The Metal Complexes of Natural Compounds, Usnic Acid and Naringenin Immobilized on Mesoporous Silica: Solid Phase Extraction and Oxidative Catalytic Properties

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Summary: The novel semi-natural Schiff bases were synthesized with the reaction of the natural compounds usnic acid and naringenin extracted and purified in natural sources and chemically modified silica gel. Cu(II), Ni(II), Co(II) and Mn(II) complexes of the ligands were synthesized and the silica-supported ligands and their metal complexes were characterized by FT-IR, TG/DTA, SEM, EDX, ICP-OES and elemental analyses techniques. The solid-phase extraction behaviours of the novel silica-supported ligands were examined. It was found that the hybrid materials showed the very efficient adsorption properties to Cu(II), Cd(II), Pb(II) and Cr(III) metal ions maximum at pH=8-9. The metal ions could be recovered again nearly 100 % from the silica-supported ligands in the recycling experiments. The catalytic efficiencies of the metal complexes in the oxidation reactions of cyclohexane, cylohexene, cyclooctane and styrene subtrates were examined under microwave irradiation in the present of H_2O_2. The complexes showed very good catalytic activities in the oxidation reactions of the various tested substrates.

Keywords: Usnic acid, Naringenin, Schiff base, Silica gel, Solid-phase extraction, Catalysis.

Introduction

The Schiff base ligands which are the Lewis bases can form the stable 4, 5 or 6 coordinated complexes with preferably phenolic-OH groups near the azomethine group with some metal ions [1,2]. The size, charge and ionization potential of metal ions affect the stability of coordination compounds. The structures of coordiantion compounds of Schiff bases formed with divalent metal ions can be in planar, tetragonal, tetrahedral or octahedral geometries. Ligands surround a metal as a cluster of ions and molecules and are therefore widely used in the preparation of various complexes. Hence, Schiff bases and their metal complexes are widely used in the various areas including catalysis, agriculture, cosmetics, pharmaceuticals and industrial chemistry [1, 2, 11, 12, 3–10]. Schiff bases and coordination compounds have also attracted attention due to their various biological activities such as antibacterial [13], antifungal [8], antiviral [14], insecticidal [15, 16], plant growth regulator [8, 17], antiinflammatory and analgesic [18, 19], antitumoral and cytotoxic [18–21]. Solid phase extraction allows the enrichment and purification of any analytes from a solution via a solid adsorbent. It can be perfomed as a batch and an elution processes. The process based on the elution of a liquid through a column holding the analytes such as a cartridge, resin or a disc and then recovering the holding analytes with a suitable solvent. In recent years, solid-phase extraction has been widely used for enriching trace toxic pollutants such as pesticides in water samples [22]. Ion-exchanging resins, chelating polymers and inorganic materials are widely used as support materials in solid-phase extraction. [23] The most important characteristics of an ideal support material are their regular structure, controlled and effective capacity, suitable particle size, chemical and thermal stability. Support materials used in solid phase extraction are water-insoluble solid materials to which bonded ligands or metal complexes [24]. Some of the advantages of inorganic support materials as compared with organic support materials are good mechanical stability, fast retention of metal ions, no swelling, good selectivity [23]. Numerous reports on the adsorption of some microorganisms, natural compounds, metal salts, polymers, chelating organic materials *etc.* using solid supports such as silica gel, metal oxides, zeolites, clay, sand, activated carbon, fibers, cellulose, chitin, chitosan, ion exchange resins has been documented [25, 26]. Aromatic Schiff bases and/or their complexes formed with different metal ions are known to have catalytic activity in oxidation, hydrolysis, electro-reduction and degradation reactions [8]. Catalytic oxidation reactions are the commercially important reactions. More than half of the chemicals produced in commercial catalytic processes are subjected to the catalytic oxidation process as part of their synthesis. Besides, catalytic

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oxidation of environmental and water pollutants are one of the important area [27]. Most of the monomers used in the production of fibers, plastics and other polymer products are produced by the selective oxidation of hydrocarbons using the catalysts containing metal complexs of various ligands [9,10]. In this study, silica gel was preferred as inorganic support material because of its superior properties to other support materials. The aims of the study were a) in order to the chemical modification of the silica gel with 3-aminopropyl-triethoxysilane (APTES); b) in order to sytnthesize the new ligands of two type of the natural compounds, usnic acid and naringenin; c) to evaluate the solid phase extraction properties of these ligands by syringe technique using Cu(II), Pb(II), Cd(II) and Cr(III) metal ions in aqueous solution; d) in order to synthesize the complexes of Ni(II), Cu(II), Co(II) and Mn(II) on silica-supported semi-natural Schiff bases; e) in order to characterize the chemical structures of the synthesized ligands and their metal complexes via FT-IR, SEM, EDX, ICP-OES, TG/DTA and elemental analysis techniques; f) in order to determine the catalytic oxidation effects of silica-supported Schiff base-metal complexes under microwave power.

Experimental

Chemicals, apparatus, materials and reagents

All the reagents and the organic solvents were purchased from commercial sources and used as received, unless noted otherwise. Naringenin was purchased from Sigma-Aldrich, while usnic acid was isolated from *U. longissima* lichen species. Merck Silica gel 60 having particle size of 0.063-0.200 mm (70-230 mesh) was used as solid support. Infrared spectra were recorded using KBr discs (4000–400 cm^{-1}) on a Perkin Elmer Spectrum 400 FT-IR. Elemental analyses were performed using LECO CHNS 932 instrument. The thermal behavior data of the compounds were collected on a SII Exstar STA 6000 thermal analysis system under nitrogen atmosphere at a heating rate of 10 °C/min in the range 30-900 °C. The surface morphology of the silica-supported ligands were analyzed Zeiss Evo LS10 SEM attached with Bruker Quantax EDS. The amount of metal ions of the metal-complexes were determined by using Perkin Elmer Optima 2100DV ICP-OES coupled with AS93 autosampler after an acid-peroxide digestion in Berghof MWS3+ microwave oven. Calibration standarts of all elements were prepared from Inorganic Ventures individual certified standards (each of 1000 $mg.L^{-1}$). Instrument conditions, calibration points and emission wavelengths of the elements were determined according to the elements. Ultrapure water obtained from a Milli-Q purifier system (Millipore Corp., Bedford, MA) was used throughout the work. The catalytic reaction products were characterized and analyzed by using Perkin Elmer Clarus 600 GC equipped with MS detector fitted with Elite-5 MS and FID detector fitted with BPX5 capillary columns. Calibration standarts were prepared in dichloromethane solvent and injected to gas chromatography. External calibrations were drawn by the instrument software with the obtained data for each substrate and products. Amine modified silica-gel was produced with our previous studies [4–7, 28].

Isolation of usnic acid from Lichen material

Usnea longissima Ach. was collected from the Erzurum-Oltu region (Nothern Anatolia) of Turkey in August 2013. It was identified and a voucher specimen (ATA-KKEF-776) has been deposited in the herbarium of Ataturk University, Erzurum (Turkey). The chemical structure of usnic acid was characterized by UV, IR, ^{1}H-NMR and ^{13}C-NMR and was confirmed based on the previous spectroscopic data [29, 30].

Synthesis of SiO_2@APTES-Usnic acid (UA) and SiO_2@APTES-Naringenin (NG)

Each of usnic acid (5 mmol, 1.72 g) and naringenin (5 mmol, 1.36 g) were mixed the seperately to modified silica gel (5 g) in 50 ml of ethanolic mixture and refluxed for 24 h. The ligands (SiO_2-APTES-UA and SiO_2@APTES-NG) were filtered in vacuo, washed with acetone and distilled water, respectively and then dried at 75 °C under vacuum.

SiO_2@APTES-UA: Yellowish colour. Elemental analysis (%): C, 24.10; H, 2.32; N, 1.86. FTIR (KBr, cm^{-1}): ν; 3536 (br, Ar-OH), 1621 (br, -C=N), 1557 (br, ArC=C), 1372 (s, -C-N), 1189 (C-O), 1055 (s-br, Si-O), 788 (Si-C).

SiO_2-APTES-NG: Dark yellow colour. Elemental analysis (%): C, 15.36; H, 2.32; N, 1.93. FTIR (KBr, cm^{-1}): ν; 3536 (br, Ar-OH), 1635 (br, -C=N), 1593 (br, Ar C=C), ve 1344 (s, -C-N), 1223 (C-O), 1051 (s-br, Si-O), 788(Si-C).

Synthesis of Metal Complexes of SiO_2@APTES-UA and SiO_2@APTES-NG

In order to synthesize SiO_2@APTES-UA-M(II) complexes, SiO_2@APTES-UA ligand (1g) was individually mixed 2 mmols of $CoCl_2.6H_2O$, $CuCl_2$, $MnCl_2$ and $NiCl_2$ $6.H_2O$ in ethanol and refluxed at 65 °C for 8 hours. The mixtures was then filtered, washed over acetone and distilled water, respectivelly, and dried under vacuum.

SiO_2@APTES-UA-Co(II): Green colour. Elemental analysis (%): C,15.55; H, 2.96; N, 1.58; Co, 4.56. FTIR (KBr, cm^{-1}): ν; 3453 (br, Ar-OH), 1622 (br, -C=N), 1552 (br, ArC=C), ve 1372 (s, -C-N), 1189 (C-O), 1048 (s-br, Si-O), 788 (Si-C).

SiO_2@APTES-UA-Cu(II): Green colour. Elemental analysis (%): C, 14.96; H, 2.96; N, 1.45; Cu, 4.61. FTIR (KBr, cm^{-1}): ν; 3453 (br, Ar-OH), 1621 (br, -C=N), 1558 (br, Ar C=C), ve 1370 (s, -C-N), 1187 (C-O), 1051 (s-br, Si-O), 789 (Si-C).

SiO_2@APTES-UA-Mn(II): Brown colour. Elemental analysis (%): C, 15.17; H, 2.81; N, 1.58; Mn, 4.43. FTIR (KBr, cm^{-1}): ν; 3558 (br, Ar-OH), 1621 (br, -C=N), 1557 (br, ArC=C), ve 1372 (s, -C-N), 1187 (C-O), 1054 (s-br, Si-O), 792 (Si-C).

SiO_2@APTES-UA-Ni(II): Yellow colour. Elemental analysis (%): C, 19.15; H, 2.79; N, 4.82; Ni, 4.55. FTIR (KBr, cm^{-1}): ν; 3454 (br, Ar-OH), 1622 (br, -C=N), 1557 (br, ArC=C), ve 1372 (s, -C-N), 1189 (C-O), 1053 (s-br, Si-O), 788 (Si-C).

SiO_2@APTES-NG-Co(II): Brown colour. Elemental analysis (%): C, 12.56; H, 2.69; N, 1.56; Co, 4.50. FTIR (KBr, cm^{-1}): ν; 3556 (br, Ar-OH), 1635 (br, -C=N), 1601 (br, ArC=C), ve 1304 (s, -C-N), 1197 (C-O), 1056 (s-br, Si-O), 788 (Si-C).

SiO_2@APTES-NG-Cu(II): Brown colour. Elemental analysis (%): C, 12.61; H, 2.76; N, 1.63; Cu, 4.65. FTIR (KBr, cm^{-1}): ν; 3445 (br, Ar-OH), 1634 (br, -C=N), 1602 (br, ArC=C), ve 1311 (s, -C-N), 1199 (C-O), 1057 (s-br, Si-O), 789 (Si-C).

SiO_2@APTES-NG-Mn(II): Brown colour. Elemental analysis (%): C, 13.30; H, 2.47; N, 1.62; Mn, 4.29. FTIR (KBr, cm^{-1}): ν; 3444 (br, Ar-OH), 1635 (br, -C=N), 1594 (br, ArC=C), ve 1311 (s, -C-N), 1217 (C-O), 1059 (s-br, Si-O), 795 (Si-C).

SiO_2@APTES-NG-Ni(II): Brown colour. Elemental analysis (%): C, 12.93; H, 2.50; N, 2.25; Ni, 3.94. FTIR (KBr, cm^{-1}): ν; 3526 (br, Ar-OH), 1635 (br, -C=N), 1598 (br, ArC=C), ve 1309 (s, -C-N), 1209 (C-O), 1051 (s-br, Si-O), 789 (Si-C).

Solid Phase Extraction Properties of SiO_2@APTES-UA and SiO_2@APTES-NG

The solid phase extraction properties of SiO_2@APTES-UA and SiO_2@APTES-NG towards Cu (II), Pb (II), Cd (II) and Cr (III) ions in water samples were examined by using syringe method as applied our previous studies [4, 7, 28].

Catalytic Oxidation

Oxidation experiments were carried according to our previous study [6].

Results and Discussion

Syntheses

In the first step of the syntheis, silica gel surface was activated to form silanol groups (Si-OH) and 3-aminopropyl-triethoxysilane (APTES) compound was bonded to chemical modification of silica gel. In the second step of the study, usnic acid and naringenin were chemically bound into the modified silica gel to form the Schiff base. The last, Ni(II), Cu(II), Co(II) and Mn(II) complexes of the silica-supported Schiff bases were synthesized and characterized by FT-IR, SEM, EDX, ICP-OES, TG/DTA and elemental analysis techniques (Fig.1).

FT-IR

Some of the peaks of the functional groups can be observed intensive enough due to the predominance of the silica gel in FT-IR spectra. Another problem is that silica gel is fastly absorbs too much moisture and water often close the vibration bands of compound bonded to silica gel [31]. Vibrations of the silica-supported usnic acid and naringenin ligands and their metal complexes were observed enough (Fig S1). C=C bands of aromatic ring were seen as very weak around 1585-1600 cm^{-1}, whereas the vibration bands of aromatic –OH groups were observed as weak peaks around 3450-3550 cm^{-1}. The strectch of azomethine group (CH=N) were collected around 1620-1635 cm^{-1}. C-N, C-O, Si-O and Si-C vibrations were determined around 1350 cm^{-1}, 1200 cm^{-1}, 1050 cm^{-1} and 780-800 cm^{-1}, respectively in the fingerprint region of the FT-IR spectra. All data are consistent with the pevious reports [5–7,32] and the elemental analysis results and important FT-IR signals of the ligands and their metal complexes are presented in Table-1

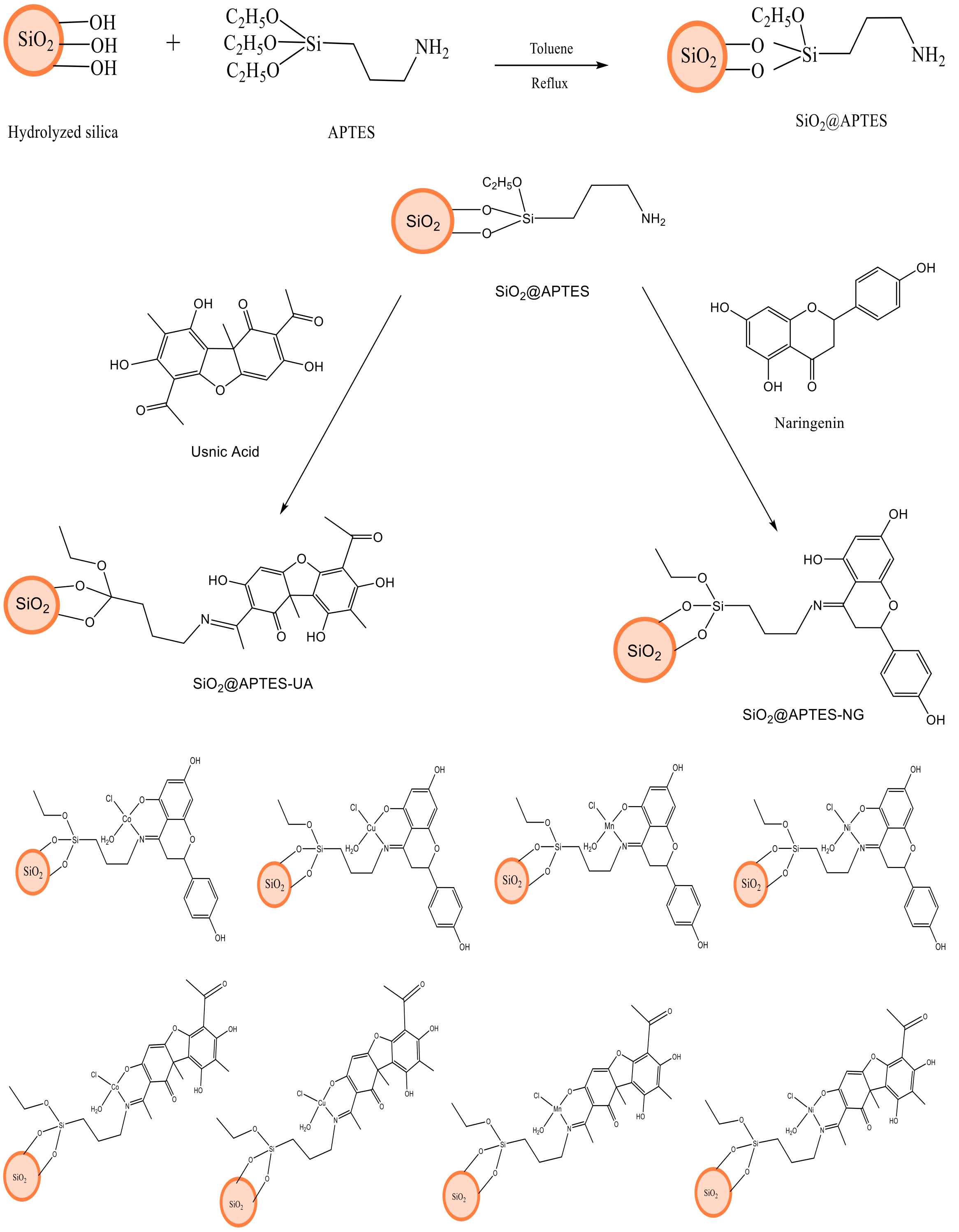

Fig. 1: Synthesis of SiO_2@APTES-UA and SiO_2@APTES-NG and the possible structures of the synthesized SiO_2@APTES-UA-M(II) and SiO_2@APTES-NG-M(II) complexes.

Table-1:Elemental Analysis results and significant FT-IR signals of the ligands and their metal complexes.

	N %	**C %**	**H %**	**Metal %**	**v(-OH)**	**v(C=C)**	**v(C=N)**	**v(C-O)**	**v(C-N)**	**v(Si-O)**	**v(Si-C)**
SiO_2@NG	-	-	-		3536	1593	1635	1223	1344	1051	788
SiO_2@NG-Co(II)	1.56	12.56	2.69	4.50	3556	1601	1635	1197	1304	1056	788
SiO_2@NG-Mn(II)	1.62	13.30	2.47	4.29	3444	1594	1635	1217	1311	1059	795
SiO_2@NG-Cu(II)	1.63	12.61	2.76	4.65	3445	1602	1634	1199	1311	1057	789
SiO_2@NG-Ni(II)	2.25	12.93	2.50	3.94	3526	1598	1635	1209	1309	1051	789
SiO_2@UA	-	-	-		3536	1557	1621	1189	1372	1055	788
SiO_2@UA-Co(II)	1.58	15.55	2.96	4.56	3553	1552	1622	1189	1372	1048	788
SiO_2@UA-Mn(II)	1.58	15.17	2.81	4.43	3558	1557	1621	1187	1372	1054	792
SiO_2@UA-Cu(II)	1.45	14.96	2.96	4.61	3453	1558	1621	1187	1370	1051	789
SiO_2@UA-Ni(II)	4.82	19.15	2.79	4.55	3454	1557	1622	1189	1372	1053	788

NG: Naringenin; UA: Usnic acid

Thermogravimetric Properties (TG/DTA)

According to TG/DTA analyses (Fig S2), the thermal characteristics of SiO_2@APTES-UA, SiO_2@APTES-NG ligands and their metal complexes are very similar. The main difference is the new band due to the formation of metal oxide forms after the degredation of organic groups in metal complexes. In general, two or three endothermic bands were observed in TG/DTA curves of the silica gel-supported imine ligands. All the metal complexes have lost a small amount of physical adsorbed water with an endothermic band between 25-80 °C. This band is thought to be formed by desorption of adsorbed water prior to TGA analysis due to the hygroscopic structure of silica gel. In TG/ DTA analysis, the bands observed up to 200 °C are estimated to be due to the water molecules coordinated to the metal complexes. Endothermic peaks ranging from 200 to 700 °C were observed as big band including the degradation of organic backbone and coordinated groups and the formation of metal oxides [1,3,6,28].

SEM/EDX

SEM images (Fig S3) showed that the surface and gaps of the silica gel particles were coated and the filled with the organic compounds, usnic acid and naringenin. The ligands and their metal complexes dispersed on silica-gel particles played very efficient roles as adsorbents in solid-phase extraction tests and good heterogeneous catalysts in the oxidation reactions. It can be said that the coordinations of chloro ligands to the metal centers were observed at around 2.6 keV in EDX spectra in order to balance ionically for all the complexes. Whereas aqua ligands were attached to the remaining coordination holes of the metals.

Solid Phase Extraction

In the solid phase extraction studies performed by syringe method, pH: 4-10 ranges were studied to determine the effect of pH on the metal ion adsorption. The maximum adsorption was observed in the range of pH: 8-9 (Fig. 2). In the case of pH≤4, imine groups were positively charged due to the acidic environment and therefore, the adsorption of positively charged metal ions was not performed well to the silica-supported adsorbents. In contrast to low pH values, the adsorptions was reduced due to metal-hydroxide formation at pH> 9. Therefore, the optimum pH range was determined as pH: 8-9. The synthesized new solid phases showed very good sorbent properties against Pb (II), Cr (III) and Cu (II) ions [4,7,28,32–34]. Recovery trials are very important for pre-concentration and purification processes, therefore, finding a suitable eluent to recover the adsorbed metal ions is the crucial point for solid phase extraction. For this purpose, HCl (2M) and HNO_3 (2M) solutions were used for the recovery of the metals and the metals recovered with about 100% yield (Table 2). The synthesis of silica-supported SiO_2@APTES-UA and SiO_2@APTES-NG ligands with high yields and high recovery rates in acidic environments indicate that these ligands are more suitable ligands for solid phase extraction [4, 7, 28, 32–34]

Table-2: Effect of different eluents on recovery of the metals ions.

	Elution	**Recovery (%)**			
		Cu(II)	**Cd(II)**	**Cr(II)**	**Pb(II)**
SiO_2@APTES-UA	**2M HCl**	**81.6**	**73.2**	**100**	**100**
	2M HNO_3	**97.7**	**58.7**	**100**	**100**
SiO_2@APTES-NG	**2M HCl**	**100**	**45.5**	**100**	**100**
	2M HNO_3	**92**	**49.9**	**100**	**100**

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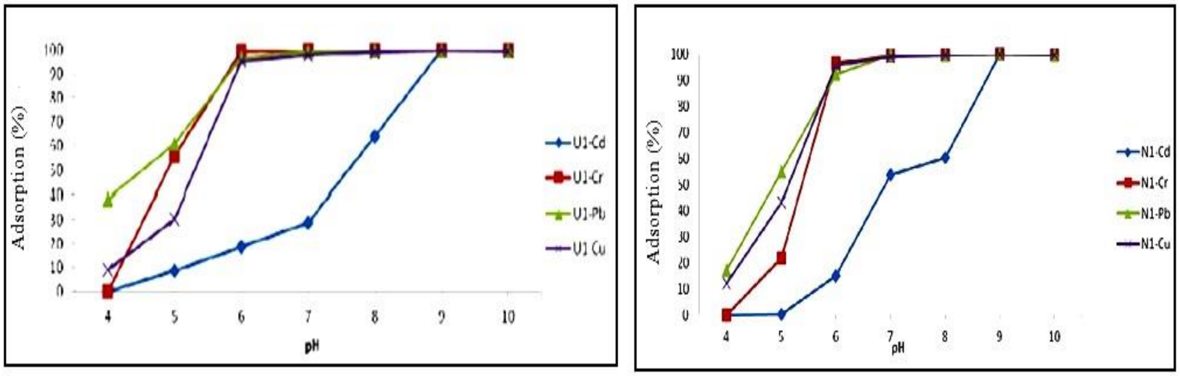


Fig. 2: The effect of pH on adsorption. U1: SiO_2@APTES-UA and N1: SiO_2@APTES-NG.

Table-3: Langmuir and Freundlich isotherm parameters.

	Metal	**Lagmuir isotherm**			**Freundlich İsotherm**		
		q_o	**b**	**R^2**	**n**	**K_f**	**R^2**
	Cr	**0,2547**	**83,8932**	**0,7247**	**1,0878**	**10,7105**	**0,9997**
SiO_2@APTES-UA	**Cd**	**0,0927**	**245,6036**	**0,6627**	**1,1080**	**9,0733**	**0,9993**
	Cu	**0,3509**	**54,1749**	**0,9539**	**1,0398**	**13,5573**	**0,9962**
	Pb	**0,0694**	**265,1750**	**0,9067**	**1,0804**	**8,8972**	**0,9998**
	Cr	**0,2040**	**109,1759**	**0,8718**	**1,1106**	**9,4426**	**0,9997**
SiO_2@APTES-NG	**Cd**	**0,2435**	**79,5853**	**0,8628**	**1,0701**	**10,9422**	**0,9998**
	Cu	**0,0980**	**234,5287**	**0,9777**	**1,0826**	**9,7653**	**0,9973**
	Pb	**0,0970**	**166,6236**	**0,7945**	**1,0549**	**10,9608**	**0,9999**

The sorption characteristics of SiO_2@APTES-UA and SiO_2@APTES-NG were evaluated with the sorption isotherm models of *Freundlich* and *Langmuir*. The monolayer *Langmuir* and the empirical *Freundlich* isotherms are usually represented in the following linearized forms:

$$lnq_e = lnK_f + \frac{1}{nlnC_e}$$

Langmuir isotherm

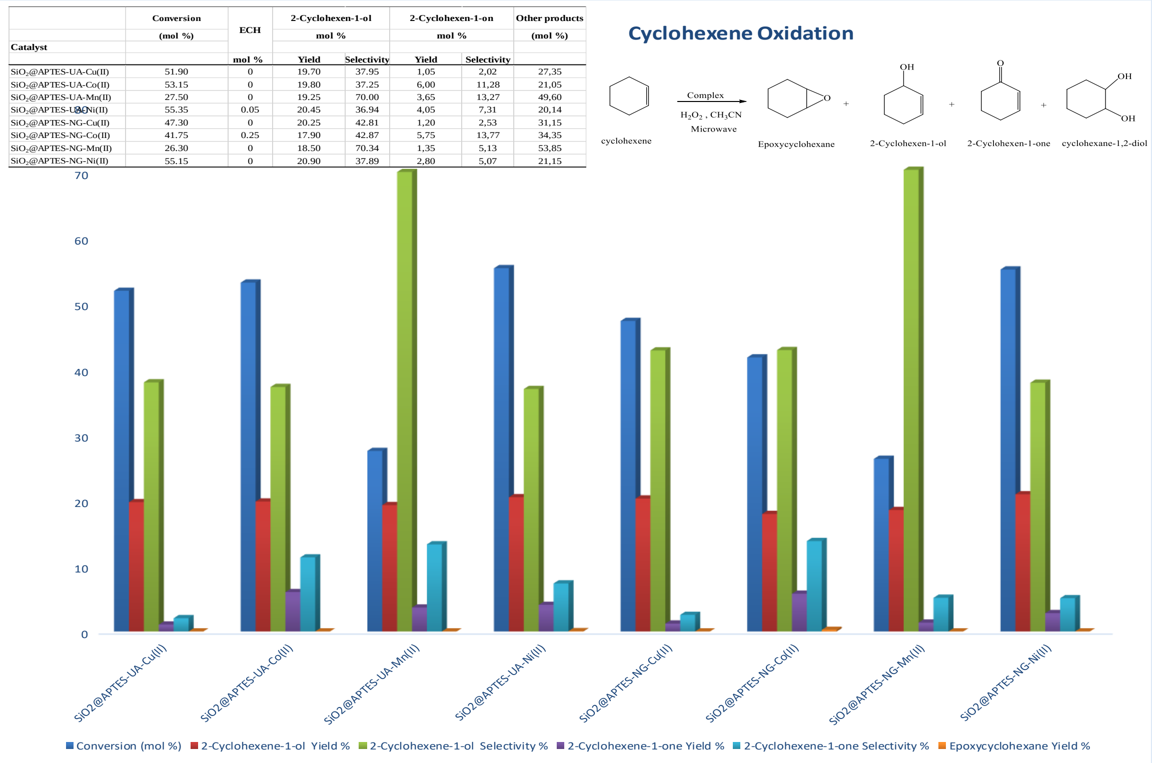
$$\frac{C_e}{q_e} = \frac{C_e}{q_o} + \frac{1}{q_o\,b}$$

Freundlich isotherm;

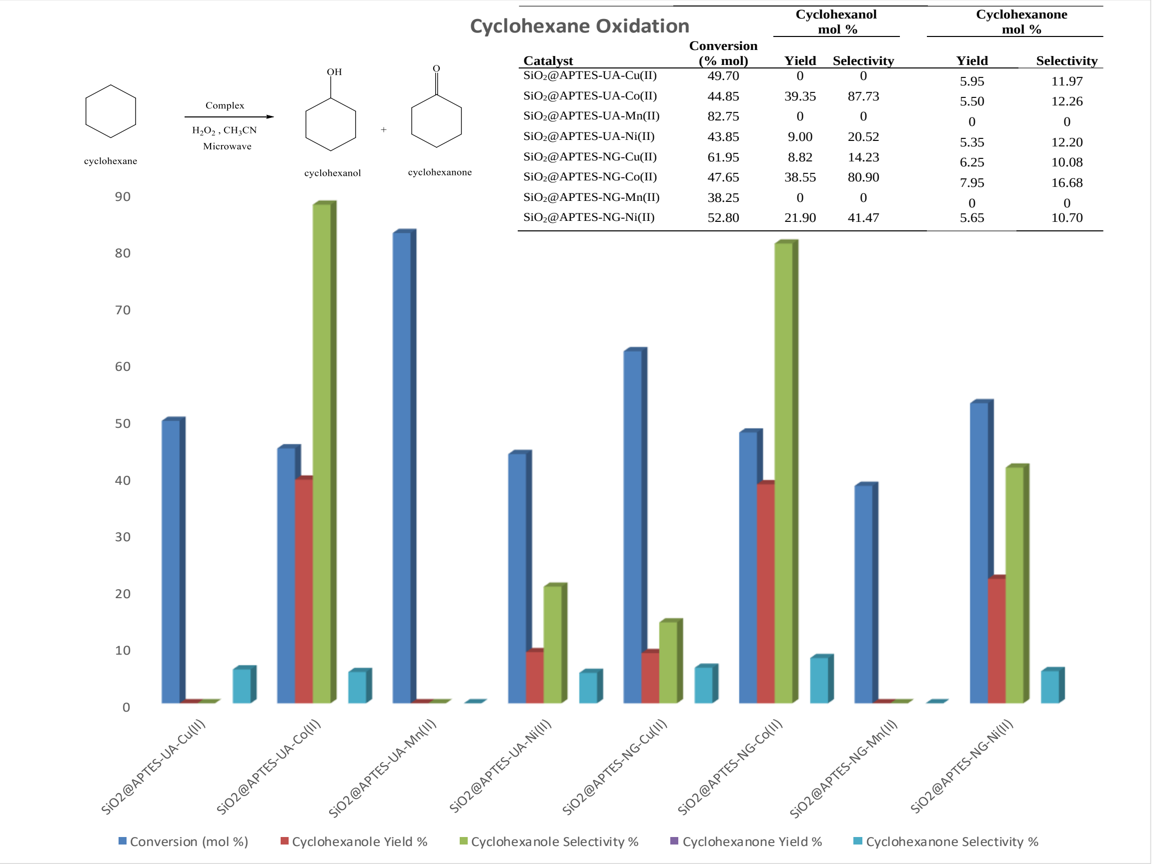
q_e is the amount of solute sorbed on the surface of the sorbent (mmol/g), C_e is the equilibrium ion concentration in the solution (mmol/L), q_o is the maximum surface density at monolayer coverage and b is the Langmuir adsorption constant (L/mmol), K_f is the Freundlich constant (mmol/g) which indicates the sorption capacity and represents the strength of the absorptive bond and n is the heterogeneity factor which represents the bond distribution. The fit of a model to the experimental data are usually evaluated in terms of linear regression coefficients where R^2 value is used as an indication for the benefit of model fit [24, 25, 27, 35, 42-46]. The linear fittings of the Langmuir isotherm model are shown in Table-3. R^2 values indicate that the Langmuir isotherm fits the experimental data better than the Freundlich model for adsorption studies. The fact shows that the mechanisms for the two adsorbents are monolayer adsorption on a homogenous surface and chemisorptions.

Catalytic Oxidation Under Microwave Power

The optimized reaction parameters such as subtrate:catalyst ratio, oxidant amount, temperature, pressure and catalysis time were applied according to our previous study [6]. The quantitative analyses of the reaction products were performed by GC-FID. In the catalytic oxidation tests, H_2O_2 was used as oxidant at 100 °C in acetonitrile medium in 1.5 h reaction time. The substrate conversion, the yields of the products and the selectivities are shown in the Fig. 4. It can be said that SiO_2@APTES-UA-Co(II) and SiO_2@APTES-NG-Co(II) complexes showed high conversions to products cyclohexanol (Cy-OH) and cyclohexanone (Cy=O) cyclohexane undergoes. Those are very good catalysts in the formation of cyclohexanol with high selectivity (Fig. 4) when compared with literature results [2, 27, 35]. On the other hand, it appears that other metal complexes of SiO_2@APTES-UA and SiO_2@APTES-NG ligands tested catalyze the conversion of cyclohexane significantly whereas their selectivities are found to be very low levels (Fig S5).



Catalyst	Conversion (mol %)	ECH mol %	2-Cyclohexen-1-ol mol %		2-Cyclohexen-1-on mol %		Other products (mol %)
			Yield	Selectivity	Yield	Selectivity	
SiO_2@APTES-UA-Cu(II)	51.90	0	19.70	37.95	1,05	2,02	27,35
SiO_2@APTES-UA-Co(II)	53.15	0	19.80	37.25	6,00	11,28	21,05
SiO_2@APTES-UA-Mn(II)	27.50	0	19.25	70.00	3,65	13,27	49,60
SiO_2@APTES-UA-Ni(II)	55.35	0.05	20.45	36.94	4,05	7,31	20,14
SiO_2@APTES-NG-Cu(II)	47.30	0	20.25	42.81	1,20	2,53	31,15
SiO_2@APTES-NG-Co(II)	41.75	0.25	17.90	42.87	5,75	13,77	34,35
SiO_2@APTES-NG-Mn(II)	26.30	0	18.50	70.34	1,35	5,13	53,85
SiO_2@APTES-NG-Ni(II)	55.15	0	20.90	37.89	2,80	5,07	21,15



Catalyst	Conversion (% mol)	Cyclohexanol mol %		Cyclohexanone mol %	
		Yield	Selectivity	Yield	Selectivity
SiO_2@APTES-UA-Cu(II)	49.70	0	0	5.95	11.97
SiO_2@APTES-UA-Co(II)	44.85	39.35	87.73	5.50	12.26
SiO_2@APTES-UA-Mn(II)	82.75	0	0	0	0
SiO_2@APTES-UA-Ni(II)	43.85	9.00	20.52	5.35	12.20
SiO_2@APTES-NG-Cu(II)	61.95	8.82	14.23	6.25	10.08
SiO_2@APTES-NG-Co(II)	47.65	38.55	80.90	7.95	16.68
SiO_2@APTES-NG-Mn(II)	38.25	0	0	0	0
SiO_2@APTES-NG-Ni(II)	52.80	21.90	41.47	5.65	10.70

Styrene Oxidation

Catalyst	Conversion (mol %)	Styerene oxide (mol %)	Other products (mol %)
SiO_2@APTES-UA-Cu(II)	1,81	5,25	92,94
SiO_2@APTES-UA-Co(II)	0,26	1,20	98,54
SiO_2@APTES-UA-Mn(II)	0,08	3,45	96,47
SiO_2@APTES-UA-Ni(II)	47,70	13,05	39,25
SiO_2@APTES-NG-Cu(II)	33,50	3,00	63,50
SiO_2@APTES-NG-Co(II)	0,28	1,20	98,52
SiO_2@APTES-NG-Mn(II)	30,15	10,35	59,50
SiO_2@APTES-NG-Ni(II)	58,65	13,45	27,90

Cyclooctane Oxidation

Catalyst	Conversion (% mol)	Cyclooctanol mol %		Cyclooctanone mol %		Other Products (mol%)
		Yield	Selectivity	Yield	Selectivity	
SiO_2@APTES-UA-Cu(II)	67.45	0	0	1,90	2,81	32.55
SiO_2@APTES-UA-Co(II)	0.95	0.50	52.63	0.40	42.10	99.05
SiO_2@APTES-UA-Mn(II)	82.85	30.00	36.21	50.00	60.35	17.15
SiO_2@APTES-UA-Ni(II)	63.10	0	0	4.30	6.81	36.90
SiO_2@APTES-NG-Cu(II)	85.10	6.50	7.63	1.00	1.17	14.90
SiO_2@APTES-NG-Co(II)	0.17	0	0	0	0	99.83
SiO_2@APTES-NG-Mn(II)	0.10	0	0	0	0	99.90
SiO_2@APTES-NG-Ni(II)	67.65	0	0	2,05	3,03	32.35

Fig. 4: The results of the catalytic oxidation.

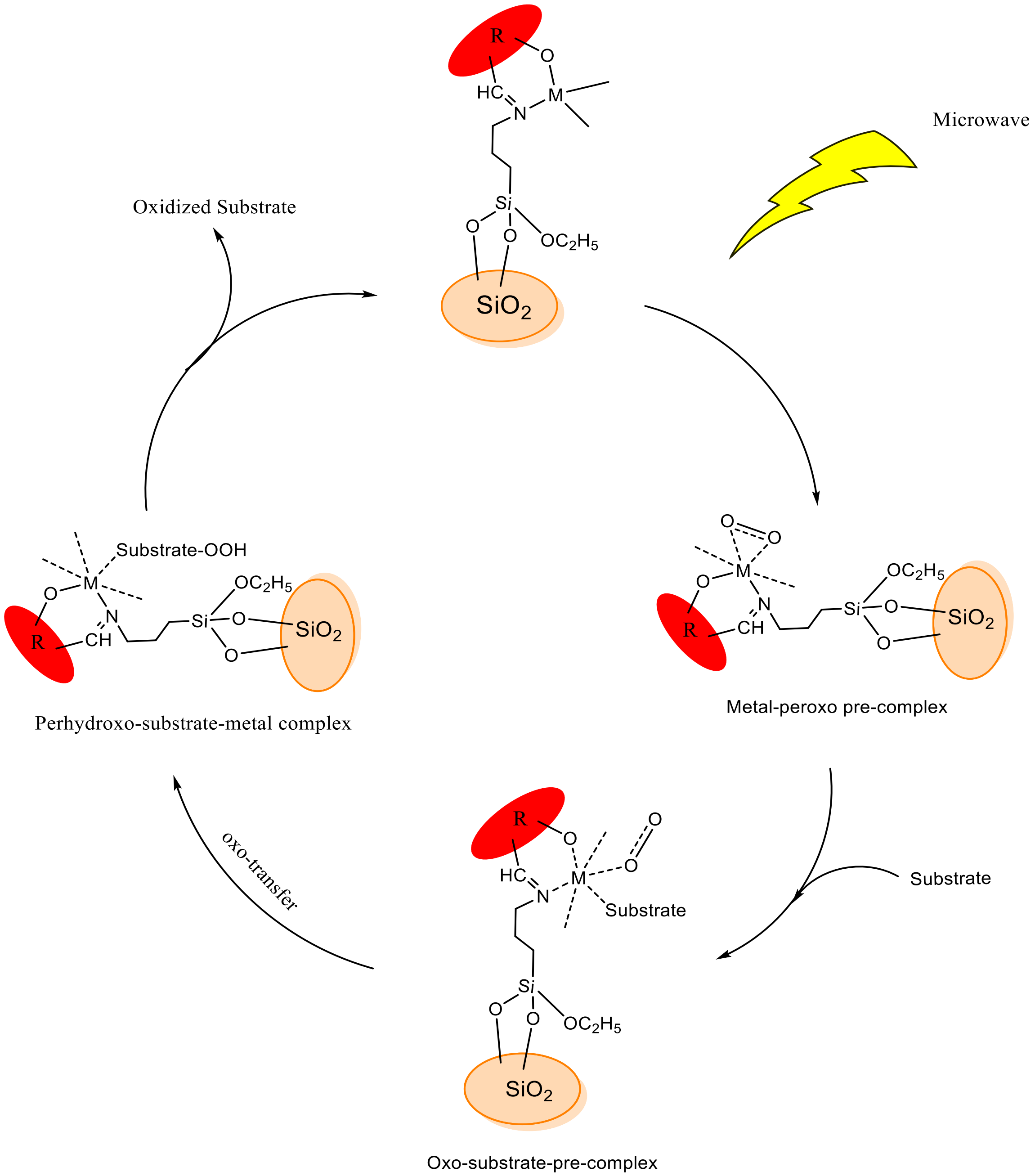


Fig. 5: Possible catalytic oxidation mechanism.

The tetra-coordinated metal complexes can be formed to octahedral geometries due to having two coordination holes which possibly accelerate the peroxo and the substrate coordinations. The pre-octahedral structure can control the oxidation mechanism like a processor. According to the possible oxidation rection mechanism; firstly, peroxo ligand and the substrates were coordinated to the metal centers. Then, the obtained octahedral structure could be possibly evolved to the trigonal prismatic molecular geometry. The trigonal prismatic molecular geometry having metal-peroxo and substrate attached pre-complexes accelerated the transfer of activated oxygen species to the substrates (Fig. 5). Microwave power was possibly accelerate the pre-oxo-substrate complexes and the forming of oxidized products coordinated to the metal centers. Possibly, tetrahedrally-coordinated Cu(II) complexes may be changed into different geometries. This flexible structure can provide the substrate and the oxo species coordination in the reaction mechanism.

The major catalytic oxidation products of cyclohexene are cyclohexene oxide, 2-cyclohexen-1-one and 2-cyclohexen-1-ol. According to GC-FID results, the catalytic conversion of cyclohexene is around 50% (Fig. 4). All the complexes showd good selectivity to 2-cyclohexen-1-ol especially Mn(II) complexes. Possibly, having different coordination structures of Mn(II), give important features of Mn(II) complexes in the oxidation mechanism of cyclohexene. These conversion rates are higher those than the previous reports [2,27,35]. In particular, the metal complexes of the SiO_2@APTES-UA and SiO_2@APTES-NG ligands act as good catalysts in the synthesis of 2-cyclohexen-1-ol. Based on the GC-FID results summarized in (Fig. 4), cyclooctane were oxidized further by using the synthesized catalysts. SiO_2@APTES-UA-Mn(II) complex showed very good catalytic activity with 60.35% selectivity of cyclooctanone [2,27,35]. The present results show that the synthesized metal complexes are not efficient and selective enough catalysts in the cyclooctane oxidation. The conversion of styrene to styrene oxide using the synthesized catalysts is remarkable considering SiO_2@APTES-UA-Ni(II), SiO_2@APTES-NG-Ni(II) and SiO_2@APTES-NG-Mn(II) complexes [2]. Posssibly, Ni(II) and Mn(II) complexes having different coordination structures give important features of in the oxidation mechanism of an organic substrates.

Conclusions

In this study, two new semi-synthetic silica-supported ligands with usnic acid and naringenin and their Cu (II), Ni (II), Mn (II) and Co (II) complexes were synthesized. The chemical structure of the new ligands and their metal complexes were characterized by FT-IR, TG/DTA, SEM, EDX, ICP-OES and elemental analysis methods. The extraction and pre-concentration of heavy metals from water by use of silica gel modified with different organic compounds as column fillers is well known in the literature[4,7,28,32–34]. Even some of the toxic metal ions have been recovered by 100%. These results showed that natural SiO_2@APTES-UA and SiO_2@APTES-NG solid phases are good heavy metal ion adsorbents. The synthesized complexes have been shown to exhibit heterogeneous catalytic properties on the oxidation of cyclohexane, cyclohexene and styrene, except for the cyclooctane oxidation. However, the catalytic properties of the metal complexes differed from each other due to the different oxidation properties of the metal ions used. [9,10,27]In particular, Cu(II) and Co(II) complexes of the ligands are known to be active in the oxidation reactions and these results are agreement wih the present results. In the view of the present results, significant contributions have been made to literature.

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