at 45^0- 50^0C. The completion of the reaction was followed by GC. The mixture was cooled; the precipitated solids and remaining metal pieces were removed by filtering on a plug of glass wool and washed with ether (2×10 mL). The combined organic extract was washed with saturated sodium bicarbonate (15 mL), saturated sodium chloride (10 mL) and dried (anhydrous Na_2CO_3). Concentration *in vacuo* and distillation yielded **7** and **8.**

6-Trimethylsilylspiro[4,5]dec-6-ene (7): B.p. 75-78°C/1 mm; **IR (neat):** 2952, 2929, 2871, 1595, 1445, 1406, 1249, 1054, 1002, 943, 836, 754, 684, 634 cm^{-1}; **^{1}H NMR (**CDCl$_3$)**: δ** 0.10 (s, 9H), 1.37 – 1.39 (m, 2H), 1.40 -1.44 (m, 2H), 1.56 – 1.59 (m, 2H), 1.65 - 1.66 (m, 6H), 1.90 - 2.03 (m, 2H), 6.03 (t, 1H, *J*=3.6Hz); **^{13}C NMR** (CDCl$_3$)**: δ** 19.2, 24.0, 27.1, 35.2, 39.0, 46.4, 137.5, 146.1; **GC-MS:** m/e (rel. intensity): 208 (2), 193 (9), 165 (3), 134 (100), 119 (9), 105 (10), 91 (22), 73 (86), 59 (35), 44 (17)

6-Trimethylsilylspiro[4,6]undec-6-ene (8): B.p.: 72-75°C/0.8mm **IR**(Neat)**:** 2921, 2858, 1645, 1446, 1247, 1151, 1099, 960, 931, 837, 754 cm^{-1}; **^{1}H NMR (**CDCl$_3$)**: δ** 0.096 (s, 9H), 1.42-1.48 (m, 4H), 1.54-1.68 (m, 8H), 1.82-1.86 (m, 2H), 2.16-2.21 (m, 2H), 6.13(t, 1H, *J* = 6.4 Hz); **^{13}C NMR** (CDCl$_3$)**: δ** 2.16, 3.53, 26.60, 27.33, 30.54, 36.51, 37.65, 51.72, 141.76, 153.51 ; **GC-MS:** m/e (rel. intensity**):** 222 (0.3), 207 (0.8), 179 (0.5), 148 (30), 133 (6), 91 (13), 73 (100), 59 (33.36), 45 (28) Anal. calcd. for $C_{14}H_{17}Si$: C, 75.59%; H, 11.78%. Found: C, 75.92%, H, 12.38%

3. RESULTS AND DISCUSSION

In expansion of the scope of the Wurtz-Fittig coupling reaction, we now report for the first time the successful synthesis of six- and seven-membered 6-trimethylsilylspiro[4,n]alk-6-enes: 6-trimethylsilylspiro[4,5]dec-6-ene (**7**) [4] and 6-trimethylsilylspiro[4,6]undec-6-ene (**8**) by the route



1: n=1
2: n=2

3: n=1
4: n=2

5: n=1
6: n=2

7: n=1
8: n=2

Scheme-1: Synthesis of Novel Spiranyl Cyclic Vinylsilanes

shown in **Scheme 1**. This route expands the scope and utility of the Wurtz-Fittig coupling reaction. The starting spiro[4,5]decan-6-one (**3**) [11] and spiro[4,6]undecan-6-one (**4**) [12] were prepared by alkylating cyclohexanone (**1**) and cycloheptanone (**2**) with 1,4-dibromobutane using potassium *tert*-butoxide in benzene solvent. The compounds **3** and **4** were reacted with hydrazine hydrate and triethylamine for their conversion to corresponding hydrazones. Monitoring the reaction by GC-MS indicated the formation of bis-spiro[4,n]alk-6-ylidene-hydrazine along with the required hydrazones of **3** and **4**. The mixture of azines and hydrazones without further purification was reacted with I_2 / DBN according to the Barton vinyl iodination method to their corresponding 6-iodospiro[4,5]dec-6-ene (**5**) and 6-iodospiro[4,6]undec-6-ene (**6**) [13]. 6-Iodospiro[4.5]dec-6-ene (**5**) is not reported in literature. However, for the vinyl bromide equivalent of **5** see [14].The literature survey indicates that there are no precedents for the conversion of spiranyl cyclic vinyl iodides to spiranyl cyclic vinylsilanes through the Wurtz-Fittig reaction, even though Yus has employed lithium metal for the synthesis of 6-trimethylsilyl-1,4-dioxaspiro[4,5]-6-decene [10] .

We have screened the alkali metals Li, Na and K as electron sources for the formation of a cyclic vinyl anion. The comparative reactivity of **5** and **6** with alkali metals is given in Table 1.

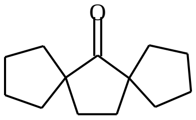
Table 1. Comparative reactivity of spiranyl cyclic vinyl iodides with alkali metals

Compound	Metal	Product	Yield, %
5	Lithium	**7**	81-84
5	Sodium	**7**	67-72
5	Potassium	**7**	63-67
6	Lithium	**8**	84-88
6	Sodium	**8**	71-75
6	Potassium	**8**	69-73

The reactions were repeated 10 times for each substrate and the range of isolated yields is indicated in Table 1. We have found that metallic lithium gave better yields over sodium and potassium.

The best results with lithium metal can be attributed to the greater solubility of the spiranyl vinyl lithium ion pairs in anhydrous ether solvent and also to the controlled reactivity due to their covalent nature originating from the polarizing power of the lithium ion. This observation is also in good conformity with the HSAB theory [15].

We have also tried to extend the methodology to prepare the five- and eight- membered spiranyl cyclic vinylsilanes. Reaction of cyclopentanone with 1,4-dibromobutane and potassium *tert*-butoxide gave the dispiro[4.1.4.2]tridecan-6-one as the major product. In case of cyclooctanone, though we have isolated the spiro[4,7]dodecanone and its hydrazone, the corresponding 6-iodospiro[4,7]dodec-6-ene could not be isolated in the conditions employed. The structure of the dispiro[4.1.4.2]tridecan-6-one was found to be:



To our knowledge, this is the first instance where spiranyl cyclic vinyl iodides are being used for the synthesis of spiranyl cyclic vinylsilanes using the Wurtz-Fittig coupling reaction. The compound **7** has been reported by Paquette through the tosyl hydrazone route [4]. To our knowledge the compound **8** has not been reported. The method we hereby report is simple and with a high yield. The spiranyl cyclic vinylsilanes **7** and **8** may serve as starting materials in the synthesis of the muscone related group of compounds [16].

4. CONCLUSIONS

A novel route for the synthesis of six- and seven- membered 6-trimethylsilylspiro[4,n]alk-6-enes by the Wurtz-Fittig type coupling reaction of the corresponding spiranyl iodides with alkali metals lithium/sodium/potassium and chlorotrimethylsilane in good yields is reported. The compounds could serve as novel spiranyl anionic synthons.

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НОВ МАРШРУТ ЗА СИНТЕЗ НА ШЕСТ И СЕДЕМ АТОМНИ ПРЪСТЕНИ НА 6-ТРИМЕТИЛ-СИЛИЛ-СПИРО [4,N] АЛК-6-ЕНИ

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(Резюме)

Съобщава се за нов маршрут за синтезата на 6-триметил-силил-спиро [4,6] дек-6-ен и 6-триметил-силил-спиро[4,n] ундек-6-ен по реакцията на Wurtz-Fittig между 6-йодоспиро[4,5]дек-6-ен and 6-йодоспиро[4,6]ундек-6-ен с алкални метали and хлор-триметил-силан с добри добиви. Съединенията служат за нов клас от спиранилни циклени жинил-йонни синтони.

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Carbon materials on the base of inorganic-organic polymer nanocomposite precursors

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Carbon materials with very good mechanical properties and SiC are produced from inorganic-organic polymer nanocomposite precursors. It was found that the main factor which determines the excellent mechanical properties of the obtained material is the interaction of the binder (PAN) with the filler (silica and zeolite). The “baking criterion” was used for estimation of the interaction between filler and binder during formation and heat treatment of the initial composites. The corellation between the „baking criterion” and the compressive strength of the obtained material was determined. Pressing of the compositions is of big significance for improving the surface contact between the binder and the filler.

Key words: inorganic-organic polymer, silicon carbide, carbon, silica.

1. INTRODUCTION

The combination of the characteristics of synthetic polymers (elasticity, reduced density and easy processability) with those of inorganic materials (hardness, thermal stability and large availability) opens new perspectives for obtaining new materials on the base of inorganic-organic composites. The synthesis and the applications of inorganic-organic nanohybrids were developed mainly in the last decade [1-7]. There are four important methods for obtaining of hybrids based on organic polymers and inorganic oxides [8]:

- The polymer and the inorganic component are formed simultaneously by a process, for example, sol - gel polymerization process [9-10];
- The polymer is formed by direct polymerization on the surface or in the pores of the already synthesized oxide material [11-12];
- The inorganic oxide compound is formed in a polymer by a sol - gel process (for example, biomineralization) [13-14];
- Both components are previously prepared and react one with another and/or form a hybrid network through interpenetrating reactions [15].

The properties of the obtained materials depend on such factors as shape and size of the filler particles, composition of binder and interaction between the components [16].

During the preparation of the composition, part of the binder molecules are adsorbed on the surface of the filler particles. These molecules could interact with the filler surface and with other substances in the adsorbed part of the binder. It was found that in order to characterize this interaction, it is appropriate to use a "baking criterion" proposed for the assessment of the baking ability of the pitches [17]. The “baking criterion” permits [18] the qualitative characterization of the degree of interaction between filler and binder and is determined by the expression:

$$\Delta K = (\frac{100.K_c - M_f K_f}{M_b K_b} - 1).100$$

where ΔK = “baking criterion”, %

K_c= amount of the solid residue of the composite, %

K_f= amount of the solid residue of the filler, %

K_b= amount of the solid residue of the binder, %

M_f= amount of the filler in the composite, %

M_b= amount of the binder in the composite, %

ΔK is the increase in the solid residue of the binder when it is in the composition with the filler, and takes into account the interaction between binder and filler during the preparation of the carbon material.

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2 EXPERIMENTAL

Raw materials

Mesoporous silica was obtained in the INCDMNR-IMNR (National Research – Development Institute for Non-ferous and Rare Metals – Bucarest, Romania) laboratory and was used as received.

The synthetic zeolite HZSM-5 was supplied by UPG (University for Oil and Gases – Ploiesti, Romania) and was used as received.

Inorganic-organic polymer nanocomposite synthesis and analysis of the products

The inorganic powder (silica, HZSM-5) was soaked in acrylonitrile (containing 1% azo-bis-isobutyronitrile based on monomer) in 50 mL glass ampoules. The monomer was introduced in different volume/weight ratios to silica (Table 1) and to HZSM-5 (Table 2), and the ampoules were purged with nitrogen for 10 min, in order to avoid the possible inhibition effect of oxygen. Then, the ampoules were sealed with a rubber tube and were tightened with a Hoffman clamp. For silica, the samples were named P1-P6 s-PAN, respectively, and for HZSM-5 zeolite, the samples were named P1-P6 z-PAN. Inhibitions were performed in the sealed ampoules in an Elma S10 Elmasonic ultrasonication bath containing water, for 1 h. After that, the ampoules were kept for 24 h at room temperature without ultrasonication. Finally, a new 1 h ultrasonication was applied. The composite materials were obtained by the introduction of the glass ampoules in an ultra-thermostated water bath at 65^{o}C. Although the initiator concentration becomes practically 0 after 10 h, the ampoules were kept 24 h for polymerization, in order to ascertain that the monomer conversion is practically complete, eliminating any doubt of monomer presence in the composite. In these conditions the polymerization of acrylonitrile within the silica or HZSM-5 pores occurred.

Thermogravimetry of the composites was performed on the Q600 TA Instruments analyzer, using air atmosphere from 20°C to 700°C using 10°C/min rate.

Analysis of heat- treated pellets "baking criterion" determination

The "baking criterion" was determined by preparation of pellets from s-PAN and z-PAN composites using pressing in a press form and baking the pellets at a heating rate of 1^{o}C/min up to 800^{o}C. The solid residue from the filler (silica or zeolite) - K_f and from the binder - K_b (PAN) was determined under the same conditions.

Pellets from composites were first heat-treated up to 1300^{o}C and then up to 1600^{o}C at a heating rate of 5^{o}C/min. All investigated composites were characterized by X-ray diffraction analysis on a Bruker D8 Advance diffractometer using CuKα radiation, and by scanning electron microscopy on a Philips 515 instrument. The average crystallite size was calculated according to the Scherrer formula by using the Topas V3 programme [19].

3. RESULTS AND DISCUSSION

Compositions of silica/PAN and zeolite/PAN were prepared in the proportions presented in Tables 1 and 2.

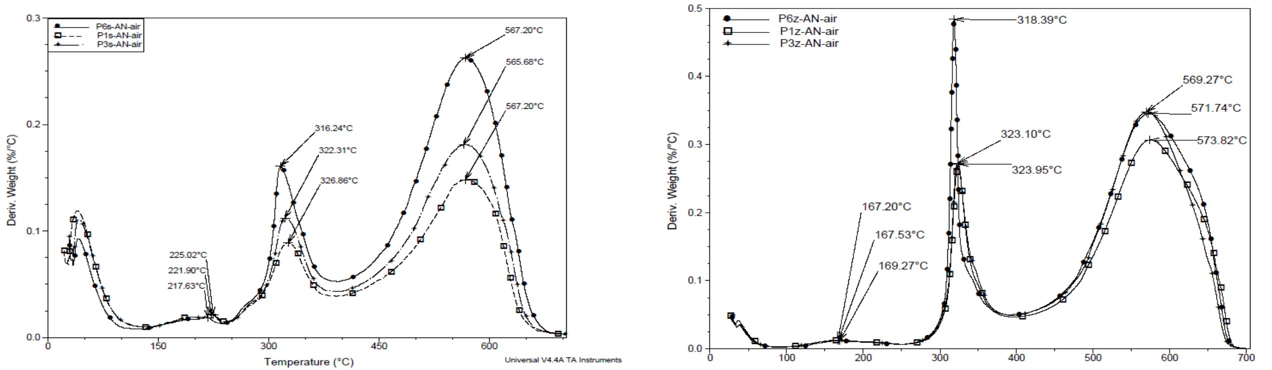
Table 1. Composition of silica and acrylonitrile samples, precursors for obtaining nanocomposites

Sample	Silica (g)	Acrylonitrile	
		(mL)	(g)
P1 silica-polyacrylonitrile	2.0	1.5	1.20
P2 silica-polyacrylonitrile	2.0	1.8	1.44
P3 silica-polyacrylonitrile	2.0	2.0	1.60
P4 silica-polyacrylonitrile	2.0	2.2	1.76
P5 silica-polyacrylonitrile	2.0	2.5	2.00
P6 silica-polyacrylonitrile	2.0	2.8	2.24

Table 2. Composition of zeolite and acrylonitrile samples, precursors for obtaining nanocomposites

Sample	Zeolite HZSM-5 (g)	Acrylonitrile	
		(mL)	(g)
P1 zeolite-polyacrylonitrile	2.0	4.5	3.60
P2 zeolite-polyacrylonitrile	2.0	4.8	3.84
P3 zeolite-polyacrylonitrile	2.0	5.0	4.00
P4 zeolite-polyacrylonitrile	2.0	5.2	4.16
P5 zeolite-polyacrylonitrile	2.0	5.5	4.40
P6 zeolite-polyacrylonitrile	2.0	5.8	4.64

DTG (diffential thermo-gravimetric) analysis of silica/PAN and zeolite/PAN composites is presented on Fig. 1. The curves indicate two main intervals of weight loss, 280-360^{o}C and 440-640^{o}C, for both composites. The first interval is due to the beginning of polymer degradation. The second interval corresponds to processes of deep degradation, which finish with cyclization of the



(a) (b)

Fig. 1. DTG curves for silica/PAN (a) and zeolite/PAN (b) composites.

polymer and formation of the final structure of the material for this stage.

Fig. 1 shows that the temperatures of the beginning of the main intervals of weight loss increase with increasing the content of the filler (silica and zeolite) in the composite. At the same time the weight loss decreases with increasing the content of filler in the composite. This is due to the extended interaction between filler and binder in the composite ias a result of the increased filler content. The results reveal a considerable influence of the interaction between the filler and the binder in the composite on the processes occurring during heat treatment of the composite.On the base of the results of the DTG analysis, the temperature of heat treatment of pellets of composites for determination of the "baking criterion" was determined as 800°C, *i.e.*, when the reaction of degradation is completed and the synthesis passes through carbonization of the polymer part of the composite.

„Baking criterion"

Investigations were carried out to assess the baking ability of PAN in composition with silica and zeolite. In Tables 3 and 4 data are presented for the "baking criterion" and the compressive strength of the composites containing different amounts of binder.

The yield of solid product from PAN after heating up to 900°C is 42.1% in argon atmosphere.

The yield of solid product from silica after heating up to 900°C is 91.1%; from the zeolite it is 81.1%, in argon atmosphere for both.

The yield of solid product from polymer in the pellets was calculated using equation:

$$\Delta Y_p = (\frac{Y_p - Y_s}{Y_p} - 1) \times 100 = (\frac{Y_p - aY_s}{bY_p} - 1) \times 100$$

where: Y_p – solid yield from pellets;

- Y_s – solid yield from pure silica at the same temperature - 900°C;
- Y_p – solid yield from pure polymer at 900°C;
- a – amount of silica or zeolite, respectively, in the composite;
- b – amount of polymer in the composite.

Table 3. Data for the heat treatment up to 800°C of pellets of silica/PAN composites

Sample	Solid yield %	Increase of solid yield from polymer in pellets, %	Compressive strength, MPa
P_{1S}	69.5	19.9	4.0
P_{2S}	68.9	23.9	5.0
P_{3S}	68.2	24.5	8.0
P_{4S}	67.2	22.3	7.0
P_{5S}	65.9	20.9	6.0
P_{6S}	63.8	15.3	6.0

Table 4. Data for the heat treatment up to 800°C of pellets of zeolite/PAN composites

Sample	Solid yield, %	Increase of solid yield from polymer in pellets, %	Compressive strength, MPa
P_{1Z}	62.2	10.4	6.0
P_{2Z}	61.9	11.4	7.0
P_{3Z}	60.3	7.1	6.0
P_{4Z}	58.8	3.2	5.0
P_{5Z}	58.7	5.2	5.0
P_{6Z}	57.6	3.7	5.0

These data indicate that due to the interaction between polymer and silica or zeolite, respectively, the solid yield from the polymer in the composite (especially as pellets) significantly increases in comparison with the solid yield from pure polymers. It seems that the increase of the solid yield depends on the proportion of the polymer and silica or zeolite, respectively, in the composite. The data show that, with the increase in binder content in the composite, ΔK increases to a definite value. The further increase of the binder amount results in a decrease of ΔK. When increasing the solid yield from polymer in the composite, the compressive strength of the obtained material increases. Obviously, there is a correlation between the solid yield from the polymer in the composite and the compressive strength of the final material. The lower increase of the solid yield from PAN in the composite with zeolite, in comparison with the composite with silica, is in the result of the much higher amount of PAN in these composites. The mechanical properties of the samples obtained for silica/PAN and zeolite/PAN composites are very good. The data show that the mechanical properties of the pellets obtained from the silica/ PAN composite, are better than these of the pellets obtained from the zeolite/PAN composite.

This is due to the higher proportion of the filler in the silica/PAN composite, which leads to stronger interaction between the filler and the binder, and a subsequent increase in the mechanical strength of the obtained material. This is also confirmed by the values of the ”baking criterion”, which correlates with the mechanical strength characteristics of the material.

In order to increase the mechanical strength and to obtain SiC, after determination of the “baking criterion”, the pellets were first heated up to 1300°C, and then up to 1600°C. As a result, the mechanical strength of the pellets was increased up to 10 MPa. In Figs. 2 and 3 the results from the XRD investigations of the pellets obtained from silica/PAN and zeolite/PAN composites heated first up to 1300°C (Fig. 2) and then up to 1600°C (Fig. 3) are presented.

Fig. 2 shows the X-ray diffraction spectra of pellets obtained from silica/PAN and zeolite/PAN composites heated up to 1300°C. In the XRD pattern (Fig. 2) of a pellet obtained from a zeolite/PAN composite, a peak at 2Θ=24° was detected. This peak corresponds to the 002 reflex of carbon and it is characteristic of the interlayer spacing in graphite. In this case the peak 002 is more narrow and asymmetric, indicative of highly ordered structure, than in the case of pellets obtained from silica/PAN composite. The main reason for this is the significantly higher filler content in silica/PAN composites in comparison with zeolite/PAN composites, because the filler particles hinder the structuring of the material and the formation of bigger crystallites during thermal treatment.

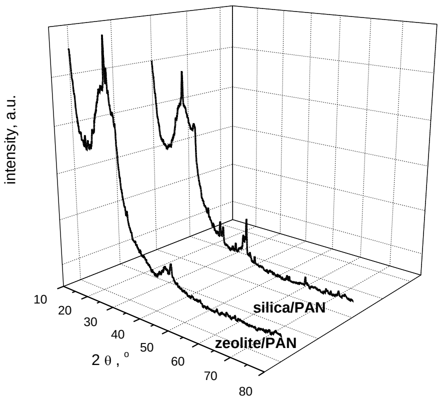


Fig. 2. X-ray diffraction patterns of pellets heated up to 1300°C.

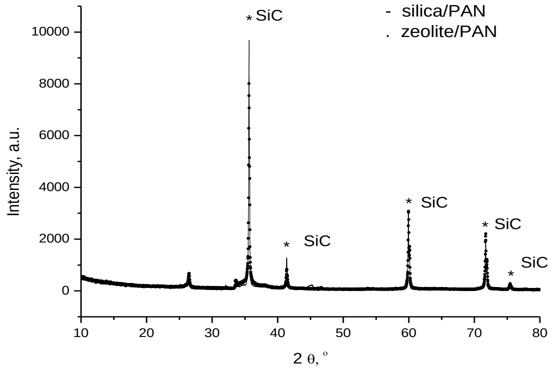


Fig. 3. XRD of the material obtained from composites silica/PAN and zeolite/PAN.

Fig. 3 shows the X-ray data for a material obtained from silica/PAN and zeolite/PAN composites and heated up to 1600°C. The data show that as a result of heat treatment, SiC is obtained from both composites (silica/PAN and zeolite/PAN).

6. CONCLUSIONS

These preliminary results point to the possibility of producing materials with high compressive strength by formation of pellets from inorganic-organic polymer nanocomposites and heating them up to 1300°C, as well as for the synthesis of SiC by heating the pellets up to 1600°C. Major factor which determines the excellent mechanical properties of the obtained materials is the interaction of the binder (PAN) with the filler (silica or zeolite) – this interaction can be estimated by means of the “baking criterion”. Pressing of the compositions is of big significance for improving the surface contact between the binder and the filler.

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ВЪГЛЕРОДНИ МАТЕРИАЛИ НА ОСНОВАТА НА ОРГАНО-НЕОРГАНИЧНИ ПОЛИМЕРНИ НАНОКОМПОЗИТНИ ПРЕКУРСОРИ

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(Резюме)

Бяха получени въглеродни материали и SiC с много добри механични свойства, използвайки органо-неорганични полимерни нанокомпозитни прекурсори. Беше установено, че основният фактор, определящ отличните механични характеристики на получения материал е взаимодействието на свързващото вещество (PAN) с пълнителя (SiO_2 или зеолит). Бе използван т. нар. „критерий за спекаемост” за оценка на взаимодействието между пълнителя и свързващото вещество в процеса на формиране на композитите и термичната им обработка. Бе установена зависимост между “критерия на спекаемост” и механичната сила на якост на получения материал. Пресоването на композициите е от голямо значение за подобряване на контакта между повърхностите на свързващото вещество и на пълнителя.

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Polymer composites on the basis of lignocellulose containing copper sulfide for electromagnetic wave protection

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Composite materials are of fundamental importance in view of their unique properties and possibilities for applications. In this connection wood polymer micro- and nanocomposites for electromagnetic wave protection on the basis of lignocelluloses modified with Cu-S reduction systems and metal and metal oxides binding substances on the basis of recycled polyol from polyethylenterephtalate and isocyanates are highly effective new materials with special properties. An original method for *in situ* coordinative binding of cupro ions with lignocellulose using a three-component cuprous reduction system was developed. Binders from polyester polyols on the basis of waste polyethyleneterephtalate magnetic tapes after glycolysis, and polyisocyanate (p-MDI) were obtained. The reactions of complex formation as well the synthesis of metal and metal oxide binder systems for lignocellulose were investigated. Composites of modified flour and binders were produced by pressing. The optimum conditions - 110ºC, 20 min and 15000 kg/cm^2 pressing were established. Modified wood polymer composites possess good physical-mechanical characteristics, low electrical resistivity and high electromagnetic wave protection. Coordinative binding of copper ions with the oxygen atoms of cellulose OH groups and aromatic nucleus in the lignin macromolecule was observed. The new nanocomposites with microwave electromagnetic absorption properties could be used in radiotechnics, electronic industry, automobile building and others.

***Keywords**: lignocellulose, wood, nanocomposites, cuprous sulfide, electromagnetic wave protection*

INTRODUCTION

In recent years, increased use of wood polymer composites in technique and everyday life is observed. In this respect nanoscience and technology give unique possibilities for creating various combinations of new materials. The metal-containing nanocomposites and polymeric nanocomposites in particular, with their unique physical and chemical properties, as well as broad areas of application, have attracted great interest [1].

Composites based on polymers with conductive fillers are in the research focus of numerous studies as a part of a growing research trend. Polymers based on renewable materials with addition of chosen materials can be directly used as advanced materials [2].

Composites with improved parameters, including toughness, thermostability, and other specific properties, can be obtained by adding mineral fillers, metals, and fibers to polymers. Recent progress is being marked by the development of nanocomposite materials comprising a low percent of filler that have much larger intrinsic surface area, hence better parameters than conventional composites [3].

A great variety of inorganic layered materials can be used both as matrices or additives to polymers, with possibilities for obtaining a wide range of new hybrid nanocomposite materials [4].

An original method for obtaining metal-containing polymers by thermal decomposition of precursors (mainly metal carbonyls) in solution or melt has been published. A strong interaction between the nanoparticles and the polymer chain occurs in such nanocomposites at the level of chemical bonding. Electronically dense individual or aggregated metal-containing particles have been observed [5,6].

Recently, special attention has been paid to nanocomposites containing metal-organic derivatives on the basis of macromolecular metal complexes of ruthenium, palladium, platinum, etc. [7,8,9,10].

Nanocomposites allow the production of superconducting articles. It has been noted that the investigations in this field open possibilities of

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obtaining new materials with unique properties [10, 11, 12].

The method of direct precipitation of colloidal dispersed additive layers and their encapsulation into the polymer matrix has been recommended as one giving a lot of possibilities for the application of the obtained materials [13]. A new method for *in-situ* synthesis of precious nanoparticles using cellulose supports has been developed [14].

Methods for modification of fabrics with electroconductive pigments on the basis of copper sulfide polymer dispersion have been developed; these include new electro-conductive polyacrylonitrile (PAN) pigments with coordinative binding of nanostate copper sulfide into the PAN matrix for microwave protection [15].

Recently, investigations connected with copper sulfide coating on polyacrylonitrile with a chelating agent of triethanolamine [16] and ethylenediaminetetraacetic acid [17] by an electroless deposition method and its EMI shielding effectiveness have received great interest. The literature study showed that obtaining of new metal-containing nanocomposite polymeric materials with improved electroconductivity and microwave absorption ability is a question of increased interest and is very useful for the production of articles that can provide electromagnetic wave protection.

In this study, copper sulfide-containing nanolignocelluloses with improved electro-conductivity and microwave absorption ability were developed and on this basis polymer composites with special properties for electromagnetic wave protection were obtained.

The investigations aimed at:

- developing methods for obtaining of copper sulfide lignocellulose nanocomposites;
- establishing the probable mechanisms and schemes of delaying and subsequent inclusion of copper sulfides in the lignocellulose matrix;
- obtaining and characterization of recycled polyols on the basis of PET film tapes and corresponding binder substances;
- obtaining and characterization of wood polymer Cu(I) containing composites.

EXPERIMENTAL

Development of methods for obtaining of copper sulphide lignocellulose nano-composites

The development of methods for obtaining copper sulfide lignocellulose nano-composites is based on the fact that copper (Cu^{+1}) sulfide as an additive to polymers imparts high electroconductivity. The latter, as an indirect index for dielectric losses, shows that the corresponding new materials will possess microwave absorption properties. A higher effect could be achieved with nano copper sulfide, which is situated as a net in the lignocellulose matrix. In this sense the development of methods is based on performing chemical modification on different kinds of lignocellulose materials – wood flour (WF), wood fibrous materials (WFM), and waste cellulose fibers WCF) – with aqueous solutions of copper compounds and sulfur-containing reduction systems in suitable quantities and ratios under definite process conditions. Such conditions will give possibilities for a reduction of Cu^{+2} to Cu^{+1} ions to take place with subsequent coordinative precipitation in lignocellulose matrices.

In the present work the following lignocellulose materials were used:

- wood flour (WF);
- wood fibrous material (WFM), produced in Lesoplast AD, Troian (Bulgaria);
- waste cellulose fibers (WCF) by paper production.

Basic Variants for Chemical Modification Process on Lignocelluloses

By previous experiments (varying the kind and composition of components) two variants for experimentation were set:

- using a three-component system (cupric sulfate pentahydrate ($CuSO_4$. $5H_2O$); sodium thiosulfate pentahydrate ($N_2S_2O_3.5H_2O$); glyoxal (OCHCHO));
- using a two-component system (cupric sulfate pentahydrate ($CuSO_4.5H_2O$); sodium thiosulfate ($N_2S_2O_3.5H\ _2O$).
- The following indicators for optimization of the methods were used:
- amount of waste water;
- content of copper and sulfur in the waste water;
- content of copper and sulfur in the modified lignocelluloses.

IR spectra of non-modified and modified samples were recorded on a Perkin Elmer FTIR – GX apparatus, having a spectral range of 4000 to 350 cm^{-1} and a resolution of 4 cm^{-1}.

Modification with a Three-Component System

The three-component system comprised cupric sulfate pentahydrate ($CuSO_4.5H_2O$), sodium thiosulfate ($N_2S_2O_3.5H_2O$); and glyoxal (OCHCHO) can be characterized as follows:

Table 1. Copper-containing Lignocelluloses, Modified with a System of Three Components

№	Conditions of modification	Copper in sample, %	Sulfur in sample, %	Copper in filtrate, mg/l	Sulfur in filtrate, mg/l	Specific electric volume resistance, Ω.m
1.	Non - modified wood fibers (WF)	0.0006	0.33	-	-	8.25×10^8
2.	Non - modified waste cellulose fibers (WCF)	0.0007	0.25	-	-	5.7×10^7
3.	Non - modified wood flour (WF)	0.0009	>0.05	-	-	8.7×10^8
4.	Modified wood fibers (WF)	3.786	>0.05	362.0	103.0	1.65×10^8
5.	Modified waste cellulose fibers (WCF)	4.319	1.92	5.0	69.0	1.11×10^7
6.	Modified wood flour (WF	5.058	1.79	1380.0	116.0	1.95×10^8

- the reduction process had a very strong effect on the wood fibrous materials (WFM), and therefore the sulfur content in the modified material was insignificant;
- on the waste cellulose fibers (WCF) the Cu^{+2} ions were reduced to Cu^{+1};
- on the modified wood flour (WF) the reduction yielded not only Cu_2S but also copper particles, hence the reduction process was most strongly expressed in that case.

Lower copper and sulfur contents in waste waters were observed with modified wood fibrous materials (WFM) in comparison with those of modified wood flour (WF).

The specific electric resistance decreased in the order 0.5 to 1.0 after modification of the three different lignocelluloses.

The results obtained with the three-component system cuprous sulfate ($CuSO_4.5H_2O$), sodium thiosulfate ($N_2S_2O_3.5H_2O$), and glyoxal (OCHCHO) unambiguously pointed to the possibility of obtaining Cu- containing lignocelluloses.

Establishment of probable mechanisms and schemes of delaying and subsequent connection of copper sulfide in the lignocellulose matrix

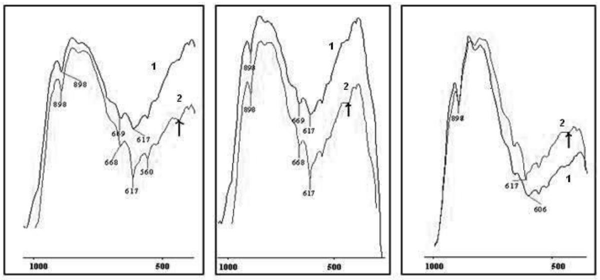
The scheme of the reduction process is as follows:

$Cu^{+2} + 1e^- \rightarrow Cu^{+1}$

$2S^{+2} - 2.2e^- \rightarrow 2S^{+4}$

$2CuSO_4 + 2Na_2S_2O_3 = Cu_2S + 2Na_2SO_4 + 3SO_2$

A peak at 400 cm^{-1}, representative of metal-oxygen ligands, was observed in the IR spectra of modified wood flour and of modified wood fibers (Fig. 1, a,b,c).



a **b** **c**

Fig. 1. IR spectrum of: a) non-modified (1) and modified (2) wood flour with system of three components (40% addition based on wood flour); b) non-modified (1) and modified (2) wood fibers with system of two components (30% added based on wood fibers); and c) non-modified (1) and modified (2) wood fibers with system of two components (40% added based on wood fibers).

These ligands are probably resulting from the coordinative binding of copper ions to oxygen atoms of cellulose -OH groups (Fig. 2) and aromatic nucleus in the lignin macromolecule (Fig. 3).

A similar model for Cu^{+2} complexes with the lignin model compound vanillin was given by Kozlevcar (2005). The binding of copper ions via methoxy oxygen atom and deprotonated hydroxy oxygen atom in nuclear species confirmed the binding role of copper to lignin (Zhang 2005). It is possible for lignocellulose materials to give evidence of physical adsorption to copper ions.

Obtaining and characterization of recycled polyols on the basis of PET film tapes and corresponding binder substances; and obtaining and characterization of wood polymer cuprous containing composites.

Obtaining of binder substances on the basis of PET magnetic tapes

The PET waste tapes were recycled by glycolysis using diethylene glycol, adipine acid and glycerol. The obtained polyols were characterized by hydroxyl number (DIN 53240); acid number and viscosity at 25ºC (DIN 3219).

The synthesis of the polyurethane binder was conducted on the basis of recycled polyols and dipheylmethane-4-4-diisocyanate (MDI) under conditions for obtaining of binders with free isocyanate groups. Such binders will be able to interact with the hydroxyl groups of lignocellulose materials. The reaction was conducted at an equivalent ratio 1:1 of the two components, at 80ºC in vacuo with subsequent drying at the same temperature for 24 hours with a view to promote the polymerization process. The obtained product was ground in a laboratory mill and was characterized by DSC, isocyanate content (DIN53185) and rheological characteristics.

Obtaining and methods for characterization of wood polymer composites (WPC)

Materials: Wood flour (BDS 3718) – conifer wood, particle size 140 µm, acidity 0,030 %, tarry substances 2%, specific volume 8 dm^3/kg, humidity 5%, cork content 0.34%;

Wood flour modified using the three-component system $CuSO_4$: $Na_2S_2O_3$: $C_2H_2O_2$ = 1.6:1.4:1, at a hydro module of soaking 1:10, 100°C temperature for 30 min. Laboratory-made WPC by pressing.

WPC were characterized with regard to: physical and mechanical properties such as tensile strength, elongation at break, modulus of elasticity and others (apparatus Zwick 2000, Zwick GmbH & Co. KG, Ulm, Germany) and electroconductivity by determination of specific electrical volume resistance (apparatus Teralin III, BDS HD 429 S1:2003).

The following parameters for determination of electromagnetic characteristics of wood polymer composites were used: complex dielectric permittivity (έ), reflection coefficient on module |Γ́| and damping coefficient α, dB/cm.

Results and discussion

Aromatic polyester polyols (APP)

The results of the characterization of the obtained APP are presented in Table 2.

Binder substances (BS)

The synthesis of a polyurethane binder was conducted on the basis of recycled polyols and diphenylmethane-4-4-diisocyanate (MDI) at an equivalent ratio 1:1 of the two components. The results from the DSC of BS are summarized in Table 3. On the basis of these results, BS number 4 is recommended for obtaining of WPC because the exothermic peak of 127.5ºC is at a lower temperature and with wider interval. Comparing this with other binder substances it is clear that there is a higher possibility for a reaction between the hydroxyl groups of lignocellulose materials and NCO groups of BS and therefore for obtaining of WPC with high physical-mechanical indexes.

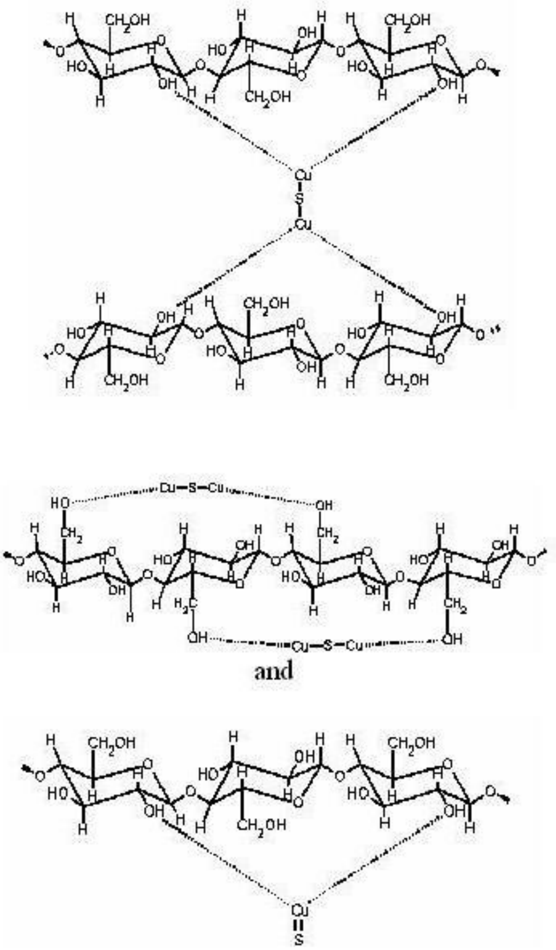


Fig.2. Copper-sulfide cellulose nanocomposites

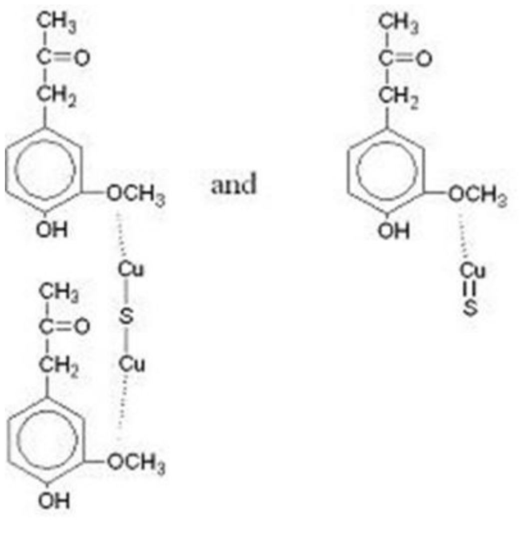


Fig.3. Copper-sulfide lignin nanocomposites

Table 2. Indexes of APP

Index	Measure	Recipe of APP			
		APP1	APP2	APP3	APP4
OH-number	mgKOH/g	416	341	326	325
acid number	mgKOH/g	0.36	0.85	0.60	0.79
Viscosity by oscillation	mPa.s	860	1160	1540	6360
Viscosity by rotation	mPa.s	760	1100	1500	5980

Table 3. Indexes of BS by DSC

Binder substance	Index		
	Temperature of glass., [°C]		Temperature of reaction ability, [°C]
	1	2	
BS №1	45.7	78.3	152.5
BS №2	52.4	67.9	158.7
BS №3	37.6	39.8	140.5
BS№4	37.2	76.4	127.5

Wood polymer composite materials

The parameters of the obtained WPC are given in Table 4, the physical-mechanical indexes of the WPS – on Figs. 4-7, and the specific electrical volume resistance – on Fig. 8.

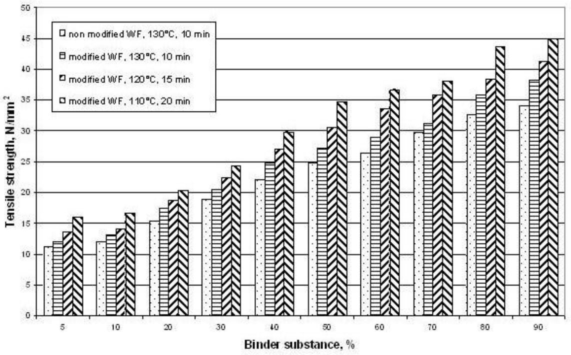


Fig. 4. Tensile strength as a function of BS%

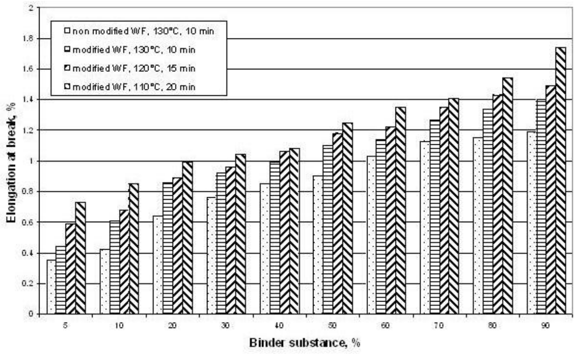


Fig.5. Elongation at break as a function of BS%

Series 1 includes WPC based on non-modified wood flour (WF) and BS (5% to 90%) after pressing at 130ºC for 10 min;

Series 2 includes WPC based on modified wood flour (WF) and BS (5% to 90%) after pressing at 130ºC for 10 min;

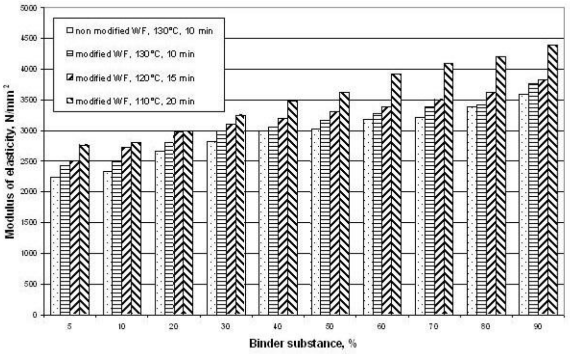


Fig. 6. Modulus of elasticity as a function of BS%

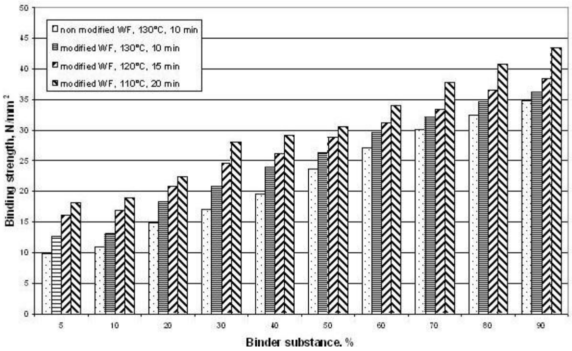


Fig. 7. Bending strength as a function of BS%

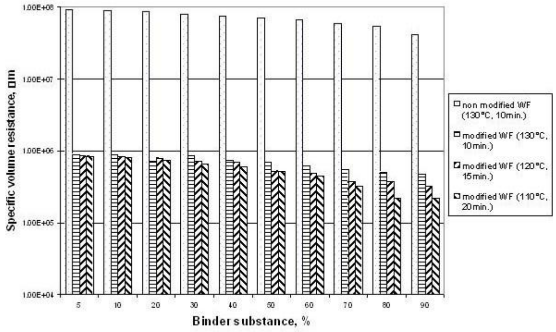


Fig. 8. Specific volume resistance as a function of BS%

Series 3 includes WPC based on modified wood flour (WF) and BS (5% to 90%) after pressing at 120ºC for 15 min;

Series 4 includes WPC based on modified wood flour (WF) and BS (5% to 90%) after pressing at 110ºC for 20 min;

The experimental data shown in Fig. 4 reveal the following correlations:

- the tensile strength of WPC based on non-modified WF after pressing at 130°C for 10 min increases at a higher quantity of BS;
- the tensile strength of WPC based on modified WF for all variants of pressing exceeds that of WPC based on non-modified WF.

The highest values are achieved at 110 °C for 20 min and 90 % BS.

Table 4. Parameters of the obtained WPC

		Components, %			Pressing conditions				Components, %		Pressing conditions	
№	Sample	WF		BS	T	Duration	№	Sample	Modified WF	BS	T	Duration
		Non mod.	Mod.		(°C)	(min)					(°C)	(min)
1	M1P	95	–	5	130	10	21	M21P	95	5	120	15
2	M2P	90	–	10	130	10	22	M22P	90	10	120	15
3	M3P	80	–	20	130	10	23	M23P	80	20	120	15
4	M4P	70	–	30	130	10	24	M24P	70	30	120	15
5	M5P	60	–	40	130	10	25	M25P	60	40	120	15
6	M6P	50	–	50	130	10	26	M26P	50	50	120	15
7	M7P	40	–	60	130	10	27	M27P	40	60	120	15
8	M8P	30	–	70	130	10	28	M28P	30	70	120	15
9	M9P	20	–	80	130	10	29	M29P	20	80	120	15
10	M10P	10	–	90	130	10	30	M30P	10	90	110	15
11	M11P	–	95	5	130	10	31	M31P	95	5	110	20
12	M12P	–	90	10	130	10	32	M32P	90	10	110	20
13	M13P	–	80	20	130	10	33	M33P	80	20	110	20
14	M14P	–	70	30	130	10	34	M34P	70	30	110	20
15	M15P	–	60	40	130	10	35	M35P	60	40	110	20
16	M16P	–	50	50	130	10	36	M36P	50	50	110	20
17	M17P	–	40	60	130	10	37	M37P	40	60	110	20
18	M18P	–	30	70	130	10	38	M38P	30	70	110	20
19	M19P	–	20	80	130	10	39	M39P	20	80	110	20
20	M20P	–	10	90	130	10	40	M40P	10	90	110	20

The same correlations (Figs. 5-7) are observed for the indexes - elongation at break, modulus of elasticity and bending strength.

Differences however are observed between modified and non-modified WF. It is worth noting that the optimal indexes of elongation at break, modulus of elasticity and bending strength are observed with series 4 (WPC obtained at 110ºC for 10 min with 90% BS). Physical-mechanical indexes of WPC in all series increase upon increasing % BS quantity.

The experimental data shown in Fig. 8 reveal the following correlations:

- the specific electrical volume resistance insignificantly decreases with the increase in the % content of BS in series 1 with non-modified WF;
- for series 2, 3 and 4 the specific electrical volume resistance of modified WF significantly decreases in comparison with non-modified WF. The best results are achieved with series 4.

Highest electroconductivity (lowest values of specific electrical volume resistance) is achieved with WPC (obtained with modified WF 5 % and BS 90 %, after pressing at 110 ^{o}C for 20 min).

WPC (series 4) were subjected to electromagnetic wave characterization (microwave absorption properties – electromagnetic wave damping – from 9 to 6 dB and standing wave coefficient – from 2,57 to 1.13). These data show that WPC with a Cu-containing lignocellulose nanocomposite component and N-containing binder substance (BS) possess high electromagnetic wave absorption. The obtained results confirm the idea for coordinative binding of Cu_2S with the N-containing polymer components.

CONCLUSIONS

Treatment with a system of three components, comprising cupric sulfate pentahydrate ($CuSO_4.5H_2O$), sodium thiosulfate pentahydrate ($Na_2S_2O_3.5H_2O$), and glyoxal (OCHCHO) at ambient pressure and 90^{o} C is very effective for modification of waste cellulose fibers and to some extent wood flour.

IR spectral data confirmed the coordinative binding of copper ions with the oxygen atoms of OH groups in cellulose and in the aromatic nucleus of the lignin macromolecule.

A treatment for modification of wood flour with a three-component cuprous reduction system was conducted. Wood nanocomposites containing Cu-3.21% and S-1.07% were obtained.

Binder substances were prepared on the basis of recycled polyols from PET waste tapes and diphenylmethane-4-4-diisocyanate (p-MDI).

On the basis of non-modified and modified wood flour and binder substances Cu-containing nanocomposites with high electroconductivity and electromagnetic wave absorption were prepared.

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ПОЛИМЕРНИ КОМПОЗИТИ ЗА ЕЛЕКТРОМАГНИТНА ВЪЛНОВА ЗАЩИТА НА ОСНОВА НА ЛИГНОЦЕЛУЛОЗА СЪДЪРЖАЩА МЕДЕН СУЛФИД

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(Резюме)

Композитните материали предизвикват голям интерес поради техните уникални свойства и възможности за приложение. В тази връзка дървесноползимерните микро- и нанокомпозити за електромагнитна вълнова защита на основата на лигноцелулози, модифицирани с Cu -S системи и метал оксидни свързващи вещества на база рециклирани полиоли от полиетилен терефталат и изоцианати, са високо ефективни нови материали със специфични свойства. Разработен е оригинален метод, основаващ се на кординативно свързване in situ на купро йони с лигноцелулоза чрез трикомпонентна редукционна система.

Получени са свързващи вещества от полиоли, на основата на отпадни полиетилен терефталатни магнитни ленти чрез гликолиза, и полиизоцианат (p-MDI). Изследвани са реакциите на комплексообразуване и тези на синтез на металоксидните свързващи системи за лигноцелулози.

Получени са композити от модифицираното брашно и свързващите вещества чрез пресоване. Установени са оптималните условия на пресоване - 110^o C, 20 минути и 1500 kg/cm^2 Модифицираните дървесноползимерни композити притежават високи физикомеханични показатели, ниско електрическо съпротивление и висока електромагнитна вълнова защита.

Установено е кординативно свързване на медните йони с кислородните атоми на целулозните OH групи и ароматните ядра в макромолекулите на лигнина.

Новите нанокомпозити с висока електромагнитна вълнова абсорбция могат да бъдат използвани в електротехниката, електрониката, автомобилостроенето и в много други отрасли на техниката и бита.

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Extractive spectrophotometric determination of palladium(II) with o-methyl phenyl thiourea from synthetic mixtures

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A novel method is proposed for the solvent extraction spectrophotometric determination of palladium(II) using low concentration of *o*-methylphenyl thiourea (OMPT). OMPT in chloroform quantitatively extracts trace concentration of palladium(II) at 0.8 moldm^{-3} hydrochloric acid media which requires only 10 s equilibriation time, the absorbance of yellow coloured palladium(II)-OMPT complex is measured at 340 nm. Complex is stable for more than 70 h. The composition of extracted species is 1:1, determined by mole ratio, job's continuous variation method and it is confirmed by log-log plot. Beer's law is obeyed in the range of 0.01 μgcm^{-3} to 15.0 μgcm^{-3}.The molar absorptivity and sandell's sensitivity are2.85x10^{3}dm^{3}mole^{-1}cm^{-1}and 0.037 μgcm^{-2}. Method is free from large number of interferences from cations and anions. The method is applied for separation of palladium(II) from multicomponent mixtures and hydrogenation catalyst.

Keywords: Palladium(II), *o*-methylphenyl thiourea, extractive spectrophotometry.

1. INTRODUCTION

Palladium(II) and its alloys have a wide range of applications in chemical industries. With the increasing use of palladium(II) in jewellery and cosmetic dentistry in the form of alloys [1, 2], the need arose for development of selective, sensitive, simple, rapid method for quantitative separation and determination of palladium(II). Several analytical techniques Viz. AAS, ICP-MS, X-ray fluorescence and spectrophotometric methods are available for determination of palladium(II). Amongst the methods available for determination of palladium(II) the spectrophotometric methods are preferred because these are cheaper, easy to handle, requires less time and with desired accuracy.

2-hydroxy-1-naphthelene carboxaldehyde hydrazine carboxamide [3] has been used for spectrophotometric determination of palladium(II). Beer's law obeyed over the range of 0.55 μgcm^{-3} to 2.50 μgcm^{-3}. A red colored complex of palladium(II) with PAR [4] is formed at pH 9.0 to 11.0 and quantitatively extracted into molten naphthalene. This method has interferences from cobalt(III), iron(II) and bismuth(III) and was removed by masking with EDTA. 1,3-Bis(hydroxymethyl)benzimidazole-2-thione [5] was used for extractive spectrophotometric determination of palladium(II) from hydrogenation catalysts. palladium(II) complexed with 1-(2-pyridylazo)-2-napthol (PAN) [6] in aqueous solution was extracted into chloroform. Components of nonferrous alloys interfere in determination of palladium (II).3-phenoxybenzaldoxime [7] was used for extractive photometric determination of palladium(II) and method was applied for determination of palladium(II) from catalysts and synthetic mixtures. Hexane 2-5-dione-bis-(ethylenediamine) [8] forms pink colored complex with palladium(II), was quantitatively extracted at pH 3.5. Extractive spectrophotometric determination method was developed for palladium(II) using 2-hydroxy-3-nitro-5-methyl acetophenone oxime [9]. Palladium(II) was quantitatively extracted from pH 0.0-4.0. The proposed method for extraction spectrophotometric determination of palladium(II) using OMPT as a new reagent when compared with other extractive spectrophotometric methods it is found to be more sensitive and selective [10-25] (Table 1).

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Table 1.
Comparison of present method with other extractive spectrophotometric determination methods of palladium(II)

Reagents	λ_{max} / nm	Acidity / pH	Beer's Law validity range(ppm)	Solvent	Molar Absorptivity (Lit Mol^{-1} cm^{-1})	M:L	Remark	Ref.No
di-2-pyridyl ketone benzoylhydrazone(DPKBH)	455	H_2SO_4 media	0-0.01	benzene	9.38x10^3	--------	Low beer's range	10
Potassium, *O,O'*-Diethyldithiophophate(Kdtp)	298	1-13	0-3.4	chloroform	2.9x10^4	1:2	Alternate shaking and standing 20 min	11
2,2'-Bipyridyl 2-Pyridylhydrazone(DPPH)	585	0.5-1.5	NM	chloroform	1.9x10^4	1:1	10 min shaking	12
4-(3,5-Dichloro-2-pyridylazo)-1,3-diaminobenzene(3,5-C12 PADAB)	600	1-2 M H_2SO_4	0.24-2.16	benzene	8.6x10^4	NM	Low beer's range, 15 min shaking	13
2-(5-methyl-2-pyridilazo)-5-diethylaminophenol	553	0.1M H_2SO_4	0.008-0.32	toulene	---------	--------	Low beer's range, Au(III), Pt(II), V(V), W(VI), interfere	14
3,4-dihydro-4,4,6-trimethyl-2(1H)-Pyrimidine-Thione(DTPT)	420	5.5	0.4-24.6	chloroform	3.90 x10^4	1:2	CN$^-$ interfere	15
3,4,5-Trimethoxybenzaldehyde Thiosemicarbazone(TBTSC)	370	0.9M HCl	0-12	chloroform	8.35x10^4	1:2	Twice extraction by 3 ml chloroform each	16
2,2'-dithioaniline (DTDA)	397	3.0	0.003-0.2	IBMK	1.47x10^6	1:1	Low beer's range	17
3- Hydroxy -2- methyl-1-phenyl-4-pyridone(HX)	345	2.5	0.28-8.0	chloroform	1.89 x10^4	1:2	35 min shaking	18
2-arylthio-p-nitroacetophenone	730	7-8M Acetic acid	2.5-20	chloroform	1.61x10^4	------	Higher Acidity, 15 min shaking	19
Pyridoxal-4-phenyl-3-thiosemicarbazone(PPT)	460	3.0	0.4-6.4	benzene	2.2 x10^4	1:1	Twice extraction by 10 ml chloroform each, interferring cations and anions masked.	20
4-(2'-Furalidineimino)-3-Methyl-5-Mercapto-1,2,4 triazole(FIMMT)	410	5.4	5-50	n-butanol	1.4x10^3	1:1	Many interfering ions masked	21
Benzyloxybenza;ldehyde thiosemicarbazone(BBTSC)	365	5.0	5-60	cyclohexanol	4.0 x10^3	1:1	Simple and sensitive	22
2-hydroxy-5-methylacetophenoneisonicotinoylhydrazone(HMAINH)	385	0.01-0.015M H_2SO_4	2.0-9.0	chloroform	5.32 x10^3	1:1	Few diverse ions studied , No application of the method	23
Monothiobenzolylmethane(3-mercapto-1,3-diphenyl-2-propen-1-one)(HSDBM)	470	3.5-6.5	0.6-3.6	benzene	NM	1:2	Low beer's range, 10 min shaking, interfering ions masked	24
Thiomichler's ketone(TMK)	518	2.5 x10^{-2}M (Clo_4^-)	0.002-0.1	chloroform	NM	NM	3 min homogeneous centrifugal extraction 4000 rpm, low beer's range	25
O-Methyl phenyl thiourea(OMPT)	340	0.8M HCL	0-12.5	chloroform	2.85 x10^3	1:1	Selective and sensitive	PM

NM : not mentioned, PM : present method.

2. EXPERIMENTAL

Instrumentation

A digital spectrophotometer model EL-159 [Elico Make] with matched 10mm quarts cells was used for absorbance measurements.

Reagents

All of the reagents used were of analytical reagent grade unless otherwise stated. A standard stock solution of palladium (II) has been prepared by dissolving 1.0 g palladium (II) chloride ($PdCl_2$)(Loba.Chem.) in 1.0 moldm^{-3} hydrochloric acid and diluted to 250 cm^3 in a calibrated flask with water and was standardized by gravimetric method [27]. A working standard solution of palladium(II) 60 μgcm^{-3} was prepared by diluting the standard stock solution with water. O-methyl phenyl thiourea [OMPT] has been prepared using method reported by Frank and Smith [28]. The working reagent solution (1.0 x 10^{-4}moldm^{-3}) of *OMPT* was prepared in chloroform. Other standard solutions of different metal ions were prepared by dissolving their respective salts in water and diluted suitably. Double distilled water was used throughout the work.

Recommended procedure

To an aliquot of solution containing 60 μg Pd(II) in a 25 cm^3 calibrated flask, enough hydrochloric acid and water were added to adjust acidity 0.8 moldm^{-3} with respect to hydrochloric acid and diluted up to mark with distilled water. The aqueous solution was equilibriated with 10 cm^3, 1.0 x10^{-4} moldm^{-3} *o*-methyl phenyl thiourea [OMPT] in chloroform for 10 s, in a 125 cm^3 separatory funnel. These two phases were allowed to separate and yellow colored palladium (II)-OMPT complex in organic phase was dried over anhydrous sodium sulphate. The total volume of organic phase was made 10 cm^3 and absorbance of palladium(II)-OMPT complex in organic phase was measured at 340 nm against the reagent blank.

3. RESULTS AND DISCUSSION

Absorption Spectra

The palladium(II)-OMPT complex in chloroform shows the absorption maxima at 340 nm, whereas absorption spectrum due to reagent blank is negligible (Fig. 1) therefore, all the absorbance measurements were made at 340 nm against reagent blank for further spectrophotometric determination of palladium(II)

Effect of acidity

The extraction of palladium(II) was studied using different mineral acid media [hydrochloric, sulphuric, nitric and perchloric acid] using 1.0 x 10^{-4}mol dm^{-3} reagent (OMPT) in chloroform, in a range of 0.1 to 10.0 mol dm^{-3} acid concentrations. Complexation was observed in all acids studied but complete complexation of palladium(II)-OMPT complex with maximum absorbance was observed in the range 0.8 – 8.0 mol dm^{-3} hydrochloric acid media (Fig. 2) Therefore 0.8 mol dm^{-3} hydrochloric acid concentration was used for further extraction study.

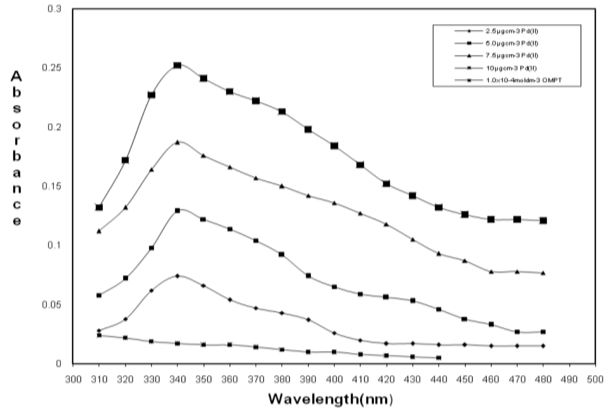


Fig 1. Absorption spectra of Pd(II)-OMPT Complex vs. OMPT reagent blank. Pd (II)-2.5 μg cm^{-3},5.0 μg cm^{-3},7.5 μgcm^{-3} ,10.0 μgcm^{-3}; OMPT- 1.0x10^{-4} mol dm^{-3} ; hydrochloric acid - 0.8 moldm^{-3}, shaking time 10s.

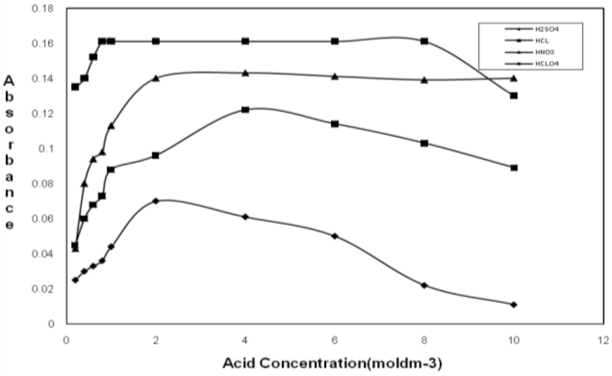


Fig 2. Effect of acidity on extraction of Pd(II)-OMPT complex. Pd(II)-6.0 μg cm^{-3}, OMPT 1.0 x 10^{-4} mol dm^{-3}, $\lambda_{max,}$ 340 nm, shaking time 10s.

Choice of solvent

Toluene, xylene, benzene, n-hexane, n-butanol, n-butylacetate, chloroform were tried for the extraction of palladium(II)-OMPT complex (Fig.3). Amongst the solvents employed for solvent extraction spectrophotometric determination of palladium(II) chloroform was selected with maximum extraction effectively.

Effect of reagent concentration

The effect of reagent concentration was studied by varying OMPT concentration from 1.0 x 10^{-5} mol dm^{-3} to 1.0 x 10^{-3} mol dm^{-3} in chloroform. It was observed that the absorption of palladium (II)-OMPT complex increases with increase in concentration of reagent from 1.0 x 10^{-5} mol dm^{-3} to 1.0 x 10^{-4} mol dm^{-3} after this range it become constant with no any adverse effect of excess reagent concentration on absorbance of palladium(II)-OMPT complex (Fig. 4).

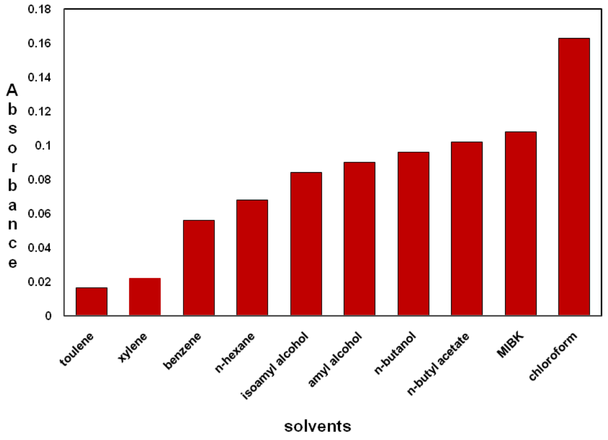


Fig 3. Effect of various solvents on extraction of Pd(II)-OMPT complex. Pd(II) 6.0 µgcm^{-3}; OMPT-1.0 x 10^{-4} mol dm^{-3} , hydrochloric acid 0.8 mol dm^{-3} , λ_{max} = 340 nm, shaking time 10s.

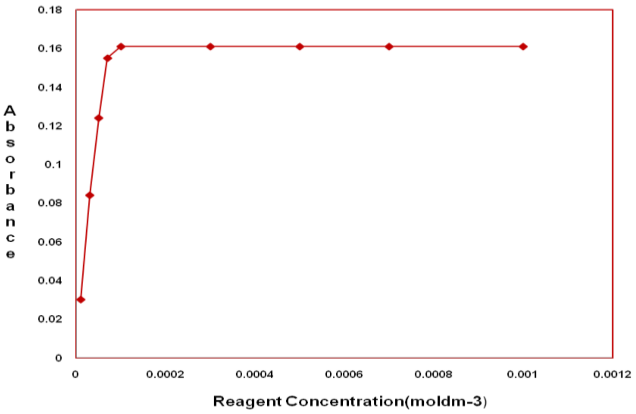


Fig 4. Effect of reagent concentration on extraction of Pd(II)-OMPT complex. Pd(II) 6.0 µg cm^{-3}; OMPT 1.0 x 10^{-5} to 1.0 x 10^{-3} mol dm^{-3}, hydrochloric acid 0.8 mol dm^{-3}, shaking time 10s.

Effect of equilibration time and stability of complex

The study of change in absorbance with variation in equilibration time was carried out over 5 s to 30 min. It has been observed that extraction was completed in 5s and there was no any adverse effect of prolonged equilibration on extraction of palladium(II)-OMPT complex up to 30 min. Hence 10s equilibration time was fixed for further study, also absorbance of Pd(II)-OMPT complex was stable for more than 70h.

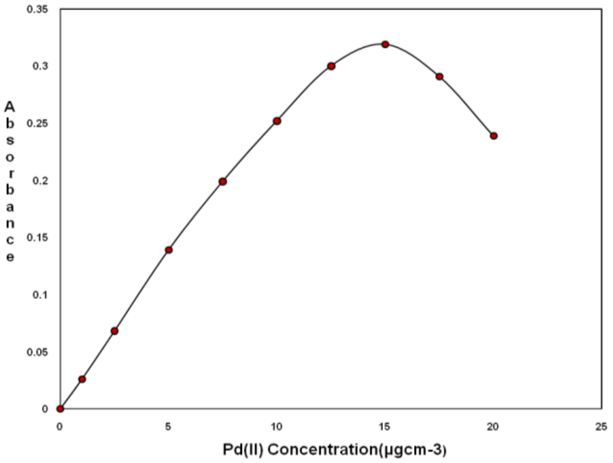


Fig 5. Applicability of Beer’s law to Pd(II)-OMPT complex. Pd(II) 0.01 to 20.0 µg cm^{-3}; OMPT-1.0x10^{-4} mol dm^{-3}, hydrochloric acid 0.8 mol dm^{-3}, λ_{max}= 340 nm, shaking time 10s.

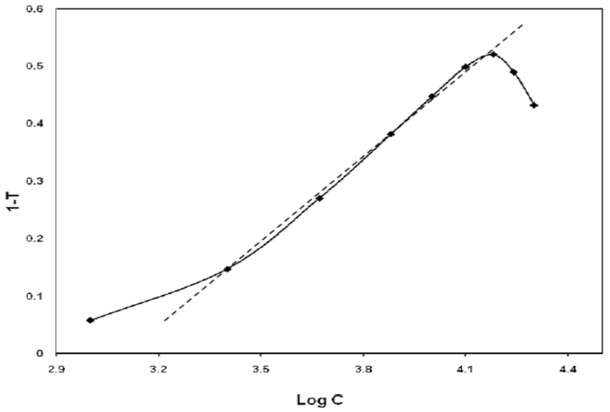


Fig 6. Ringbom’s plot for Pd(II)-OMPT complex. Pd(II) 1000 to 22500 µg dm^{-3}, OMPT 1.0x10^{-4} mol dm^{-3}, hydrochloric acid 0.8 mol dm^{-3}, λ_{max} = 340 nm, shaking time 10s.

Beer’s law, molar absorptivity, sandell’s sensitivity and correlation coefficient

Beer’s law is obeyed over the concentration range of 0.01 µgcm^{-3} to 15.0 µgcm^{-3} for palladium(II)-OMPT complex at 340 nm (Fig. 5) The molar absorptivity and sandell’s sensitivity are 2.85 x 10^{3} $dm^{3}mol^{-1}cm^{-1}$ and 0.037 µgcm^{-2} respectively. The optimum range as defined by Ringbom’s [26] plot (Fig. 6) is 3.1 to 13.0 µgcm^{-3}, slope of Ringbom’s plot from fig.6 is 0.4655. Hence, the ratio between the relative error in concentration and photometric error is p = 4.655, and for one percent photometric error, p=0.01, hence the relative error in concentration is 0.04655. The correlation coefficient value of Pd(II)-OMPT complex with an independent variable as concentration in µgcm^{-3} and a dependent variable as absorbance, was found to be 0.99, indicates a clear linearity between these variables. The slope value and intercept for the best fitted line were obtained are 0.02394 and 0.01036. Therefore the content of palladium(II) in real samples can be determined using the straight line equation

$$Y=0.02394X + 0.01036.$$

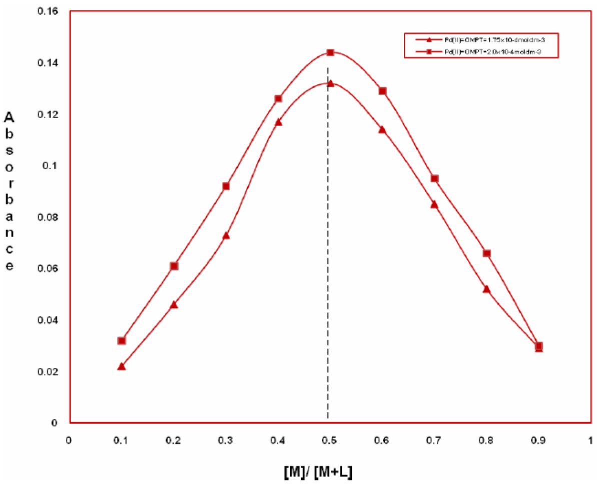


Fig 7. Pd(II):OMPT species by job's variation method. Pd(II)=OMPT= 1.75 x 10^{-4}(▲)and 2.0x10^{-4} (■) mol dm^{-3}, hydrochloric acid-0.8 moldm^{-3}, λ_{max} = 340 nm, shaking time 10s.

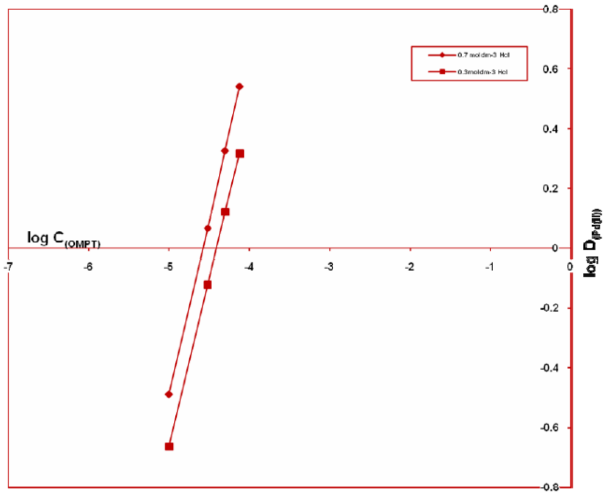


Fig 9. Plot of log $D_{Pd(II)}$ vs. log $C_{(OMPT)}$. Pd(II)-6.0µg cm^{-3}, OMPT- 1.0 x 10^{-4} mol dm^{-3}, hydrochloric acid - 0.7 mol dm^{-3} and 0.3 mol dm^{-3}, λ_{max} = 340 nm, shaking time 10s.

Stiochiometry of the complex

Probable composition of extracted species was ascertained by plotting graph of log$D_{(Pd(II))}$ against log$C_{(OMPT)}$ at 0.7 moldm^{-3} and 0.3 moldm^{-3} hydrochloric acid concentrations. The plots are linear with slopes 1.14 and 1.11 respectively (Fig. 9). The probable composition was 1:1 (Pd(II): OMPT). This composition was also verified by mole ratio method (Fig. 8) and also confirmed by job's continuous variation method (Fig. 7).

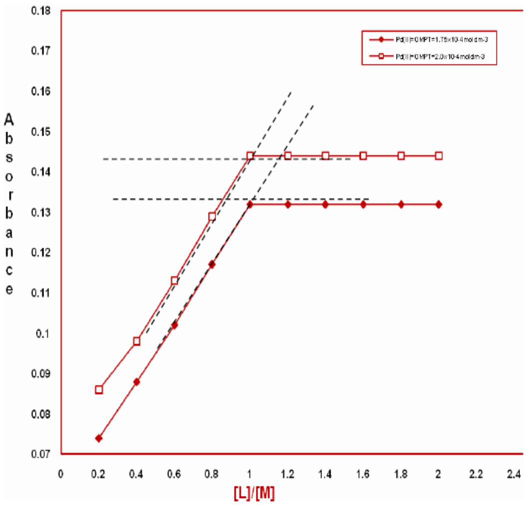


Fig 8. Pd(II):OMPT species by mole ratio method. Pd(II) = OMPT= 1.75 x 10^{-4} (♦) and 2.0x10^{-4} (□) mol dm^{-3}, λ_{max} = 340nm, hydrochloric acid 0.8 moldm^{-3}, shaking time 10s.

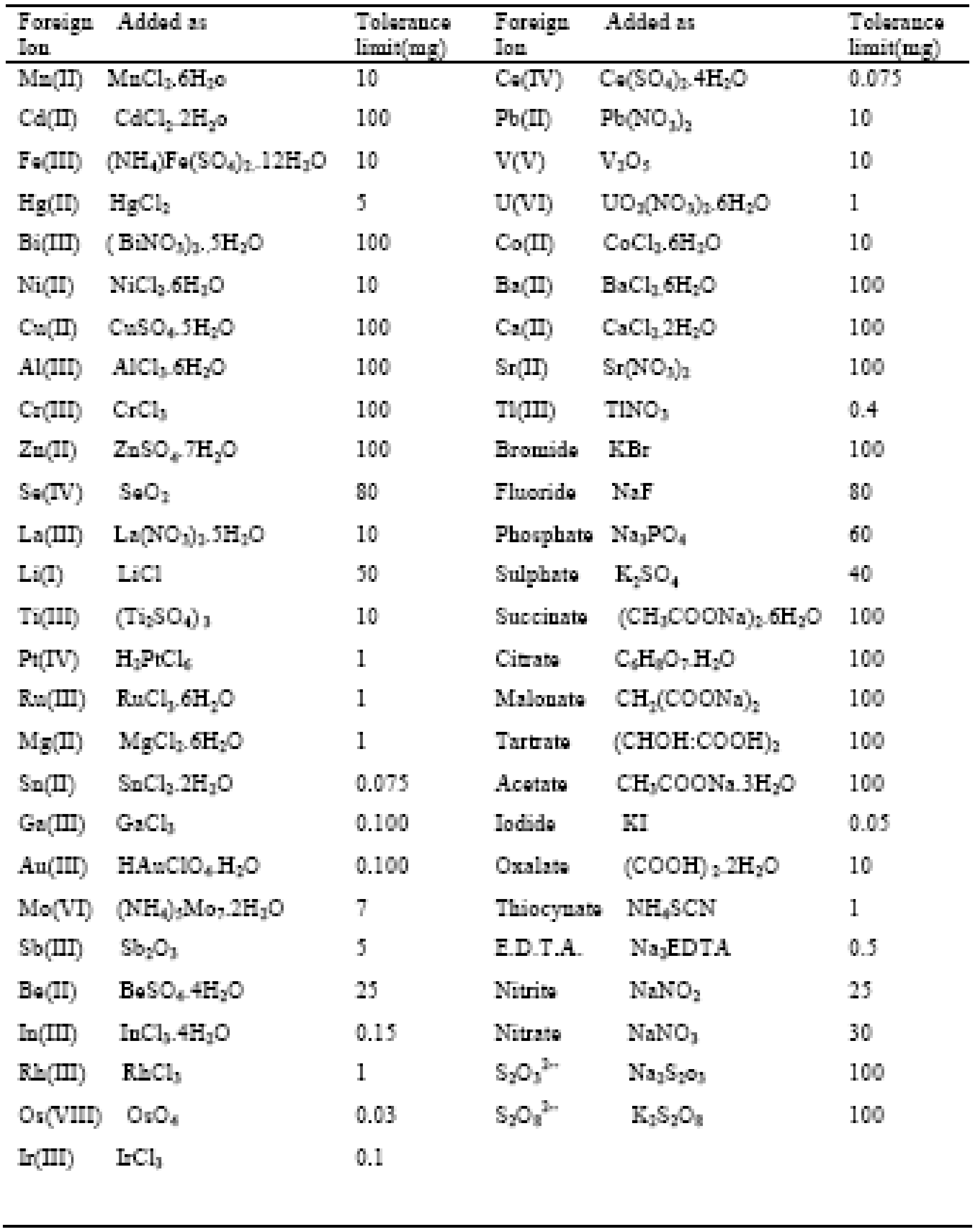
Influence of foreign ions

The effect of the various foreign ions was investigated in order to find tolerance limit of these ions in extraction spectrophotometric determination of Pd(II) (Table 2). The only interfering ion was silver (I) because of its precipitation as silver chloride.

Precision, accuracy and detection limit

To access the reproducibility and accuracy of the method, absorbance measurements with ten different identical solutions containing 60 µg palladium (II) were determined by proposed method. The average of these ten readings and standard deviation were determined. Standard deviation was found to be not more than 0.0013 and relative standard deviation was less then 0.82% respectively. It is evident from these results that the method is precise and accurate. The detection limit for palladium(II) for proposed method is

Table 2. Influence of foreign ion
Pd(II) 6.0 μgcm^{-3}, OMPT 1.0x10^{-4} moldm^{-3}, hydrochloric acid 0.8 moldm^{-3},
λ_{max} 340 nm, shaking time 10s.



Foreign Ion	Added as	Tolerance limit(mg)	Foreign Ion	Added as	Tolerance limit(mg)
Mn(II)	$MnCl_2.6H_2o$	10	Ce(IV)	$Ce(SO_4)_2.4H_2O$	0.075
Cd(II)	$CdCl_2.2H_2o$	100	Pb(II)	$Pb(NO_3)_2$	10
Fe(III)	$(NH_4)Fe(SO_4)_2.12H_2O$	10	V(V)	V_2O_5	10
Hg(II)	$HgCl_2$	5	U(VI)	$UO_2(NO_3)_2.6H_2O$	1
Bi(III)	$(BiNO_3)_3.5H_2O$	100	Co(II)	$CoCl_2.6H_2O$	10
Ni(II)	$NiCl_2.6H_2O$	10	Ba(II)	$BaCl_2.6H_2O$	100
Cu(II)	$CuSO_4.5H_2O$	100	Ca(II)	$CaCl_2.2H_2O$	100
Al(III)	$AlCl_3.6H_2O$	100	Sr(II)	$Sr(NO_3)_2$	100
Cr(III)	$CrCl_3$	100	Tl(III)	$TlNO_3$	0.4
Zn(II)	$ZnSO_4.7H_2O$	100	Bromide	KBr	100
Se(IV)	SeO_2	80	Fluoride	NaF	80
La(III)	$La(NO_3)_3.5H_2O$	10	Phosphate	Na_3PO_4	60
Li(I)	LiCl	50	Sulphate	K_2SO_4	40
Ti(III)	$(Ti_2SO_4)_3$	10	Succinate	$(CH_2COONa)_2.6H_2O$	100
Pt(IV)	H_2PtCl_6	1	Citrate	$C_6H_8O_7.H_2O$	100
Ru(III)	$RuCl_3.6H_2O$	1	Malonate	$CH_2(COONa)_2$	100
Mg(II)	$MgCl_2.6H_2O$	1	Tartrate	$(CHOH:COOH)_2$	100
Sn(II)	$SnCl_2.2H_2O$	0.075	Acetate	$CH_3COONa.3H_2O$	100
Ga(III)	$GaCl_3$	0.100	Iodide	KI	0.05
Au(III)	$HAuClO_4.H_2O$	0.100	Oxalate	$(COOH)_2.2H_2O$	10
Mo(VI)	$(NH_4)_5Mo_7.2H_2O$	7	Thiocynate	NH_4SCN	1
Sb(III)	Sb_2O_3	5	E.D.T.A.	Na_2EDTA	0.5
Be(II)	$BeSO_4.4H_2O$	25	Nitrite	$NaNO_2$	25
In(III)	$InCl_3.4H_2O$	0.15	Nitrate	$NaNO_3$	30
Rh(III)	$RhCl_3$	1	$S_2O_3^{2-}$	$Na_2S_2o_3$	100
Os(VIII)	OsO_4	0.03	$S_2O_8^{2-}$	$K_2S_2O_8$	100
Ir(III)	$IrCl_3$	0.1			

determined, as amount corresponding to thrice the standard deviation blank value and the limit of detection is 0.13 μg cm^{-3}.

4.APPLICATIONS

Determination of palladium(II) in synthetic mixtures corresponding to alloys

Various synthetic mixtures were prepared in laboratory and palladium(II) was determined using recommended procedure. The results are in agreement with those obtained by direct atomic absorption spectrometry. These results are reported in Table 3.

Determination of palladium(II) from hydrogenation catalyst

Proposed extraction spectrophotometric determination method was applied for the determination of palladium(II) in hydrogenation

Table 3. Separation of palladium (II) from synthetic mixtures corresponding to alloys

Composition of alloy (%)	Amount of palladium(II)			S.D	R.S.D(%)
	Taken (μg)	Found (μg) AAS	Found (μg) PM [a]		
Oakay alloy (Pd 18.2; Pt 18.2; Ni 54.2; V 9.1)	60	59.96	59.94	0.345	0.58
Jewelry alloy (Pd 95.0; Rh 4.0; Ru 1.0)	60	59.95	59.92	0.896	1.50
Stibopalladinate alloy (Pd 75.0; Sb 25.0)	60	59.97	59.95	0.745	1.24
Pd-Cu alloy (Pd 60; Cu 40)	60	59.95	59.92	0.486	0.81

PM[a] : Present method, average of five determinations.

Table 4. Determination of palladium (II) in hydrogenation catalyst

Hydrogenation catalyst	Amount of palladium(II)			S.D.	R.S.D. (%)	C.L. α = 0.95
	Taken (μg)	Found (μg) AAS	Found (μg) PM [a]			
Palladium on activated charcoal (Pd-C, 30%Pd)	30	29.88	29.80	0.155	0.52	0.25
Palladium on activated charcoal (Pd-C, 5.0%Pd)	5.0	4.95	4.95	0.033	0.66	0.052
Palladium on barium sulphate (Pd-$BaSo_4$, 5.0%Pd)	5.0	4.94	4.93	0.020	0.41	0.032

catalysts (Table 4), Palladium on activated charcoal [29] (Pd-C,30%), palladium on barium sulphate [29] (Pd-$BaSo_4$,5%), palladium on activated charcoal [29] (Pd-C,5%). About 0.3 gm of the catalyst sample was treated twice with 10 cm^3 portion of aqua regia, then evaporated to 5 cm^3, and on cooling distilled water was added to it .it was filtered using whatmann filter paper no.41 and filtrate was transferred into 250 cm^3 calibrated flask.

The residue was washed with 20 cm^3 of 2.0 mol dm^{-3} nitric acid and then with distilled water. Finally the sample was made up to mark with distilled water and suitable aliquots of this solution were then analyzed as per recommended procedure for palladium (II) determination. The results obtained are in agreement with those obtained by direct atomic absorption spectrometry (Table 4).

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ЕКСТРАКЦИОННО СПЕКТРОФОТОМЕТРИЧНО ОПРЕДЕЛЯНЕ НА ПАЛАДИЙ (II) С О-МЕТИЛ-ФЕНИЛКАРБАМИД В СИНТЕТИЧНИ СРЕДИ

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(Резюме)

Предложен е нов метод за екстракционно спектрофотометрично определяне на паладий,използвайки ниски концентрации на о-метил-фенилкарбамид (OMPT). Последният реактив извлича количествено из хлороформ следи от паладий (II) в среда на 0.8 mol dm^{-3} солна киселина. Равновесието се достига само за 10 секунди. Абсорбцията на жълто-оцветения комплекс паладий (II)-OMPT се определя при 340 nm. Комплексът е стабилен за повече от 70 часа. Моларното съотношение на екстрахираните компоненти е 1:1 и е потвърдено в двойно-логаритмични координати. Законът на Beer се спазва в интервала от 0.01 до 15.0 µg cm^{-3}. Моларната абсорбция и чувствителността по Сандел са 2.85x10^{3} dm^{3}mole^{-1}cm^{-1} and 0.037 µgcm^{-2}. Методът не се влияе от голям брой катиони и аниони. Той може да се прилага за разделяне на паладий (II) от много-компонентни смеси и катализатори за хидриране.

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Removal of Mn(II), Fe(III) and Cr(III) from aqueous solutions using Bulgarian clinoptilolite

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The main purpose of the present work was to study the adsorption of Mn(II), Fe(III) and Cr(III) from aqueous solutions onto natural and pretreated Bulgarian clinoptilolite from Beli plast deposit. Batch adsorption studies were carried out to evaluate the effect of contact time, temperature, solution pH and initial concentration of investigated ions. The equilibrium adsorption data were fitted to linear Langmuir, Freundlich and Dubinin-Radushkevich models and maximum adsorption capacities were calculated. The adsorption of the investigated ions followed pseudo-second-order reaction kinetics, as well as a Freundlich isotherm. The results clearly showed that the treatment with NaCl improved the adsorption capacity of natural clinoptilolite. It was found that the removal of all investigated ions from a multicomponent aqueous solution was significantly affected by the presence of competing ions.

Key words: clinoptilolite; adsorption equilibrium; kinetics; metal ions

1. INTRODUCTION

There is heavy metal contamination in the aqueous waste streams of many industries, such as metal plating facilities, mining operations, and tanneries. Especially Mn(II), Fe(III) and Cr(III) are common pollutants found in many industrial wastewaters. The presence of heavy metals in the environment can be detrimental to a variety of living species. Therefore their elimination from waters and wastewaters is important to protect public health [1]. Heavy metals are non-biodegradable and tend to accumulate in organisms, causing numerous diseases and disorders. Numerous processes exist for the removal of dissolved metals, including ion exchange, chemical precipitation, coagulation, phytoextraction, ultrafiltration, reverse osmosis, electrodialysis and adsorption. Among various treatment methods, ion exchange seems to be the most attractive one when effective low-cost ion exchangers are used. Generally, ion exchange and adsorption are preferred for heavy metal ions removal due to easy handling [2,3]. Zeolites, which represent the largest group of microporous materials, are crystalline inorganic polymers based on a three-dimensional arrangement of SiO_2 and AlO_4 tetrahedra connected through their oxygen atoms to form large negatively-charged lattices with Brønsted and Lewis acid sites. The use of zeolitic materials for the environmental protection is stimulated by their good physico-chemical properties, e.g. selective adsorption, non-toxic nature, availability and low cost. Pretreatment of natural zeolites by acids, bases, surfactants, etc. is an important method to improve their ion-exchange capacity [4-6]. A great deal of research on natural zeolites has been focused on the most commonly occurring types, especially clinoptilolite and mordenite. Many researchers have investigated various aspects of heavy metal removal from wastewater and synthetic aqueous solutions by clinoptilolite and other zeolites [2,3,6-10]. As is seen from the literature review, zeolites can be used for the removal of some metal ions from wastewaters. The ion-exchange process is influenced by several factors, such as concentration and nature of cations and anions, temperature, pH level, crystal structure and composition of the zeolites. The composition, purity and mineralogical characteristics of clinoptilolite may vary widely from one deposit to another and even within the same deposit. For this reason clinoptilolite samples from different regions show different behavior in ion-exchange processes [3,8,10].

The aim of this study was to investigate the efficiency of clinoptilolite from a Bulgarian deposit in the removal of Mn(II), Fe(III) and Cr(III) from aqueous solutions and to estimate the optimal operation parameters of the process. Such studies

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are important for the future practical use of this natural material in wastewater treatment.

2. EXPERIMENTAL

A sample of clinoptilolite was taken from the Beli plast deposit in the Eastern Rhodopes Mountain, Bulgaria. The clinoptilolite was crushed and classified to a size range 0.2-1.0 mm. Then it was washed several times with distilled water, filtered, dried in an oven at 378 K for 24 h and stored in closed containers for further tests. The clinoptilolite sample was characterized by X-ray diffraction and chemical analysis. The chemical composition of the samples was determined by conventional analytical methods for silicate materials [11]. Characterization of the texture parameters of clinoptilolite was carried out by low-temperature adsorption of nitrogen at 77 K using a conventional volumetric apparatus. The clinoptilolite sample was outgassed at 473 K for 6 h under vacuum (10^{-3} Torr) before N_2 adsorption.

Natural clinoptilolite (CL) was treated with 2 mol/L NaCl solution (clinoptilolite/solution ratio of 100 g/L) at 363 K over a period of 7 h in a thermostat. After a cool-down period, the sample was filtered, washed several times with distilled water and dried at 378 K for 6 h. In this way Na-modified clinoptilolite (CL_Na) was obtained.

The adsorption properties of CL and CL_Na with respect to Mn(II), Fe(III) and Cr(III) ions were determined by the batch method. Experiments were carried out using stoppered 50-mL Erlenmeyer flasks containing 0.25 g clinoptilolite sample and 25 mL of an aqueous solution of the metal ion(s) under study. The mixture was shaken at 295 K on an automatic shaker. On reaching equilibrium, the adsorbent was removed by filtration through a Millipore filter (0.2 μm). The initial and equilibrium concentrations of the metal ions were determined by flame AAS on a Pye Unicam SP 192 flame atomic absorption spectrometer (UK). The kinetics of adsorption was studied by placing 0.25 g adsorbent in 25 mL of a 50 mg/L aqueous solution of a metal ion at pH 4.0 at 295 K**.** The contact time varied between 1 and 300 min. The effect of acidity on the removal efficiency of the adsorbents was investigated over the pH range 2.0–5.0 employing an initial concentration of 5 mg/L for all investigated ions at 295 K. Thus, to determine the effect of the initial metal ion concentration on the adsorption capacity of CL and CL_Na, initial concentrations in the range 5–150 mg/L at pH 4.0 were chosen.

The removal efficiency (%) and the amount of metal ions adsorbed by clinoptilolite samples at equilibrium (Q_e, mg/g) were calculated using the expressions:

$$\text{Removal efficiency } (\%) = (C_0 - C_e)*100/C_0 \quad (1)$$

$$Q_e = (C_0 - C_e)* V/m \quad (2)$$

where $\boldsymbol{C_0}$ and $\boldsymbol{C_e}$ are the initial and equilibrium concentrations of the investigated ions (mg/L), respectively. $\boldsymbol{V}$ is the solution volume (L) and $\boldsymbol{m}$ is the adsorbent weight (g).

Analytical grade reagents were used in all experiments. The working solutions containing different concentrations of Mn(II), Fe(III) and Cr(III) ions were prepared by stepwise dilution of the stock solutions (Titrisol Merck, Germany). All adsorption experiments were replicated and the average results were used in data analyses.

3. RESULTS AND DISCUSSION

The chemical composition of natural clinoptilolite is as follows (wt %): SiO_2: 70.03; Al_2O_3: 12.91; Fe_2O_3: 1.89; Na_2O: 1.35; K_2O: 3.62; CaO: 2.36; MgO: 0.38; H_2O: 6.02, other 1.44%, as described in our previous study [5]. The Si/Al ratio of the sample as calculated from this composition is 5.4, which is within the typical range 4–5.5 given for clinoptilolite [8,10]. Based on the results of X-ray diffraction, Bulgarian clinoptilolite used in this study is composed of 83 % clinoptilolite, 5% cristobalite, 7% heulandite, 2% quartz, 2% albite and 1% microcline. The nitrogen adsorption isotherm was used for evaluation of textural parameters of natural clinoptilolite and the following values were obtained: specific surface area – 26.0 m^2/g, total pore volume – 0.082 cm^3/g and average pore diameter - 20.4 nm.

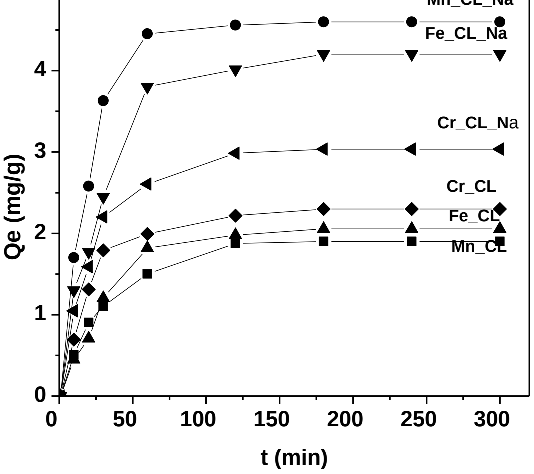

Fig. 1. Kinetics of adsorption of Mn(II), Fe(III) and Cr(III) onto CL and CL_Na (C_0 50 mg/L, stirring time 2 h, pH 4.0).

The experimental results of the kinetic study of Mn(II), Fe(III) and Cr(III) adsorption onto clinoptilolite samples are presented on Fig. 1. The amount of adsorbed metal ions onto both samples increases with the contact time and reaches a maximum value after 2 hours. Thus, we fixed two hours as the optimum contact time. Fig. 1 shows that the adsorption rate for all investigated ions after NaCl treatment of natural clinoptilolite is appreciably higher. In order to elucidate the adsorption kinetics of the investigated metal ions, three kinetic models: pseudo-first-order, pseudo-second-order and intraparticle diffusion, were applied to the experimental data. The pseudo-first-order [12] and pseudo-second-order [13] equations are expressed as shown in equations 3 and 4, respectively:

$$\log (Q_e - Q_t) = \log (Q_e) - k_1 t/2.303 \quad (3)$$

$$(t/Q_t) = (1/k_2 Q_e) + (1/Q_e)t \quad (4)$$

where Q_t is the amount of metal ions adsorbed at various times $\boldsymbol{t}$ (mg/g); and $\boldsymbol{k_1}$ is the rate constant of pseudo-first-order adsorption (1/min); Q_e is the equilibrium adsorption capacity (mg/g); $\boldsymbol{k_2}$ is the rate constant of pseudo- second-order adsorption (g/mg min). The values of k_1 can be calculated from the slope of the plots of $\log (Q_e - Q_t)$ versus t; the values of k_2 can be calculated from the slope of the plots of t/Q_t versus t. The intercepts of these curves were used to determine the equilibrium capacity Q_e. The values obtained are presented in Table 1. The theoretical Q_e values estimated from the pseudo-first-order kinetic model differed significantly from the experimentally obtained ones and the corresponding correlation coefficients (R^2) were found to be lower than those for the pseudo-second-order model. On the other hand, the theoretical values obtained from the pseudo-second-order kinetic model were very close to the experimental Q_e values. Thus we proved that the adsorption of all investigated ions can be described by the pseudo-second-order kinetic mechanism.

Table 1. Kinetic parameters for the adsorption of Mn(II), Fe(III) and Cr(III) onto CL and CL_Na

Adsor bents	Metal ions	Pseudo-first-order constants			Pseudo-second-order constants			Intraparticle diffusion constants			
		Q_e (mg/g)	k_1 (l/min)	R^2 (-)	Q_e (mg/g)	k_2 (g/mg min)	R^2 (-)	k_{id} mg/gmin$^{1/2}$)	C	R^2 (-)	Q_e,exp (mg/g)
CL	Mn(II)	1.699	0.067	0.936	2.070	0.075	0.995	0.152	0.474	0.946	1.903
	Fe(III)	1.690	0.056	0.986	2.288	0.047	0.993	0.170	0.395	0.910	2.051
	Cr(III)	1.853	0.049	0.997	2.401	0.042	0.999	0.159	0.849	0.910	2.005
CL_Na	Mn(II)	2.725	0.068	0.989	4.807	0.078	0.998	0.302	1.944	0.922	4.602
	Fe(III)	3.534	0.081	0.987	4.608	0.085	0.992	0.328	1.077	0.903	4.217
	Cr(III)	2.052	0.082	0.992	3.205	0.093	0.996	0.210	1.096	0.926	3.354

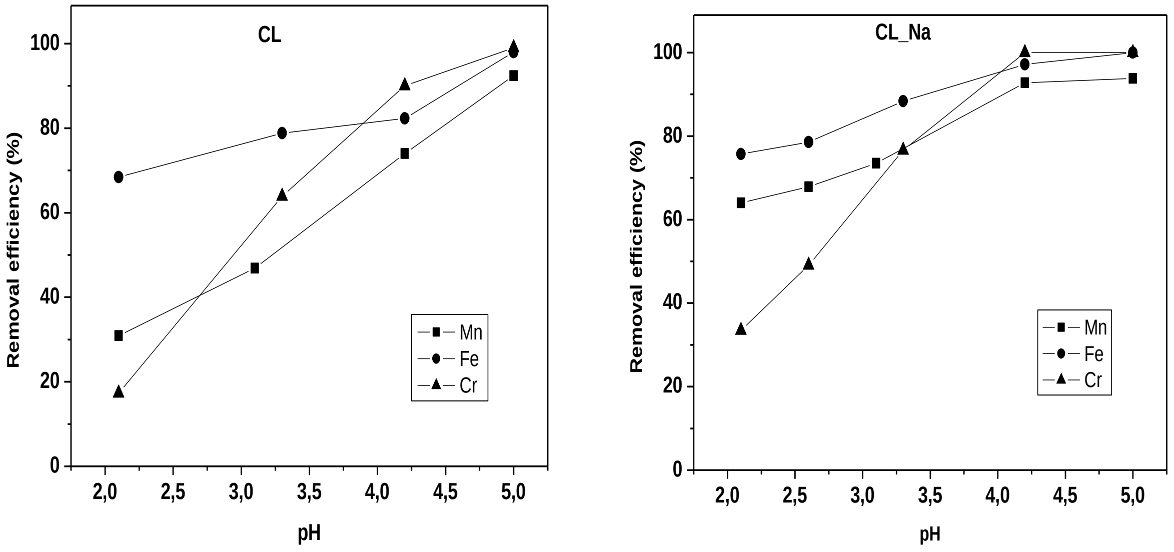

Fig. 2. Removal efficiency (%) as a function of pH for Mn(II), Fe(III) and Cr(III) adsorption onto CL and CL_Na (C_0 5 mg/L, stirring time 2 h).

In order to assess the nature of the diffusion process reasonable for the adsorption of investigated ions onto the clinoptilolite samples, attempts were made to calculate the pore diffusion coefficients.

The intraparticle diffusion equation [14] may be written as shown in equation 5:

$$Qt = k_{id}t^{1/2} + C \tag{5}$$

where C is the intercept, and k_{id} is the intraparticle diffusion rate constant (mg/g min$^{1/2}$). By using this model, the plots of Qt, versus $t^{1/2}$ should be linear if the intraparticle diffusion is involved in the adsorption process. The values of k_{id} and C are presented in Table 1. The deviation of the straight lines from the origin indicates that intraparticle diffusion cannot be accepted as the only rate-determining step for the adsorption of the investigated ions on CL and CL_Na, but other kinetic models may also control the rate of adsorption, all of which may be simultaneously operating. The correlation coefficients for the intraparticle diffusion model are also lower than that of the pseudo-second-order kinetic model. These results confirm that the pseudo-second-order mechanism is predominant for the adsorption of Mn(II), Fe(III) and Cr(III) onto CL and CL_Na.

The pH of the aqueous solution is an important controlling parameter in the adsorption process. It is known that increasing the pH decreases the extent of competition between the hydroxonium ions and metal ions in the solution for surface adsorption sites, thereby resulting in increased amounts of adsorbed metals by the adsorbents. Thus, it is possible to manage metal removal from aqueous solutions by changing the pH value. The effect of pH on the metal adsorption by clinoptilolite samples is presented on Fig. 2. The removal efficiency of Mn(II), Fe(III) and Cr(III) strongly depends on the acidity of the initial solutions. Most affected by pH changes for CL and CL_Na is the adsorption of Cr(III). pH values between 4.5 and 5 are considered as the most favourable for all systems.

The adsorption of Mn(II), Fe(III) and Cr(III) onto clinoptilolite samples as a function of temperature was studied by varying the temperature from 293 to 333 K, while keeping all other parameters constant (C_0 50 mg/L, pH 4.0). The amount of adsorbed metal ions increased with increasing temperature. The increase in adsorption with temperature indicates an endothermic process. This may be attributed either to the increase in the number of active surface sites available for adsorption on the adsorbent, or to the desolvation of the adsorbed species and the decrease in the thickness of the boundary layer surrounding the adsorbent, so that the mass transfer resistance of the adsorbate in the boundary layer decreases. The thermodynamic parameters, such as changes in the adsorption standard free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) were calculated using the following equations:

$$K_d = Q_e/C_e \tag{6}$$

$$\Delta G^0 = -RT \ln K_d \tag{7}$$

$$\ln K_d = \Delta S^0/R - \Delta H^0/RT \tag{8}$$

where K_d is the equilibrium constant, R is the gas constant (J/mol K) and $\boldsymbol{T}$ is the temperature (K). The enthalpy change, ΔH^0, and the entropy change, ΔS^0, are determined from the slope and intercept of the plots of $\ln K_d$ versus $1/T$, respectively. The values of ΔG^0, ΔH^0 and ΔS^0 parameters are presented in Table 2. The negative changes in the standard free energy indicate that adsorption of the investigated metal ions on CL and CL_Na is feasible and spontaneous. The positive values of ΔH^0 thermodynamically substantiate the assumption that the adsorption of the investigated ions on the two clinoptilolite samples is endothermic. The positive values of ΔS^0 show the existence of some structural changes at the solid–liquid interface. Also, the positive ΔS^0 favours both the complexation and stability of adsorption.

Adsorption isotherms obtained under equilibrium conditions are very important in designing adsorption systems, since such isotherms describe the distribution of adsorbed molecules between the liquid and solid phases in the equilibrium. The experimental adsorption isotherms obtained in the present study are presented on Fig. 3. According to the data shown in Fig. 3, the amounts of Mn(II), Fe(III) and Cr(III) adsorbed by CL_Na are higher when compared to CL. The exposure of natural clinoptilolite to a NaCl solution leads to the production of a sodium-rich sample. Na-rich forms of clinoptilolite are known to have an enhanced exchange capacity, because a part of the more tightly bound K and Ca cations are also exchanged when treated with Na solutions [15,16]. There are several isotherm equations available for evaluation of experimental adsorption equilibrium data. In the present study, the experimental equilibrium data for the adsorbed metal ions onto the investigated adsorbents were analyzed using the Langmuir (9), Freundlich (10) and Dubinin–

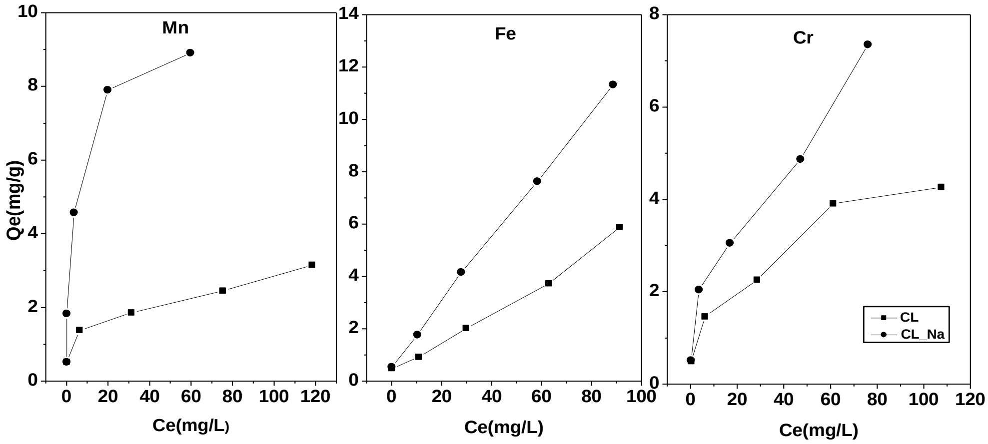

Fig. 3. Adsorption isotherms of Mn(II), Fe(III) and Cr(III) at pH 4.0 onto CL (■) and CL_Na (●)

Table 2. Thermodynamic parameters of Mn(II), Fe(III) and Cr(III) adsorption onto clinoptilolite samples.

Adsorbents	Metal ions	ΔG^0 (kJ/mol) 293K	ΔG^0 (kJ/mol) 313K	ΔG^0 (kJ/mol) 333K	ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)
CL	Mn(II)	-17.61	-18.60	-19.83	0.70	61.66
	Fe(III)	-20.85	-22.03	-23.50	0.94	73.38
	Cr(III)	-18.66	-19.99	-21.32	0.74	66.23
CL_Na	Mn(II)	-27.13	-28.64	-30.54	0.93	94.49
	Fe(III)	-22.70	-23.98	-25.57	0.94	79.61
	Cr(III)	-17.99	-18.99	-20.22	0.47	62.16

Radushkevich (11) isotherm models. The linear forms of these isotherms are as follows:

$$C_e/Q_e = 1/K_L Q_0 + C_e/Q \qquad (9)$$

where C_e is the concentration of NH_4^+ ions in the equilibrium solution (mg/L), Q_e is the amount of NH_4^+ adsorbed (mg) by per unit mass of adsorbent (g), Q_0 , the maximum adsorption capacity (mg/g); K_L, the constant of the Langmuir equation related to the enthalpy of the process.

$$\ln Q_e = \ln k_F + (1/n) \ln C_e \qquad (10)$$

where k_F and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

$$\ln Q_e = \ln Q_0 - \beta\varepsilon^2 \qquad (11)$$

where β is the constant of the adsorption energy (mol^2/J^2), and ε is the Polanyi potential, described as:

$$\varepsilon = RT \ln(1+1/C_e) \qquad (12)$$

where R is the gas constant (J/mol K) and T is the temperature (K). The mean adsorption energy E (KJ /mol) can be calculated from parameter β as follows:

$$E = 1/(-2\beta)^{1/2} \qquad (13)$$

The corresponding correlation coefficients and the isotherm constants are calculated and presented in Table 3. The Freundlich model yielded a much better (r^2 = 0.992-0.998) fit than that of the Langmuir (r^2 =0.938-0.998) and Dubinin–Radushkevich models (r^2 = 0.897-0.973). The highest equilibrium adsorption capacity Q_0 towards all investigated ions was obtained for the adsorbent CL_Na. The values for the CL vary from 3.17 mg/g [for Mn(II)] to 12.44 mg/g [for Fe(III)]. For the modified adsorbent CL_Na the values are as follows: from 7.17 mg/g (for Cr(III)] to 38.64 mg/g [Fe(III)]. Obviously, the adsorbent CL_Na proved to be better than CL. Fe(III) is characterized by the highest adsorption capacity for both adsorbents.

The Langmuir parameters can be used to predict the affinity between adsorbate and adsorbent using the dimensionless separation factor R_L, which is defined as:

$$R_L = 1/(1 + K_L C_0) \qquad (14)$$

The values of R_L for the natural and Na-modified clinoptilolites varied within the ranges 0.012 - 0.980 (for CL) and 0.066 – 0.733 (for CL_Na). All values were within the 0–1 range, indicating favourable adsorption for all ions investigated. In addition, the values of the separation factor demonstrated that natural and modified clinoptilolites are potential adsorbents for the removal of Mn(II), Fe(III) and Cr(III) from aqueous solutions. The Freundlich model shows a similar adsorption capacity sequence as the Langmuir isotherm according to the $\boldsymbol{k_F}$ values. In the study reported here, the values of n were all in the range from 1.17 to 4.53, indicating favourable adsorption onto the clinoptilolite samples [17].

The value of *E* from the D-R model is very useful in predicting the type of adsorption and gives information about chemical and physical adsorption. It is known that energy of adsorption in the range of 2–20 kJ/mol could be considered physisorption in nature [18,19]. As shown in Table 3, the values obtained in the present work are in the range 1.25 - 4.44 KJ/mol. This indicates that the type of adsorption for all investigated ions onto CL and CL_Na is essentially physical.

It is important to assume that the mechanism of metal ions adsorption on clinoptilolite samples cannot be directly related to the Langmuir, Freundlich or Dubinin–Radushkevich models. However, from Table 3, it may be concluded that the adsorption isotherm of the investigated ions exhibits mainly Freundlich behaviour, which indicates heterogeneous surface binding. It confirms the existence of different types of possible adsorption sites on the clinoptilolite surface with different energy if the site was on an edge or was located in a defect position.

From a practical point of view, most effluent solutions are likely to contain a range of metal ions rather than a single ionic type. Under such circumstances, it becomes essential to study not only single-component adsorption, but also the effects of present co-cations on the adsorption capacity of adsorbents [20]. For such studies, a model multi-component aqueous solution containing the three metal ions (Mn(II), Fe(III) and Cr(III)) with initial concentration 20 mg/L was prepared in order to investigate the influence of competing ions on the individual adsorption on CL and CL_Na. The results obtained are presented in Table 4. The adsorption of the three ions investigated was significantly affected by the presence of competing ions. The amount adsorbed from multi-component solutions with concentration 20 mg/L, decreased by 33%, 21% and 35% for Mn(II), Fe(III) and Cr(III), respectively (for CL), and by 30%, 18% and 31% for Mn(II), Fe(III) and Cr(III) respectively (for CL_Na), compared to their respective single-component solutions (see Table 4). It may be concluded that despite the similar properties of the investigated metal ions, each of them interacts only with specific adsorption sites of the adsorbents [21].

Table 3. Langmuir, Freundlich and Dubinin-Radushkevich parameters for the adsorption of Mn(II), Fe(III) and Cr(III) onto CL and CL_Na.

Adsorbent	Metal ions	Langmuir			Freundlich			Dubinin-Radushkevich		
		Q_0 (mg/g)	K_L (L/mg)	R^2	k_F (L/mg)	n (-)	R^2	Q_m (mg/g)	E (KJ/mol)	R^2
CL	Mn(II)	3.171	0.057	0,977	0.866	4.534	0.992	2.12	4.44	0.897
	Fe(III)	12.439	0.569	0.978	1.118	1.176	0.997	3.97	1.25	0.900
	Cr(III)	4.673	0.004	0.974	0.943	2.73	0.994	2.74	2.00	0.898
CL_Na	Mn(II)	9.100	0.095	0.998	2.594	2.849	0.996	6.62	3.74	0.973
	Fe(III)	38.640	0.007	0.966	3.242	1.169	0.998	8.07	1.27	0.917
	Cr(III)	7.173	0.073	0.938	1.299	2.693	0.998	4.42	2.65	0.939

Table 4. Adsorption of Mn(II), Fe(III) and Cr(III) from single- and multi-component metal solution onto clinoptilolite samples (C_0 20 mg/L, pH 4.00, stirring time 2 h).

Adsorbent	Metal ion	Adsorbed amount (mg/g)	
		single-component solution	multi-component solution
CL	Mn(II)	1.38	0.93
	Fe(III)	0.92	0.73
	Cr(III)	1.47	0.95
CL_Na	Mn(II)	1.83	1.28
	Fe(III)	1.78	1.46
	Cr(III)	2.06	1.41

4. CONCLUSIONS

The adsorption of Mn(II), Fe(III) and Cr(III) onto natural and NaCl-treated Bulgarian clinoptilolite was studied. A contact time of 2 h was sufficient to attain equilibrium with both adsorbents. The experimental parameters such as solution pH, contact time, initial concentration and temperature influenced the removal of the investigated metal ions. Comparison of the equilibrium adsorption data with Langmuir, Freundlich and Dubinin–Radushkevich isotherm models showed that the Freundlich model described the process more accurately. The treatment with NaCl improved the adsorption capacity of natural clinoptilolite. The maximum adsorption capacities of CL and CL_Na were found to be 3.17, 4.67 and 12.44 mg/g for Mn(II), Cr(III) and Fe(III), respectively (for CL) and 9.10, 7.17and 38.64 mg/g for Mn(II), Cr(III) and Fe(III), respectively (for CL_Na). The values of ΔS^0, ΔH^0 and ΔG^0 for the removal of the investigated ions by the clinoptilolite samples were calculated. The negative values of the changes in Gibbs free energy indicated that adsorption of Mn(II), Cr(III) and Fe(III) onto CL and CL_Na was spontaneous and exothermic. The pseudo-second-order kinetic model better predicted the adsorption kinetics of the investigated ions onto clinoptilolite samples. The amounts of metal adsorbed from multi-component solutions were significantly lower than those adsorbed from single solutions.

Based on the experimental results, Bulgarian clinoptilolite from Beli plast deposit could be used as a low-cost adsorbent for the removal of Mn(II), Fe(III) and Cr(III) ions from different kinds of contaminated waters and it may be an alternative to more expensive adsorption materials.

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ПРИЛОЖЕНИЕ НА БЪЛГАРСКИ КЛИНОПТИЛОЛИТ ЗА ИЗВЛИЧАНЕ НА Mn(II), Fe(III) И Cr(III) ОТ ВОДНИ РАЗТВОРИ

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Постъпила на 28 март, 2011 г.; приета на 26 септември, 2011 г.

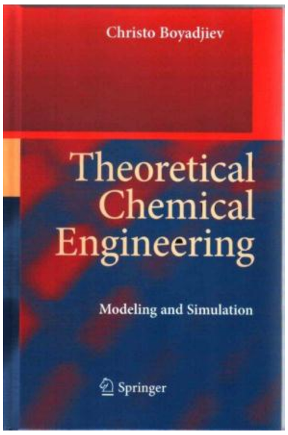
(Резюме)

Целта на настоящата работа е изследване на адсорбцията на Mn(II), Fe(III) и Cr(III) от водни разтвори върху природен и модифициран български клиноптилолит от находището в Бели пласт. Проведени са адсорбционни изследвания в статичен режим с цел да се установи влиянието на времето на контакт, температурата, pH на изходните разтвори и началната концентрация на изследваните йони. Получени са равновестните адсорбционните изотерми и е изследвано тяхното съответствие с теоретичните модели на Лангмюир, Фройндлих и Дубинин Радушкевич. Адсорбцията на Mn(II), Fe(III) и Cr(III) се описва най-добре с модела на реакции от псевдо-втори порядък и изотермата на Фройндлих. Модификацията на природния клиноптилолит с NaCl повишава адсорбция му капацитет. Установено е, че извличането на изследваните метални йони от мулти-компонентен разтвор се влияе значително от присъствието на конкурентни йони.

Bulgarian Chemical Communications, Volume 44, Number 2 (pp. 188 – 188) 2012

Book review

Christo Boyadjiev. **Theoretical Chemical Engineering (Modeling and Simulation)**
Springer-Verlag, Berlin Heidelberg, 2010.



Chemical engineering is an applied science dealing with the powerful methodologies of mathematics, physics, chemistry and engineering sciences. Since it is designed to transfer the fundamental results of chemical research activity to practical applications chemical engineering has to solve many practical tasks, usually associated with the very complicated conditions in practice, i.e. complicated geometry in the real apparatuses, turbulent multiphase flows, high rates of the processes, etc., the different simplified approaches for process modeling are used with different level of complexity.

Usually the similarity theory is helpless to solve correctly the scale-up problems. That is why mathematical models contribute to the best approximations to the reality to make scaling-up more reliable.

The monograph “Theoretical Chemical Engineering” written by Prof. Christo Boyadjiev, DSc has the ambitious goal to cover all of the directions of modeling and mathematical descriptions of the most frequently met processes in chemical industry and the flow sheets in chemical industry as a whole.

It started with considerations on the models describing the flow patterns and their impact on the transport phenomena in relatively simple geometries. The cases of physical transport processes as well as the cases of chemical reactions occurring in the liquid phase are discussed. A big merit of this part of the book is the detailed description of the non-linear transport phenomena and their effect on the net mass transfer. The hydrodynamic stability is considered in this context.

A significant part of the book is dedicated to the mathematical methods used for solving the differential transport equations coupled with the procedures of parameter identification, particularly for inverse problems.

Comparative analysis of the variety of mathematical models – starting from the lowest level of comprehensiveness, like the experiment design methods to the highest level of partial differential equations for defined flows and shapes is made.

The optimization methods are considered in the context of optimal design and control of total plants in chemical technology.

It could be emphasized that the main part of the book is based on own research results of the author, showing a broad variety of expertise.

The book will be useful either for researchers or for students as a tool for solution of various chemical engineering tasks.

If someone wants to know what does chemical engineering is, he can read this book.

V. Beschkov.

Bulgarian Chemical Communications, Volume 44, Number 2 (pp. 189 – 189) 2012

ERRATUM

The authors and their affiliations of the article “Catalytic synthesis of diphenylmethyl ethers (DPME) using Preyssler acid $H_{14}[NaP_5W_{30}O_{110}]$ and silica-supported Preyssler catalysts” published in Bulgarian Chemical Communications, volume 44, issue 1, pp. 11-19 should be read as follows:

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CONTENTS

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СЪДЪРЖАНИЕ

BULGARIAN CHEMICAL COMMUNICATIONS

Instructions about Preparation of Manuscripts

General remarks: Manuscripts are submitted in English by e-mail or by mail (in duplicate). The text must be typed double-spaced, on A4 format paper using Times New Roman font size 12, normal character spacing. The manuscript should not exceed 15 pages (about 3500 words), including photographs, tables, drawings, formulae, etc. Authors are requested to use margins of 3 cm on all sides. For mail submission hard copies, made by a clearly legible duplication process, are requested. Manuscripts should be subdivided into labelled sections, e.g. **Introduction, Experimental, Results and Discussion**, *etc*.

The title page comprises headline, author's names and affiliations, abstract and key words.

Attention is drawn to the following:

a) **The title** of the manuscript should reflect concisely the purpose and findings of the work. Abbreviations, symbols, chemical formulas, references and footnotes should be avoided. If indispensable, abbreviations and formulas should be given in parentheses immediately after the respective full form.

b) **The author**'s first and middle name initials, and family name in full should be given, followed by the address (or addresses) of the contributing laboratory (laboratories). **The affiliation** of the author(s) should be listed in detail (no abbreviations!). The author to whom correspondence and/or inquiries should be sent should be indicated by asterisk (*).

The abstract should be self-explanatory and intelligible without any references to the text and containing not more than 250 words. It should be followed by key words (not more than six).

References should be numbered sequentially in the order, in which they are cited in the text. The numbers in the text should be enclosed in brackets [2], [5, 6], [9–12], etc., set on the text line. References, typed with double spacing, are to be listed in numerical order on a separate sheet. All references are to be given in Latin letters. The names of the authors are given without inversion. Titles of journals must be abbreviated according to Chemical Abstracts and given in italics, the volume is typed in bold, the initial page is given and the year in parentheses. Attention is drawn to the following conventions:

a) The names of all authors of a certain publications should be given. The use of "*et al.*" in the list of references is not acceptable.

b) Only the initials of the first and middle names should be given.

In the manuscripts, the reference to author(s) of cited works should be made without giving initials, e.g. "Bush and Smith [7] pioneered...". If the reference carries the names of three or more authors it should be quoted as "Bush *et al*. [7]", if Bush is the first author, or as "Bush and co-workers [7]", if Bush is the senior author.

Footnotes should be reduced to a minimum. Each footnote should be typed double-spaced at the bottom of the page, on which its subject is first mentioned.

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