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Keywords: Crystal Structure; Thorium-doped lead zirconate; Doping; Perovskite

The pure lead zirconate (PbZrO₃) and low concentrations thorium-doped samples with general formula (Pb_{1-x}Th_xZrO₃) where *x*=0.05, 0.1, 0.2, 0.25 mole were synthesized by the conventional solid state method and sintering procedures. Experimental XRD-measurements indicated that Thorium dopant can substitute successfully on the A-sites of lead zirconate without damaging the main crystal structure which found to be orthorhombic phase with *Cmmm* space group. Scannin electron microscopy indicated that the average grain size of thorium-doped-lead zirconate ranged in between 0.35 and 1.43 μ m. A Visualized studies were made to confirm success of thorium doping in the A-sites of perovskite structure. Theoretical investigations done were concerned by matching and comparison of bond distances ,torsions on angles of investigated compound to clarify success of thorium doping on the perovskite structure. Thermal analyses TGA&DTA were also attempted and incorporated to clarify the effect of thorium doping on thermal behavior of doped perovskite. Furthermore the effect of low concentration thorium dopings on the magnetic order, grain size and vibrational modes frequencies of infrared-spectra were studied.

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Introduction

Perovskite antiferroelectric (AFE) materials usually display larger field-induced strains, higher energy storage density, considerable pyroelectric coefficient and giant electro-caloric effect due to its unique electric-field-induced phase transformation characteristics between ferroelectric (FE) and AFE. Hence, AFE materials have potential applications in micro-actuators, IR-detectors, digital memories, high energy storage capacitors and cooling devices. Pure PbZrO₃ (PZ) with a Curie point of 230 C is the most stable AFE material at room temperature.⁵ PZbased materials in bulk and film forms are also the most extensively investigated AFE materials at present. There are a lot of reports on PZ-based AFE materials, such as: (Pb,La)ZrO₃ (PLZ), (Pb,Ba)ZrO₃ (PBZ), (Pb,Sr)TiO₃ (PST), $(Pb_{0.97}La_{0.02})(Zr,Ti,Sn)O_3$ (PLZST) and $(Pb_{0.99}Nb_{0.02})$ (Zr,Ti,Sn)O₃ (PNZST), and so on.⁶⁻¹⁴ Most of the compounds with the general formula ABO3 have the perovskite structure¹⁵ in which "A" may be a mono-, di-, or tri-valent cation and "B" may be a penta-, tetra-,or tri-valent cation.¹⁶. Solid solutions of lead zirconate-titanate (PbZrO₃ – PbTiO₃ system) attract the attention of researchers and developers in various fields of science and technology because of their potential applications in memories, microwave tunable capacitors, micro-electromechanical systems (MEMS), pyroelectric sensors and electro-optical switches¹⁷⁻²⁷ It is also reported that the antiferroelectric (AFE) to ferroelectric transition leads to significant

energy storage for a dc field. This feature of PbZrO₃ makes it a specific material for energy storage applications.²⁸

Preparation of lead zirconate or (PZ) by conventional processes requires the use of high temperatures at which PbO volatility becomes significant. It is reported that the full development of pure PbZrO₃ phase occurs after sintering at temperatures above 1200c° for at least 2h in controlled PbO atmospheres.²⁹⁻³² PZ powders can also be prepared by wet-chemistry based process routes, which include chemical co-precipitation^{33,34}, micro-emulsion³⁵ and sol-gel technique.²⁹

Matthes et al.³⁵ prepared PZT thin films by the deposition a sol slurry, this method consists of a PZT-sol on acetic acid basis and PZT powder .Kong et al.³⁶ prepared PZ by a highenergy ball milling process using oxides as starting materials.

Bharadwaja et al.³⁷ studied the X-ray diffraction (XRD) for lead zirconate and La-doped lead zirconate thin films and reported that pure lead zirconate thin films showed a pseudo-cubic (110) orientation, whereas all the La-modified films showed a pseudo-cubic (111) orientation. The XRD analysis for lead lanthanum zirconate titanate (PLZT) thin films has been studied³⁸ and showed that the PLZT thin films are polycrystalline and the lattice parameter *a* decrease slightly with increasing La concentrations.

Boutarfaia³⁹ studied XRD, differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) for *x*PbZrO₃-(0.95-*x*)PbTiO₃-0.05Pb(Fe_{1/5},Ni_{1/5},Sb_{3/5})O₃, it was reported that, the endothermic peak observed at about 240 °C is due to Pb₃O₄ decomposition and a appreciable weight loss of 2.5% is found with TGA, and another endothermic

signal at 560 °C which is related to Pb_3O_4 final decomposition.

The scanning electron microscope (SEM) has been studied³³ for $PbZrO_3$ and showed the sub-micrometer and spherical nature of the $PbZrO_3$ powder.

Akimov⁴⁰ studied the IR spectra of lead zirconate- titanate with a rhombohedral and a tetragonal structures and it has been established that with increase in the content of lead titanate in solid solutions of lead zirconate-titanate with a tetragonal structure, the frequency of the ferroelectric- active mode shifts toward higher frequencies.

The essential goal of present studies are studying the effect of low concentration thorium doping tetra-valent dopant on the A-site of perovskite on:

a) crystal structural of pure and Th-doped lead zirconate tetragonal- orthorhombic phases .

b) micro-structural feature and grain size of Th-doped samples ($Pb_{1-x}Th_xZrO_3$).

c) magnetic order and thermal behavior of Th-doped-samples .

d) spectroscopic IR-absorption spectral frequencies of Th-doped samples .

Experimental

Samples Preparation

The pure lead zirconate (PbZrO₃) and thorium-doped samples with general formula (Pb_{1-x}Th_xZrO₃) where x = 0.05,0.1,0.2,0.25 mole were synthesized by the conventional solid state method and sintering procedure using appropriate amounts of PbCO₃, zirconyl carbonate, ZrOCO₃ and ThO₂ each of having purity >99%. The mixtures were ground in an agate mortar for 1h. The finely ground powder were subject to heating at 800 C° for 20 hrs then reground and pressed into pellets under compressive strength 8 ton/m² having the pellet dimensions (thickness 0.2 cm & diameter 1.2 cm). Sintering was carried out at 850 C° for 48 hrs. Then the furnace is cooled down slowly to room temperature. 10% more off-stoichiometric Pb₃O₄ were used in order to compensate lead deficient due to its sublimation during sintering process.

X-Ray diffraction (XRD)

The X-ray diffraction measurements (XRD) were carried out at room temperature on the fine ground powders of pure lead zirconate (PbZrO₃) and thorium-doped samples with general formula (Pb_{1-x}Th_xZrO₃) where x = 0.05, 0.1, 0.2, 0.25 mole in the range (2 θ =10-90°) using Cu-K α radiation source and a computerized [Steo-Germany] X-ray diffractometer with two theta (2 θ) scan technique. A visualized studies of crystal structure were made by using Diamond Molecular Structure version 3.2 package, Germany and Mercury 2.3-BUILD RC4-UK . A visualization study made

is concerned by matching and comparison of experimental and theoretical data of atomic positions, bond distances, oxidation states and bond torsion on the crystal structure formed. Some of these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data_request/cif</u>, or by emailing data request @ccdc.cam.ac.uk, or by contacting ICSD-Fiz-Karlsruhe-Germany.

Scanning Electron – Microscope (SEM):

Scanning electron microscope (SEM) measurements were carried out using small pieces of prepared samples on different sectors to estimate the actual molar ratios by using "TXA-840,JEOL-Japan" attached to XL30 apparatus with EDX unit, accelerant voltage 30kv, magnification 10x up to 500.000x and resolution 3 nm. The samples were coated with gold.

Thermal Analyses Measurements

The thermo-gravimetric analysis (TGA) and the differential thermal analysis (DTA) measurements were carried out on the green mixtures of the prepared samples using a computerized Shimadzu (Japan) TGA/DTA analyzer and Al₂O₃ as reference for DTA measurements. The heating rate was 3 degree/min and the cooling rate was 1 degree/min.

Solid Infrared Absorption Spectra Measurements

The IR absorption spectra of the samples were recorded using "Perkin Elmer" Infrared Spectrophotometer, Germany in the range 200-1500 cm⁻¹ using spec. Pure KBr matrix.

Magnetic Order Measurements

The electron spin resonance spectra (ESR) were recorded at x-band frequencies on a "Bruker-Germany" ESR Spectrometer at room temperature at the National Research Center, Egypt. The magnetic field was swept from 0 to over 8 KG and the calibrated energy was 1 KG with a digital gaussmeter. Several selected samples were investigated.

RESULTS AND DISCUSSION

Phase Identification

Fig.1 displays the X-ray diffraction patterns of pure lead zirconate (PbZrO₃) and Th-doped PbZrO₃ (Pb_{1-x}Th_xZrO₃) perovskite where x=0.05, 0.1, 0.2, and 0.25 mole. Analysis of the corresponding 2 θ values and the inter-planar spacing *d* (Å) proved that, the compound mainly belongs to orthorhombic crystal structure with *Cmmm* space group.

The unit cell dimensions were calculated using the parameters of the most intense X-ray reflection peaks and were found to be a=11.8642 Å, b=12.09 Å and c=8.6345 Å for the pure PbZrO₃. Even though PZ was first reported

to be tetragonal⁴¹ at room temperature, single-crystal studies revealed the structure to be orthorhombic.⁴² The present XRD patterns of PZ are in full agreement with results reported by Fang et al.³⁴ and Kong et al.³⁶



Figure 1. Room temperature XRD-patterns: (a) $PbZrO_3$; (b) $Pb_{0.95}Th_{0.05}ZrO_3$; (c) $Pb_{0.9}Th_{0.1}ZrO_3$; (d) $Pb_{0.8}Th_{0.2}ZrO_3$; (e) $Pb_{0.75}Th_{0.25}ZrO_3$.

It was observed that *c*-axis exhibits slight length compression by increasing Th-content as shown in Fig.(1a) due to ionic radius of Th-ion (Th⁴⁺=102 pm) which is smaller than that of Pb-ion such that, Pb²⁺=120pm.



Figure 1a. Variation of c-axis lattice parameter as function of thorium content .

Although most of the compounds with the general formula ABO₃ have the perovskite structure¹⁵ in which "A" may be a mono-, di-, or trivalent cation and "B" may be a penta-, tetra-, or trivalent cation.¹⁶ In the present investigation tetravalent thorium successes within the investigated range to replace lead (Pb^{+m}, where 2 < m < 4) in the main crystalline structure of perovskite without damaging the original orthorhombic perovskite crystal.

Structure Visualization

To confirm the success of tetravalent thorium to replace lead on the lattice structure of perovskite (A-site) a visualized crystal structure investigations were made depending upon single crystal data of lead zirconate supplied from ICSD-data bank Karlsruhe-Germany code number ICSD# 86443⁴³ see Figs.2a,b.



Figure 2a 2D-frame net and side view of thorium-doped lead zirconate perovskite unit cell.

Fig.2a shows 2D-frame net structure of orthorhombic perovskite structure displaying the different geometries of (Pb/Th)=A-sites and Zr=B-sites beside displaying the different orientation of polyhedron-zirconate inside unit cell of perovskite structure as clear in Fig.2b.



Figure 2b. Unit cell of Th-doped zirconate displaying ZrO₆-polyhedral units

Fig.2c shows the indexed XRD-profile for pure lead zirconate with I_o index = {318} which lies at $2\theta \sim 35.8$. The most intense reflection peaks (fingerprint) of lead zirconate were represented by red circles as clear in Fig.2_c. It was noticeable that at two theta $(2\theta) \sim 51.4$ there is doublet

Atom ₁	Atom ₂	Sym. Oper.1	d ₁₋₂	Atom ₃	Sym. Opr.2	d ₁₋₃	Angle 213^
Pb1 Th1	01	-x, -y, z	1.9461	01	x, y, z	1.9461	180.000
	01	-x, -y, z	1.9461	05	x, y, z	2.1570	124.046
	05	x, y, z	2.1570	05	х, -у, -z	2.1570	111.908
	05	x, y, z	2.1570	05	-x, y, -z	2.1570	97.369
Pb2 Th2	06	0.5-x, 0.5-y, z	2.4102	06	0.5+x, 0.5-y, -z	2.4102	118.991
	06	0.5-x, 0.5-y, z	2.4102	06	0.5-x, -0.5+y, -z	2.4102	115.995
	06	0.5-x, 0.5-y, z	2.4102	O6	0.5-x, 0.5-y, -z	2.4102	85.581
	06	0.5-x, 0.5-y, z	2.4102	O6	0.5+x, -0.5+y, -z	2.4102	180.000
Pb4 Th4	06	0.5-x, -0.5+y, 1-z	2.2861	06	0.5+x, -0.5+y, 1-z	2.2861	67.935
	O6	0.5-x, -0.5+y, 1-z	2.2861	O6	0.5+x, 0.5-y, 1-z	2.2861	101.369
	O6	0.5-x, -0.5+y, 1-z	2.2861	O6	0.5-x, 0.5-y, 1-z	2.2861	64.710
	O6	0.5-x, -0.5+y, 1-z	2.2861	O6	0.5-x, 0.5-y, z	2.2861	112.065
Pb5 Th5	05	0.5-x, 0.5-y, z	2.4836	05	0.5-x, 0.5-y, -z	2.4836	51.553
	05	0.5-x, 0.5-y, z	2.4836	05	х, у, -z	2.4836	180.000
	05	0.5-x, 0.5-y, z	2.4836	05	x, y, z	2.4836	128.447
	05	х, у, -z	2.4836	05	x, y, z	2.4836	51.553

Table 1. Selected bond distances and angles inside crystal lattice of Th-doped-lead zirconate .

Table 2. Selected bond distances and angles inside crystal lattice of Th-doped-lead zirconate

Atom ₁	Atom ₂	Sym. Oper.1	d ₁₋₂	Atom ₃	Sym. Opr.2	d ₁₋₃	Angle 213 [^]
Zr1	O3	x, y, z	1.5066	01	x, y, z	1.8329	140.289
	01	x, y, z	1.8329	05	x, y, z	2.2210	56.003
	O5	х, -у, z	2.2210	05	x, y, z	2.2210	79.761
Zr2	O2	x, y, z	1.5781	O4	x, y, z	1.6000	153.370
	O4	x, y, z	1.6000	05	-x, y, z	2.0079	94.843
	O5	-x, y, z	2.0079	05	x, y, z	2.0079	73.944
	O6	-x, y, z	2.0294	O6	x, y, z	2.0294	78.010
01	Zr1	x, y, z	1.8329	Zr1	х, -у, -z	1.8329	122.436
	O5	x, y, z	1.9338	05	х, -у, -z	1.9338	135.099
02	Zr2	-x, y, -z	1.5781	Zr2	x, y, z	1.5781	145.486
	O5	-x, y, -z	1.9460	05	х, у, -z	1.9460	76.71
03	Zr1	x, -y, 1-z	1.5066	Zr1	x, y, z	1.5066	158.142
04	Zr2	-x, y, 1-z	1.6000	Zr2	x, y, z	1.6000	161.253
05	01	x, y, z	1.9338	O2	x, y, z	1.9460	109.573
	O2	x, y, z	1.9460	Pb1 Th1	x, y, z	2.1570	74.958
	Zr2	x, y, z	2.0079	Pb1 Th1	x, y, z	2.1570	106.153
	Pb1 Th1	x, y, z	2.1570	05	х, у, -z	2.1600	59.954
	Zr1	x, y, z	2.2210	05	-x, y, z	2.4152	136.875
06	Zr2	x, y, z	2.0294	Zr10.5	-x, 0.5-y, z	2.0946	164.190
	Zr1	0.5-x, 0.5-y, z	2.0946	Pb4 Th4	-0.5+x, 0.5+y, z	2.2861	98.639
	Pb4 Th4	-0.5+x, 0.5+y,z	2.2861	Pb2 Th2	-0.5+x, 0.5+y, z	2.4102	82.106
	Pb2 Th2	-0.5+x, 0.5+y,z	2.4102	06	x, 1-y, z	2.4468	59.495

peak characteristics for lead zirconate perovskite structure indexed by {318), the same doublet peak was observed also nearly in the same location in the visualized theoretical patterns constructed for thorium-doped zirconate as clear in Fig.2d which confirm that thorium can substitute successfully on A-sites of perovskite structure without destroying the original orthorhombic phase .

The comparison between theoretical pattern Fig.2d and the experimental XRD-profile of thorium-doped lead zirconate Fig.2c one may conclude that there are moderate to strong fitting between the both profiles which confirm success of thorium doping within investigating range (0.05-0.25 mole).

Tables.1 and 2 show some selected bond distances and angles inside unit cell of Th-doped –perovskite zirconate.

From Table 1 one can observe that there are five types of A-sites (Pb/Th) according to the data found with five different environment namely ; Pb₁/Th₁ ,Pb₂/Th₂, Pb₃/Th₃, Pb₄/Th₄ and Pb₅/Th₅, it was noticed that the bond distances estimated for type one of A-sites (Pb₁/Th₁) were recorded and exhibited minimum bond distances with neighbouring oxygen atoms as clear in Table.1. Since Pb₁/Th₁-O₁ =1.94 Å and Pb₁/Th₁-O₅ = 2.157Å, while maximum bond distance were recorded for Pb₅/Th₅-O₅ which found to be equal 2.4836 Å.

These results are in full agreement with Coker et al.⁴⁴ who reported that the average bond distances recorded inside the crystal lattice of lead zirconate were found 2.47 Å for lead type 1 Pb₁-O and 2.58Å for lead type 2 Pb₂-O respectively .



Figure 2c. Indexed XRD-profile recorded for pure lead zirconate

The analysis of bond distances and angles inside unit cell of Th-doped-lead zirconate indicated that there are two types of zirconium environment nominated as Zr_1 and Zr_2 as described in Table 2. This is beside six types of oxygen environment symbolized as O_1 , O_2 , O_3 , O_4 , O_5 and O_6 respectively.



Figure 2d. Visualized XRD-profile recorded for Th-doped lead zirconate

It was noticed that the bond distances between Zr-O recorded minimum for (Zr_1 -O₃ =1.50 Å) and maximum one is for Zr_1 -O₅ with bond length = 2.22 Å while the other type was found to be 1.57 is for Zr_2 -O₂ and 2.029 for Zr_2 -O₆ respectively.

From Table 2 it was observed also that there are six types of oxygen symbolized as O_1 , O_2 , O_3 , O_4 , O_5 and O_6 are found inside lattice recorded bond distance values 1.83, 1.57, 1.5, 1.6, 2.007 and 2.029 Å for O_1 -Zr₁, O_2 -Zr₂, O_3 -Zr₁, O_4 -Zr₂, O_5 -Zr₂ and O_6 -Zr₂ Å respectively.

These results are compatible with average bond distances recorded for the two types of zirconium (Zr_1 and Zr_2)-Oxygen inside crystal lattice was reported⁴⁴ for lead zirconate with small differences due to thorium doping

effect. The authors⁴⁴ recorded the following bond distances for the two different types of zirconium Zr_1 - $O_2 = 2.111$ Å, Zr_1 - $O_1 = 2.098$ Å, Zr_2 - $O_3 = 2.162$ Å, Zr_2 - $O_4 = 2.140$ Å and Zr_2 - $O_5 = 2.044$ Å respectively.

The analysis of visualized structure concerning by XRDpattern, bond distances, angles, torsion and lattice volume confirmed that stability of doped-lead zirconate lattice is relatively high specially there is no violation in most data recorded for thorium-doped- lead zirconate and consequently reflects success of thorium doping in the investigated range (x=0.05-0.25 mole).

SEM Measurements

Fig. 3 shows the SEM-micrographs for pure and Th-doped PbZrO₃ with (x=0.05, 0.1, 0.2 and 0.25) applied on the ground powders that prepared by solid state route (SSR) and it shows the sub-micrometer and spherical nature of the PbZrO₃ powder. The average grain size was calculated and found in between 0.35 and 1.43 μ m.

These results are in agreement with results reported by Rao et al.³² and Fang et al.³⁴ in which the conventionally PbZrO₃ powder is covering the size range from 0.2 to 1.3 μ m. From Fig.3a-e it is so difficult to observe inhomogeneitiy within the micrograph due to that the powders used are very fine and the particle size estimated is too small. It was noticeable that the surfaces of all samples have bubbling nature as clear in Figs.3_{a-e} due to precursor of the lead zirconate contains both of zirconium and lead as carbonates .And as result of raising temperature carbonates decomposes converting into CO₂ which make as bubbling agent .



The grain size for Th-doped PbZrO₃ was calculated according to Scherrer's formula:

 $B=0.87\lambda/D\cos\theta$ (1)

where *D* is the crystalline grain size in nm, θ is the half of the diffraction angle in degree, λ is the wavelength of X-ray source (Cu-K_x) in nm, and B is the degree of widening of

diffraction peak which is equal to the difference of full width at half maximum (FWHM) of the peak at the same diffraction angle between the measured sample and standard one. From SEM-maping, the estimated average grain size was found to be in between 0.35 and 1.43 μ m which is relatively large in comparison with that calculated applying Scherrer's formula for pure 123-phase ($D \sim 0.39 \ \mu$ m). This indicates that, the actual grain size in the material bulk is smaller than that detected on the surface morphology.

Furthermore, in our EDX (energy disperse X-ray) analysis, Th^{4+} was detected qualitatively with good approximate to the actual molar ratio but not observed at PbZrO₃ grain boundaries which confirm that, thorium (IV) has diffused regularly into material bulk Th-doped PbZrO₃ perovskite-phase and induces in the crystalline structure of PbZrO₃ perovskite through solid state reaction.

Infrared Absorption Spectra Measurements

Fig. 4 shows the solid Infrared spectra for pure and Thdoped PbZrO₃ powders, the spectra for pure PbZrO₃ displays some characteristics bands at 417,551,750 and 812 cm^{-1} which have been assigned generally to ZrO₃ torsions and those at 551 and 750 cm^{1-} are due to Zr-O stretching and the other weak and much weaker bands appearing at higher wavenumbers result from the valent oscillation of metal-O bands.⁴⁵



Figure 4. Infrared absorption spectra (a) $PbZrO_3$; (b) $Pb_{0.95}Th_{0.05}ZrO_3$; (c) $Pb_{0.9}Th_{0.1}ZrO_3$; (d) $Pb_{0.8}Th_{0.2}ZrO_3$; (e) $Pb_{0.75}Th_{0.25}ZrO_3$

For Th-doped lead zirconate , absorption bands of FT-IR spectrum are related to the lattice vibration of BO₆ (B¹/₄Zr) octahedron groups,⁴⁶⁻⁴⁸ a strong and broad band within 700–400 cm⁻¹ indicated the presence of ZrO₆ oxygen-octahedral groups, absorption bands within 700–500 and 500–400 cm⁻¹ represented the stretching frequencies of ZrO₆ oxygen-octahedral groups. Therefore, these observed infrared spectrum bands were all the characteristic bands of the perovskite PZ structure, further proving that the formation of perovskite-phase PZ via the solid state chemical reactions in heterogeneous multi-material powder mixtures.⁴⁹ It was noticed that some of Zr–O bond length decreased, so the bond force constant of *K* increased, and vibration frequency of ZrO₆ oxygen-octahedral groups got bigger, thus the

strongest adsorption band shifted to a higher wave number for synthesized powders.

Based on these observations, it could be inferred due to which the crystal structure of synthesized powders is distorted. Thus the powders have high activity, which can reduce sintering temperature.

Electron Spin Resonance (ESR) Measurements

Fig. 5 displays the electron-spin resonance (ESR) spectra recorded for pure and Th-doped PbZrO₃ powders with (x = 0.0, 0.05, 0.1 and 0.2 mole), the *g*-values parallel and perpendicular to the symmetry axis and the effective *g*-values which nominated as (g_{iso}) are calculated as shown in Table 3.



Figure 5. ESR-signals recorded for pure and selected thorium doped zirconates; (a) PbZrO₃; (b) Pb_{0.95}Th_{0.05}ZrO₃; (c) Pb_{0.9}Th_{0.1}ZrO₃; (d) Pb_{0.8}Th_{0.2}ZrO₃.

It was obvious to observe that the values of (g_{iso}) is inversely proportional to the dopant ratio, recording minimum value $(g_{iso}) = 2.13$ for highest dopant content Th=0.2 mole.

Table 3.The effective g-values (g_{iso}) of some prepared samples of Th-doped PbZrO₃.

Material	g _{iso} values
PbZrO ₃	2.31
Pb0.9Th0.05ZrO3	2.28
Pb _{0.8} Th _{0.1} ZrO ₃	2.24
Pb0.75Th0.25ZrO3	2.13

This decrease in the paramagnetic content is due to that thorium dopant has tetra-valent oxidation state which means the outer shell is vacant since the electronic configuration of thorium is [Rn] $6d^27s^2$, for tetra-valent thorium (Th⁴⁺)=[Rn] $6d^07s^0$ and consequently the diamagnetic character is increased remarkably as Th-doping ratio increased.



Figure 6. TGA/DTA curves: (a) PbZrO₃; (b) Pb0.95Th0.05ZrO₃; (c) Pb0.9Th0.1ZrO₃; (d) Pb0.8Th0.2ZrO₃.

Analysis of its ESR spectra indicates that Th⁴⁺ substitution occurs at the Pbⁿ⁺ at many different ESR-distinguishable locations. All factors, namely could be for the Pb⁴⁺>Pb²⁺, Pb³⁺>Pb²⁺ or Pb⁴⁺>Pb²⁺ Pb⁴⁺>Pb³⁺ conversions which are responsible for the large microstrains and the deterioration of crystalline structure is observed in these ceramics, which seemed to play a crucial role for reading large piezoelectric anisotropy within thorium-doped perovskite system. Although Pb³⁺ is not real valency for lead but it is really observed in visualised calculation as average oxidation state for lead (Pb⁴⁺ and Pb²⁺) inside crystal lattice .

These results are partially in agreement with the results of Rosales et al.⁵⁰ who investigated the effect of Eu-and Tidoping on the ESR spectra of lead manganate perovskite structure.

Thermal Analyses Measurements

The TGA and DTA analyses were carried out on the green mixtures of pure and Th-doped $PbZrO_3$ powders with (x=0.0, 0.05, 0.1 and 0.2 mole) symbolized as a, b, c and d respectively in Fig. 6.

From TGA/DTA curves Fig.6 the TGA analysis can be divided into four steps. The first step occupies the region from room temperature up to 230°C for which the weight loss occurred is attributing to the humidity of samples and partial decomposition of both of ZrOCO₃ and PbCO₃ The second region lies between 240~390 °C at which lead carbonate decomposed moderately into PbO and CO₂.³⁹. The third region of temperature ranging from 390-680 °C at which the weight loss occurred attributing to the onset of the crystallization process and partial volatilization of lead oxide.^{39,51} The last region is between 680~800 °C for complete decomposition of both of Zr(CO₃)₂ and PbCO₃ into metal oxide accompanied with solid state reaction of solid metal oxide (Pb-oxide,ThO₂ and ZrO₂).

The same trend was observed⁵²⁻⁵⁴ for the endothermic peak, which always observed at approximated range of ~ 780-820 °C which refers to the phase formation and this range could be shifted up or down according to the system composition under investigations.

Conclusions

The conclusive remarks within this article can be summarized under the following points;

Tetravalent thorium got success in the investigated range to replace lead in the main crystalline structure of perovskite without damaging the original orthorhombic perovskite crystal.

The analysis of visualized structure determined by XRDpattern, bond distances, angles, torsion and lattice volume confirmed that stability of doped-lead zirconate lattice is relatively high, specially there is no violation in most data recorded for thorium-doped- lead zirconate and consequently reflects success of thorium doping in the investigated range (x=0.05-0.25 mole)

The SEM measurements indicated that the average grain size of thorium-doped-lead zirconate ranged in between 0.35 and 1.43 μ m.

Decreasing of paramagnetic content is due to the diamagnetic character is increased remarkably as Th-doping ratio increased .

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Received: 30.09.2010. Accepted: 16.10.2012.



SYNTHESIS AND CHARACTERIZATION OF NANOCOMPOSITES HAVING CATALYTIC ACTIVITIES USING MICROWAVE TECHNIQUES

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Keywords: 4-Hydroxobenzoic acid; Cobalt(II) ions; X-ray powder diffraction; Spectroscopic data; Thermal analysis; Nanocomposites; Biological evaluation;

A new cobalt(II) 4-hydroxobenzoate, $[Co_2(C_7H_5O_3)_2(H_2O)_4]2H_2O$ was synthesized as binuclear complex and characterized by elemental analyses (CHN), spectroscopic (infrared, electronic, x-ray powder diffraction, scanning electron microscopy SEM,) studies, magnetic susceptibility measurements and thermal analysis. This complex is a new type of 4-hydroxybenzoate bridged metal complex in which the carboxylate ligand is *p*-hydroxobenzoic acid. Bridging co-ordination modes for the carboxylates were indicated by the presence of ($v_{asym}-v_{sym}$) vibrations in the infrared spectra nearly the same as observed for ionic compounds. The magnetic moment value of cobalt(II) 4–hydroxybenzoate determined in at 300 K is 4.45 BM which refer to octahedral geometry. Thermo gravimetric analysis (TGA) of the hydrated water molecules shows that the first degradation step is associated with the release of water molecules followed by the decomposition of the 4-hydroxobenzoate, nitrato and coordinated water molecules. According to Horowitz-Metzger (HM) and Coats-Redfern methods, the kinetic parameters for the non-isothermal degradation of this complex were calculated using thermogravimetric data.

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Introduction

4-Hydroxybenzoic acid is a mono-hydroxybenzoic acid, a phenolic derivative of benzoic acid. It is a white crystalline solid, slightly soluble in water and chloroform but more soluble in polar organic solvents such as alcohols and acetone. 4-Hydroxybenzoic acid is primarily known as the basis for the preparation of its esters, known as parabens, which are used as preservatives in cosmetics and some ophthalmic solutions. It is isomeric with 2-hydroxybenzoic acid, known as salicylic acid, a precursor to aspirin. 4-Hydroxybenzoic acid can be found naturally in *Cocos nucifera*.¹ It is one of the main catechins metabolites found in human beings after consumption of green tea infusions.²



Formula 1: Structure of 4-hydroxybenzoic acid

The chemistry of metal carboxylates continues to be an area of intense research in view of its diverse applications, ranging from the relevance of metal carboxylate complexes as model systems for the metal-active sites in bioinorganic chemistry^{3,4} to their use as novel materials in material science. Metal oxides can be readily prepared from metal carboxylate by thermal decomposition methods.⁵ Metal carboxylates exhibit fascinating structural features. The

structure diversity of metal carboxylate complexes can be attributed to the versatile ligational behaviour of the carboxylate group which can function like a bidentate ligand binding with single metal atom or alternatively as a bridging bidentate ligand coordinating two metal atoms or as a monodentate ligand.⁶⁻⁸ The metal carboxylates have high affinity to chelate with the transition metal ions, hence are attracting attention due to potential applications in areas viz. biology, catalysis, thermal, electrical, optical, magnetic, etc.9-14 The structural diversity encountered in metalcarboxylate complexes can be attributed to the versatile ligational behavior of the carboxylate group which can function like a bidentate ligand binding to a single metal or alternatively as a bridging bidentate ligand coordinating to two metals or as a monodentate ligand^{15,16} The carboxylate group is able to coordinate to metal ions by different modes (Scheme 1).¹⁷

- (i) When the carboxylate group coordinates the metal ion in a monodentate manner, the difference between the wavenumbers of the asymmetric and symmetric carboxylate stretching bands, $\Delta v = v_{as}COO^{-} v_{s}COO^{-}$), is larger than that observed for ionic compounds.
- (ii) When the ligand chelates, Δv is considerably smaller than that for ionic compounds, while on the asymmetric bidentate coordination, the values is in the range characteristic of monodentate coordination.¹⁸
- (iii) The characteristic wavenumber difference, Δv , is larger than that for chelated ions and nearly the same as observed for ionic compounds. Based on the above results, it was possible to distinguish the coordination mode of the COO⁻ group.



Scheme 1. Possible coordination modes of the carboxylate group

Cobalt(II) of 4-hydroxybenzoic acid complex is a little known. Ammonium (NH4⁺) and sodium 4-hydroxybenzoate were prepared as solid compounds soluble in water. The binuclear cobalt(II) complex with p-hydroxybenzoic acid has not been studied before. The main purpose of the present work has been the study of some physicochemical properties, thermal degradation and the ability of binuclear cobalt(II) phydroxybenzoic acid to act as a bio-mimetic heterogeneous catalyst for selective oxidation of various alcohols with H₂O₂. The catalytic behavior of cobalt(II) complex can be discussed upon the micro-porous structure which constructed by intermolecular bridging of Co-OO-Co species. In order to obtain a wide insight into cobalt(II) hydroxybenzoic acid complex properties, the FT-IR, UVvis, magnetic measurements, SEM, XRD analysis and (TG/TGA) studies were carried out and the results are presented in connection with the kinetic parameters for the non-isothermal degradation of the two maximum DTG peaks by using Horowitz Metzger (HM) and Coats-Redfern (CR) methods. Microwave-assisted synthesis is a branch of green chemistry. The application of microwave-assisted synthesis in organic, organometallic and coordination chemistry continues to develop at an astonishing pace. Microwave irradiated reactions under solvent free or minimum solvent conditions are attractive to reduced pollution, cost effectiveness and provide high yields together with simple processing and handling.¹⁹⁻²³

Experimental

Chemicals and reagents

All chemicals and reagents used in present study were of analytical grade. 4-Hydroxybenzoic acid and cobalt (II) nitrate were received from Aldrich and Fluka chemical companies.

Microwave method for the synthesis of cobalt(II) complex

The 4-hydroxybenzoic acid ligand and the cobalt(II) nitrate hexahydrate were mixed in 1:2 (metal:ligand) ratio at pH= 8 with ammonia solution. The reaction mixture was then irradiated by the microwave oven with 10-15 mL of dry ethanol as solvent. The reaction was completed in a short time (5 min) with higher yields. The resulting product was then washed with ethanol and ether and finally dried under reduced pressure over anhydrous CaCl₂ in a desicator. The progress of the reaction and purity of the product was monitored by TLC using silica gel G (yield: 85%).

Physical measurements and analytical estimations

The elemental analyses of carbon, hydrogen and nitrogen contents were performed using a Perkin Elmer CHN 2400, while content of cobalt was determined from TG curves and by calcinating the prepared complex to most stable oxide (Co_2O_3) at 800 °C. The content of crystallization water was calculated from TG curves and by heating the complex at appropriate temperature. The molar conductivity of freshly prepared 1.0×10-3 mol/cm3 dimethylsulfoxide (DMSO) solution was measured for the dissolved cobalt(II) 4hydroxybenzoic acid complex using Jenway 4010 conductivity meter. The electronic absorption spectra of cobalt(II) complex was recorded in DMSO solvent within 900-200 nm range using a UV2 Unicam UV/Vis Spectrophotometer fitted with a quartz cell of 1.0 cm path length in Mansoura University. The infrared spectra with KBr discs were recorded on a Bruker FT-IR Spectrophotometer (4000–400 cm⁻¹). Solid reflectance spectra were measured on UV-3101 PC, Shimadzu, UV-Vis. NIR Scanning Spectrophotometer. Magnetic data were calculated using Magnetic Susceptibility Balance, Sherwood Scientific, Cambridge Science Park Cambridge, England, at Temp 25°C in Cairo University. The thermal studies TG/DTG-50H were carried out on a Shimadzu thermogravimetric analyzer under static air till 800 °C. Scanning electron microscopy (SEM) images were taken in Quanta FEG 250 equipment. The X-ray diffraction patterns for the studies cobalt(II) complex was recorded on X 'Pert PRO PANanalytical X-ray powder diffraction, target copper with secondary monochromate.

Antibacterial and antifungal activities

Antimicrobial activity of the tested samples was determined using a modified Kirby-Bauer disc diffusion method.24 Briefly, 100 µl of the best bacteria/fungi were grown in 10 mL of fresh media until they reached a count of approximately108 cells/mL for bacteria or 105 cells/mL for fungi.²⁵ 100 µl of microbial suspension was spread onto agar plates corresponding to the broth in which they were maintained. Isolated colonies of each organism that might be playing a pathogenic role should be selected from primary agar plates and tested for susceptibility by disc diffusion method.^{26,27} Of the many media available, National Committee for Clinical Laboratory Standards (NCCLS) recommends Mueller-Hinton agar due to: it results in good batch-to-batch reproducibility. Disc diffusion method for filamentous fungi tested by using approved standard method (M38-A) developed by the NCCLS²⁸ for evaluating the susceptibility of filamentous fungi to antifungal agents. Disc diffusion method for yeast developed standard method (M44-P) by the NCCLS.²⁹ Plates inoculated with filamentous fungi as Aspergillus Flavus at 25 °C for 48 hours; Gram (+) bacteria as Staphylococcus Aureus, Bacillus subtilis; Gram (-) bacteria as Escherichia Coli, Pseudomonas aeruginosa they were incubated at 35-37 °C for 24-48 hours and yeast as Candida Albicans incubated at 30 °C for 24-48 hours and, then the diameters of the inhabitation zones were measured in millimetres.²⁴ Standard discs of Tetracycline (Antibacterial agent), Amphotericin B (Antifungal agent) served as positive controls for antimicrobial activity but filter disc impregnated with 10 µl of solvent (distilled water, DMSO) were used as a negative control. The agar used is Meuller-Hinton agar that is rigorously tested for composition and pH. Further the depth of the agar in the plate is a factor to be considered in the disc diffusion method. This method is well documented and standard zones of inhabitation have been determined for susceptible values. Blank paper disks (Schleicher & Schuell, Spain) with a diameter of 8.0 mm were impregnated 10 µl of tested concentration of the stock solutions. When a filter paper disc impregnated with a tested chemical is placed on agar the chemical will diffuse from the disc into the agar. This diffusion will place the chemical in the agar only around the disc. The solubility of the chemical and its molecular size will determine the size of the area of chemical infiltration around the disc. If an organism is placed on the agar it will not grow in the area around the disc if it is susceptible to the chemical. This area of no growth around the disc is known as a "Zone of inhibition" or "Clear zone". For the disc diffusion, the zone diameters were measured with slipping calipers of the National Clinical Laboratory Standers.²⁶ Agar-based methods such as Etest disk diffusion can be good alternatives because they are simpler and faster than broth methods.^{30,31}

Results and discussions

Analytical data and conductivity measurements

The molecular weights, molecular formula and percentage of each carbon, hydrogen and nitrogen contents of cobalt(II) 4-hydroxybenzoate complex was listed in Table 1. The elemental analysis technique support the stoichiomerty between 4-hydroxybenzoic acid and cobalt(II) nitrate salt is 1:1. The microwave-assisted synthesis technique lead to complete the chemical reaction in a short time with higher yields compared to the usual method. In the microwave method homogeneity of reaction mixture was increased by the rotating of reaction platform tray. The cobalt(II) phydroxybenzoate complex has a pink color, solid and stable with hygroscopic nature at room temperature. Conductivity meter type Jenway 4010 was used to measure conductivities of cobalt(II) hydroxybenzoate complex of p-hydroxybenzoic acid ligand in DMSO with 1.0x10⁻³ mol dm⁻³ concentration. The conductivity of the free ligand was also measured at a similar condition in order to make comparison between the free ligand with its respective cobalt(II) complex. The conductance value of this complex is 50 Ω^{-1} cm⁻¹ mol⁻¹. The conductance value indicates that this complex has slightly electrolytic in nature. Slightly electrolytic complex assigned to the presence of nitrato groups inside chelation.¹⁷

Infrared spectra

The infrared spectral data of sodium p-hydroxybenzoate and cobalt(II) complex (Fig. 1) were characterized and presented in Table 2. The band at 1694 cm⁻¹ originating from –COOH stretching vibration, in the spectrum of the phydroxybenzoic acid, is replaced in the spectra of cobalt(II) complex, by two bands at 1607 cm⁻¹ and 1385 cm⁻¹, which can be ascribed to the asymmetric and symmetric vibrations of –COO- groups, respectively.³² The bands attributed to asymmetric and symmetric C-H stretching modes of the aromatic rings are observed at 3181 cm⁻¹. The bands with

the maxima at 3602 and 3381 cm⁻¹ in the spectrum of 4hydroxybenzoate of Co(II) are characteristic for v(O-H) vibrations^{32,33} of water molecules and –OH hydroxyl benzoic acid free of chelation. The bands of v(C=C) ring vibrations appear at 1535 cm⁻¹ and 784-853 cm⁻¹, and those corresponding to v(M-O) and v(M-O) stretching occur at 420-550 cm⁻¹. The Table 2 presents the values of the two band frequencies of asymmetrical and symmetrical vibrations of carboxylate group for 4-hydroxybenzoates of Co(II) and Na(I). The difference in the values, $\Delta v(OCO)$, between the frequencies $v_{as}OCO$ and v_sOCO in the cobalt(II) complex is nearly similar (222 cm⁻¹) to the sodium salt ($\Delta v =$ 232 cm⁻¹). According to the spectroscopic criteria^{32,33} the carboxylate ions appear to be Co-OO-Co bridging chelation (Formula 2). The bands at *ca*. 1560 cm⁻¹ and ~ 1385 cm⁻¹ overlapping with v_s OCO are due respectively to v(N=O) (v_1) and $v_{as}(NO_2)$ (v₅) of the coordinated nitrate. The $v_s(NO_2)$ (v₂) is detected at ca. 1100 cm⁻¹. These facts are characteristic of bidentate chelating nitrate.^{32,33} The separation $\Delta v = v_1 - v_5$ has been used as criterion of differentiation between mono and bidentate chelating nitrates, with Δv increasing as the coordination changes from mono to bidentate and/or bridging modes. The magnitude of this separation for this complex (Fig. 1) is indicative of a bidentate nitrate.³² As expected for symmetric bidentate coordination, the separation of the v_{as} (1607 cm⁻¹) and v_s (1385 cm⁻¹) of the cobalt(II) complex (222 cm⁻¹) is much smaller than those observed for uni-dentate coordination.32



Electronic spectrum and magnetic measurements

The electronic UV-vis (Fig. 2), solid reflectance spectra and magnetic measurements are important and interesting items for most chemical characterizations to draw important information about the structural aspects of the transition metal complexes.^{34,35} New bands in the visible region due to d-d absorption and charge transfer spectra from metal to ligand (M–L) or ligand to metal (L–M) can be observed and these data can be processed to obtain information regarding the structure and geometry of the complexes.³⁴. Electronic spectrum of cobalt(II) complex was recorded in DMSO with 10⁻³ mol cm⁻³.

Table 1: Elemental analysis data of Co(II) p-hydroxybenzoate complex

Complex		С, %		Н, %			Melting	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	point, °C	
[Co ₂ (C ₇ H ₅ O ₃) ₂ (NO ₃) ₂ (H ₂ O) ₄]2H ₂ O	26.85	26.28	3.86	3.48	4.47	4.41	257	

Table 2: Infrared frequencies (cm⁻¹) and tentative assignments for Co(II) and Na(I) 4-hydroxybenzoate

Compounds	Assign	Assignments							
	V(O-H)	$\delta_{(H_2O)}$	Vas(OCO)	V _{s(OCO)}	$v_{as} - v_s$	V(M-O)			
$[Co_2(C_7H_5O_3)_2(NO_3)_2(H_2O)_4]2H_2O$	3602	1607	1607	1385	222	550 501			
	3381					453 420			
Na(C7H5O3)	_	-	1610	1378	232	492			

UV-visible peaks corresponding to the $\pi \rightarrow \pi^*$ transitions in the Co(II) complex was observed at 274 and 294 nm for this complex, while the peaks belonging to $n \rightarrow \pi^*$ transitions are recorded at 316 and 390 nm wavelengths. Also, remaining peaks at 536 and 584 cm⁻¹ can be attributed to the ligand-to-metal charge transfer bands LMCT.³⁵ In paramagnetic cobalt(II) complex, often the magnetic moment (μ_{eff}) gives the spin only value $(\mu_{s.o.} = (n(n+2))^{\frac{1}{2}}$ B.M.) corresponding to the number of unpaired electron. The variation from the spin only value is attributed to the orbital contribution and it varies with the nature of coordination and consequent delocalization. The magnetic moment, configurations, stereochemistry, hybrid orbitals, number of unpaired electrons, spin-only and expected magnetic values of cobalt(II) phydroxybenzoate complex are (4.45 B.M., d⁷, octahedral, $sp^{3}d^{2}$, n=3, 3.88 B.M.). The diffuse spectrum for distorted octahedral of Co(II) complex, the diffuse spectrum displayed two bands at 16447 and 31746 cm⁻¹, assigned to ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$, and ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$ transitions, respectively.



Formula 2. Suggested structure of the studied $[Co_2(C_7H_5O_3)_2(NO_3)_2(H_2O)_4].2H_2O$ complex

X-ray powder diffraction and scanning electron microscopy

There are fourteen peaks (2θ /intensity= 5/100; 10/65; 14/23; 15/38; 18/21; 19/20; 21/25; 26/26; 27/39; 32/25; 34/19; 37/21; 43/25 and 47/19) exhibited clearly in x-ray powder diffraction patterns (Fig. 3) of $[Co_2(C_7H_5O_3)_2(NO_3)_2(H_2O)_4]2H_2O$ complex which was confirmed its crystalline structure. The values of 2θ , d value (the volume average of the crystal dimension normal to diffracting plane), full width at half maximum (FWHM) of prominent intensity peak, relative intensity (%) and particle size of cobalt(II) 4-hydroxybenzoate complex was calculated. The maximum diffraction patterns of this complex exhibited at $2\theta/d$ -value(Å)= 5/1.2871. The crystallite size could be estimated from XRD patterns by applying FWHM of the characteristic peaks using Deby-Scherrer Eqn. 1.36,37

where *D* is the particle size of the crystal grain, K is a constant (0.94 for Cu grid), λ is the X-ray wavelength (1.5406 Å), θ is the Bragg diffraction angle and β is the integral peak width. The particle size was estimated according to the highest value of intensity compared with the other peaks. These data gave an impression that the particle size located within nano scale range.



Figure 2. Electronic spectrum of the studied $[Co_2(C_7H_5O_3)_2(NO_3)_2(H_2O)_4].2H_2O$ complex



 $\label{eq:Figure 3: X-ray powder diffraction patterns of $ [Co_2(C_7H_5O_3)_2(NO_3)_2(H_2O)_4].2H_2O$ complex. $ \end{tabular}$

The morphology and particle size of $[Co_2(C_7H_5O_3)_2(NO_3)_2(H_2O)_4].2H_2O$ complex has been discussed under using scanning electron microscopy (Fig. 4). This figure show the photographs at different magnitude 1000x, 2000x, 4000x, 5000x, 10 000x and 20 000x. From the collected photos, we can concluded that the cobalt(II) complex has a clear homogeneous phase with 4 µm particle size.



Figure 4. SEM photograph of the $[Co_2(C_7H_5O_3)_2(NO_3)_2(H_2O)_4]$.2H₂O complex.

studied

Thermal and kinetic thermodynamic assessments

The data represented to the thermal decomposition of cobalt(II) of 4-hydroxybenzoate, the synthetic $[Co_2(C_7H_5O_3)_2(NO_3)_2(H_2O)_4]2H_2O,$ complex are discussed as follows; The TG curve corresponding to this complex heated in the 30-800 °C temperature range is exhibited in Fig. 5. The thermal curve of cobalt(II) complex was recorded in static air atmosphere from ambient to 800 °C, the characteristic data and stages of pyrolysis regarding the thermal behavior refer that the resulted cobalt(II) complex is thermally stable up to 500 °C. The initiation of the mass loss in TG curve ascribed to dehydration of five water molecules with 14.05 % experimental value in agreement with calculated value 14.37 %. The second step in temperature range 176-310 °C at DTG_{max}= 257 °C accompanied by losses of 2 nitrate and the last water molecules (calcd.=22.68 %; experimental = 22.06%). The third decomposition stage (decomposition of both 4-hydroxybenzoic acid moieties) appears as an endothermic peak 403 °C in the DTG curve. The residue left (calc.= 26.49%; experimental= 24.849%) in the crucible of corresponding cobalt(III) oxide Co_2O_3 which is confirmed by infrared spectrum (Fig. 6).



Figure 5: TG curve of $[Co_2(C_7H_5O_3)_2(NO_3)_2(H_2O)_4].2H_2O$ complex



Figure 6. Infrared spectrum of final residue of [Co₂(C₇H₅O₃)₂(NO₃)₂(H₂O)₄]2H₂O complex at 800 °C.

In recent years there has been increasing interest in determining the rate-dependent parameters of solid-state non-isothermal decomposition reactions by analysis of TG curves. Several equations³⁸⁻⁴⁵ have been proposed as means of analyzing a TG curve and obtaining values for kinetic parameters.

Step	Horowitz				Coats-Redfern					
	<i>E</i> , kJmol ⁻¹	Z, s ⁻¹	ΔS , J mol ⁻¹ K ⁻¹	ΔH , kJ mol ⁻¹	ΔG , kJ mol ⁻¹	<i>E</i> , kJ mol ⁻¹	Z, s ⁻¹	ΔS , J mol ⁻¹ K ⁻¹	ΔH , kJ mol ⁻¹	ΔG , kJ mol ⁻¹
2	97.4	4.12E+07	-104	93.0	148	87.1	3.28E+06	-125	82.7	149

Table 3: Kinetic parameters determined using the Coats-Redfern (CR) and Horowitz-Metzger (HM).

Many authors³⁸⁻⁴² have discussed the advantages of this method over the conventional isothermal method. The rate of a decomposition process can be described as the product of two separate functions of temperature and conversion,³⁹ using

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where α is the fraction decomposed at time *t*, k(T) is the temperature dependent function and $f(\alpha)$ is the conversion function dependent on the mechanism of decomposition. It has been established that the temperature dependent function k(T) is of the Arrhenius type and can be considered as the rate constant k.

$$k = Ae^{-\frac{E^*}{RT}}$$
(2)

where, *R* is the gas constant in $(J \text{ mol}^{-1} \text{ K}^{-1})$. Substituting Eqn. (2) into Eqn. (1), we get,

$$\frac{d\alpha}{dT} = \left[\frac{A}{\varphi}e^{-\frac{E^*}{RT}}\right]f(\alpha)$$
(3)

where, φ is the linear heating rate dT/dt. On integration and approximation, this equation can be obtained in the following form:

$$\ln g(\alpha) = -\frac{E^*}{RT} + \ln\left[\frac{AR}{\varphi E^*}\right]$$
(4)

where $g(\alpha)$ is a function of α dependent on the mechanism of the reaction. The integral on the right hand side is assigned for temperature and has not so close for solution. So, several techniques have been used for the evaluation of temperature integral. Most commonly used methods for this purpose are the differential method of Freeman and Carroll³⁸ integral method of Coat and Redfern,⁴⁰ the approximation method of Horowitz and Metzger.⁴³ In the present investigation the general thermal behavior of the $[Co_2(C_7H_5O_3)_2(NO_3)_2(H_2O)_4].2H_2O$ complex in terms of stability ranges, peak temperatures and values of kinetic parameters, are shown in Fig. 7 and Table 3. The kinetic parameters have been evaluated using the following methods and the results obtained by

these methods are compared with one another. The following two methods are discussed in brief.

Coats- Redfern equation

$$\int_{0}^{\infty} \frac{d\alpha}{\left(1-\alpha\right)^{n}} = \frac{A}{\varphi} \int_{T_{1}}^{T_{2}} e^{-\frac{E^{*}}{RT}} dT$$
(5)

The Coats-Redfern equation, which is a typical integral method, can be represented as:

For convenience of integration the lower limit T_1 is usually taken as zero. This equation on integration gives;

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = -\frac{E^*}{RT} + \ln\left[\frac{AR}{\varphi E^*}\right]$$
(6)

A plot of left-hand side (LHS) against 1/T was drawn. E^* is the energy of activation in kJ mol⁻¹ and calculated from the slop and A in (s⁻¹) from the intercept value. The entropy of activation ΔS^* in (J K⁻¹ mol⁻¹) was calculated by using the equation:

$$\Delta S^* = R \ln \left[\frac{Ah}{k_B T_s} \right] \tag{7}$$

where, $k_{\rm B}$ is the Boltzmann constant, *h* is the Plank's constant and $T_{\rm s}$ is the DTG peak temperature.⁴⁶

Horowitz-Metzger equation

The Horowitz-Metzger equation is an illustrative of the approximation methods. These authors derived the relation:

$$\lg \left[\frac{1 - (1 - \alpha)^{1 - n}}{1 - n} \right] = \frac{E^* \theta}{2.303 R T_s^2} \quad for \ n \neq 1$$
(8)

when n=1, the LHS of Eqn. 4 would be $lg[-lg (1-\alpha)]$. For

$$\lg\left[\lg\frac{w_{\alpha}}{w\gamma}\right] = \frac{E\theta}{2.303RT_s^2} - \lg 2.303 \tag{9}$$

a first-order kinetic process the Horowitz-Metzger equation may be written in the form:

where $\theta = T \cdot T_s$, $w_{\gamma} = w_{\alpha} - w$, $w_{\alpha} = \text{mass loss at the completion of the reaction; } w = \text{mass loss up to time } t$. The plot of $lg[lg(w_{\alpha}/w_{\gamma})]$ vs θ was drawn and found to be linear from the slope of which E^* was calculated. The pre-exponential factor, A, was calculated from the equation:

$$\frac{\underline{E}^{*}}{RT_{s}^{2}} = \frac{A}{\left[\varphi \exp{-\frac{E^{*}}{RT_{s}}}\right]}$$
(10)

The entropy of activation, ΔS^* , was calculated from Eqn. 3. The enthalpy activation, ΔH^* , and Gibbs free energy, ΔG^* , were calculated from;

$$\Delta H^* = E^* - RT \tag{11}$$

and

$$\Delta G^* = \Delta H^* - T \Delta S^* \tag{12}$$

respectively.

The activation energy E, increases through the degradation steps revealing the high stability of the remaining part suggesting a high stability of complexes characterization by covalence bonding. The negative of activation entropy values indicates that the activated fragment has more ordered structures. The positive of activation Gibb's free energy reveals that the free energy of the final residue is higher than that of the initial complex and the decomposition stages are non spontaneous.



Molecular modeling studies

Molecular modeling had been successfully used to detect three dimensional arrangements of atoms in free 4hydroxybenzoic acid ligand and its cobalt(II) complex. The bond lengths and bond angles values of the chelation complex were summarized and recorded in Table 4 and Figs. 8a-b. This calculation for $[Co_2(C_7H_5O_3)_2(NO_3)_2(H_2O)_4].2H_2O$ complex was obtained by using the commercial available molecular modeling software Chem Office Ultra-7. These statistical data have a good agreement with formula 2 confirmed the place of coordination towards cobalt(II) ions.





Figure 7: Plots of Coats–Redfern (CR) and Horowitz–Metzger (HM) relations for [Co₂(C₇H₅O₃)₂(NO₃)₂(H₂O)₄].2H₂O complex.

Figure 8: Molecular modeling of (a) 4-hydroxybenzoic acid and (b) its cobalt(II) complex

Table 4: The values of bond lengths and bond angles of 4-hydroxybenzoic acid and its cobalt complex

Adducts	Bond length			Bond angle			
	Atoms	Actual	Optimal	Atoms	Actual	Optimal	
Ligand	C(1)-C(2)	1.517	1.517	C(2)-C(1)-O(8)	119.898	123	
	C(1)-O(8)	1.208	1.208	C(2)-C(1)-O(9)	121.199	124.3	
	C(1)-O(9)	1.338	1.338	O(8)-C(1)-O(9)	118.898	122	
	C(2)-C(3)	1.42	1.42	C(1)-C(2)-C(3)	117.601	117.6	
	C(2)-C(7) 1.42 1.42 C(1)-C(2)-C(C(1)-C(2)-C(7)	117.601	117.6		
	C(3)-C(4)	1.42	1.42	C(3)-C(2)-C(7)	120	120	
	C(3)-(16)	1.1	1.1	C(2)-C(3)-C(4)	120	120	
	C(4)-C(5)	1.42	1.42	C(2)-C(3)-H(16)	119.998	120	
	C(4)-(13)	1.1	1.1	C(4)-C(3)-H(16)	119.998	120	
	C(5)-C(6)	1.42	1.42	C(3)-C(4)-C(5)	120	120	
	C(5)-(11)	1.355	1.355	C(3)-C(4)-H(13)	119.998	120	
	C(6)-C(7)	1.42	1.42	C(5)-C(4)-H(13)	119.998	120	
	C(6)-(14)	1.1	1.1	C(4)-C(5)-C(6)	120.001	120	
	C(7)-(15)	1.1	1.1	C(4)-C(5)-O(11)	119.998	124.3	
	O(9)-(10)	0.972	0.972	C(6)-C(5)-O(11)	119.998	124.3	
	O(11)-(12)	0.972	0.972	C(5)-C(6)-C(7)	120	120	
				C(5)-C(6)-H(14)	119.998	120	
				C(7)-C(6)-H(14)	119.998	120	
				C(2)-C(7)-C(6)	120	120	
				C(2)-C(7)-H(15)	119.998	120	
				C(6)-C(7)-H(15)	119.998	120	
				C(1)-O(9)-H(10)	106.101	106.1	
				C(5)-O(11)-H(12)	108		
Co ²⁺	C(1)-C(2)	1.497	1.497	C(2)-C(1)-O(10)	109.5	109.5	
	C(1)-O(10)	1.402	1.402	C(2)-C(1)-O(13)	109.5	109.5	
	C(1)-O(13)	1.402	1.402	C(2)-C(1)-H(60)	109.391	109.39	
	C(1)-H(60)	1.109	1.109	O(10)-C(1)-O(13)97.000	97		
	C(2)-C(3)	1.42	1.42	O(10)-C(1)-H(60)106.700	106.7		
	C(2)-C(7)	1.42	1.42	O(13)-C(1)-H(60)123.488	106.7		
	C(3)-C(4)	1.42	1.42	C(1)-C(2)-C(3)	121.4	121.4	
	C(3)-H(59)	1.1	1.1	C(1)-C(2)-C(7)	118.599	121.4	
	C(4)-C(5)	1.42	1.42	C(3)-C(2)-C(7)	120	120	
	C(4)-H(56)	1.1	1.1	C(2)-C(3)-C(4)	120	120	
	C(5)-C(6)	1.42	1.42	C(2)-C(3)-H(59)	119.998	120	
	C(5)-O(8)	1.355	1.355	C(4)-C(3)-H(59)	119.998	120	
	C(6)-C(7)	1.42	1.42	C(3)-C(4)-C(5)	120.001	120	
	C(6)-H(57)	1.1	1.1	C(3)-C(4)-H(56)	119.998	120	
	C(7)-H(58)	1.1	1.1	C(5)-C(4)-H(56)	119.998	120	
	O(8)-H(9)	0.972	0.972	C(4)-C(5)-C(6)	120.001	120	
	O(10)-Co(11)	1.8		C(4)-C(5)-O(8)	119.998	124.3	
	Co(11)-O(14)	1.8		C(6)-C(5)-O(8)	119.998	124.3	
	Co(11)-O(25)	1.8		C(5)-C(6)-C(7)	120	120	
	Co(11)-O(31)	1.8		C(5)-C(6)-H(57)	119.998	120	
	Co(11)-O(39)	1.8		C(7)-C(6)-H(57)	119.998	120	

Co(11)-O(40)	1.8		C(2)-C(7)-C(6)	120	120
Co(12)-O(13)	1.8		C(2)-C(7)-H(58)	119.998	120
Co(12)-O(16)	1.8		C(6)-C(7)-H(58)	119.998	120
Co(12)-O(28)	1.8		C(5)-O(8)-H(9)	108	108
Co(12)-O(34)	1.8		C(1)-O(10)-Co(11)	109.47	
Co(12)-O(37)	1.8		O(10)-Co(11)-O(14)	90	
Co(12)-O(38)	1.8		O(10)-Co(11)-O(25)	90	
O(14)-C(15)	1.402	1.402	O(10)-Co(11)-O(31)	180	
C(15)-O(16)	1.402	1.402	O(10)-Co(11)-O(39)	89.999	
C(15)-C(17)	1.497	1.497	O(10)-Co(11)-O(40)	89.999	
C(15)-H(55)	1.109	1.109	O(14)-Co(11)-O(25)	90	
C(17)-C(18)	1.42	1.42	O(14)-Co(11)-O(31)	90	
C(17)-C(22)	1.42	1.42	O(14)-Co(11)-O(39)	90	
C(18)-C(19)	1.42	1.42	O(14)-Co(11)-O(40)	180	
C(18)-H(54)	1.1	1.1	O(25)-Co(11)-O(31)	89.999	
C(19)-C(20)	1.42	1.42	O(25)-Co(11)-O(39)	180	
C(19)-H(52)	1.1	1.1	O(25)-Co(11)-O(40)	89.999	
C(20)-C(21)	1.42	1.42	O(31)-Co(11)-O(39)	90	
C(20)-O(23)	1.355	1.355	O(31)-Co(11)-O(40)	90	
C(21)-C(22)	1.42	1.42	O(39)-Co(11)-O(40)	90	
C(21)-H(51)	1.1	1.1	O(13)-Co(12)-O(16)	89.658	
C(22)-H(53)	1.1	1.1	O(13)-Co(12)-O(28)	90	
O(23)-H(24)	0.972	0.972	O(13)-Co(12)-O(34)	180	
O(25)-H(26)	0.992		O(13)-Co(12)-O(37)	90	
O(25)-H(27)	0.992		O(13)-Co(12)-O(38)	90	
O(28)-H(29)	0.992		O(16)-Co(12)-O(28)	90	
O(28)-H(30)	0.992		O(16)-Co(12)-O(34)	90.341	
O(31)-H(32)	0.992		O(16)-Co(12)-O(37)	90	
O(31)-H(33)	0.992		O(16)-Co(12)-O(38)	179.684	
O(34)-H(35)	0.992		O(28)-Co(12)-O(34)	90	
O(34)-H(36)	0.992		O(28)-Co(12)-O(37)	180	
O(37)-N(41)	1.316		O(28)-Co(12)-O(38)	90	
O(38)-N(41)	1.864		O(34)-Co(12)-O(37)	90	
O(39)-N(42)	1.316		O(34)-Co(12)-O(38)	90	
O(40)-N(42)	1.864		O(37)-Co(12)-O(38)	90	
N(41)-O(43)	1.316		C(1)-O(13)-Co(12)	109.472	
N(42)-O(44)	1.316		Co(11)-O(14)-C(15)	109.47	
O(45)-H(46)	0.942	0.942	O(14)-C(15)-O(16)	97	97
O(45)-H(47)	0.942	0.942	O(14)-C(15)-C(17)	109.5	109.5
O(48)-H(49)	0.942	0.942	O(14)-C(15)-H(55)	106.7	106.7
O(48)-H(50)	0.942	0.942	O(16)-C(15)-C(17)	109.5	109.5
			O(16)-C(15)-H(55)	106.7	106.7
			C(17)-C(15)-H(55)	124.049	109.39
			Co(12)-O(16)-C(15)	109.262	
			C(15)-C(17)-C(18)	120	121.4
			C(15)-C(17)-C(22)	119.998	121.4
			C(18)-C(17)-C(22)	119.998	120
			C(17)-C(18)-C(19)	120	120

C(17)-C(18)-H(54)	119.998	120
C(19)-C(18)-H(54)	120	120
C(18)-C(19)-C(20)	119.998	120
C(18)-C(19)-H(52)	119.998	120
C(20)-C(19)-H(52)	119.998	120
C(19)-C(20)-C(21)	120	120
C(19)-C(20)-O(23)	119.998	124.3
C(21)-C(20)-O(23)	119.998	124.3
C(20)-C(21)-C(22)	120.001	120
C(20)-C(21)-H(51)	119.998	120
C(22)-C(21)-H(51)	119.998	120
C(17)-C(22)-C(21)	120	120
C(17)-C(22)-H(53)	119.998	120
C(21)-C(22)-H(53)	119.998	120
C(20)-O(23)-H(24)	108	108
Co(11)-O(25)-H(26)	109.482	
Co(11)-O(25)-H(27)	109.461	
H(26)-O(25)-H(27)	0.316	
Co(12)-O(28)-H(29)	109.451	
Co(12)-O(28)-H(30)	109.468	
H(29)-O(28)-H(30)	0.547	
Co(11)-O(31)-H(32)	109.535	
Co(11)-O(31)-H(33)	109.468	
H(32)-O(31)-H(33)	0.547	
Co(12)-O(34)-H(35)	109.451	
Co(12)-O(34)-H(36)	109.444	
H(35)-O(34)-H(36)	0.547	
Co(12)-O(37)-N(41)	90	
Co(12)-O(38)-N(41)	74.951	
Co(11)-O(39)-N(42)	90	
Co(11)-O(40)-N(42)	74.951	
O(37)-N(41)-O(38)	105.05	
O(37)-N(41)-O(43)	109.47	
O(38)-N(41)-O(43)	109.47	
O(39)-N(42)-O(40)	105.05	
O(39)-N(42)-O(44)	109.47	
O(40)-N(42)-O(44)	109.47	
H(46)-O(45)-H(47)	103.7	103.7
H(49)-O(48)-H(50)	103.702	103.7

Biological activity studies

The biological assessment were studied in term of antimicrobial activities of $[Co_2(C_7H_5O_3)_2(NO_3)_2(H_2O)_4]2H_2O$ complex against gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) and gram-negative (*Escherichia coli* and

Pseudomonas aeruginosa) and two strains of fungi (*Aspergillus flavus* and *Candida albicans*). Results from the agar disc diffusion tests for antimicrobial activities of respective complex are shown in Fig. 9. The tested cobalt(II) complex displayed a different degree of antimicrobial effect (*Staphylococcus aureus* > *Bacillus subtilis* = *Escherichia coli* = *Candida albicans* > *Pseudomonas aeruginosa* > *Aspergillus flavus*) and has a degree of antimicrobial activities greater than free ligand against all organisms tested. The various reasons for lethal action of tested complex may be due to their interactions with critical intra-cellular sites causing the death of cells. The variety of antimicrobial activities of tested complex may due to a penetration through cell membrane structure of target organism. In conclusion, the interaction between the tested cobalt(II) complex in nano–structural form resulting in developing the effectiveness of biological characters of free phydroxybenzoic acid.



Figure 9. Biological assessment of cobalt(II) complex.

Conclusion

The interaction between the 4-hydroxybenzoic acid and the cobalt nitrate hydrated synthesized using microwave technique and was studied spectroscopically. New cobalt(II) complex was isolated and characterized through elemental analysis, (infrared, electronic, SEM and XRD spectra) and also thermal and kinetic thermodynamic studies. The stoichiometry of the product was found to be 1:1. Accordingly, the formed CT-complex has the formula [Co₂(C₇H₅O₃)₂(NO₃)₂(H₂O)₄].2H₂O.

Acknowledgement

This work was supported by grants from Taif University, Taif, Saudi Arabia under project Grants No. 1242-432-1.

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Received: 08.10.2012. Accepted: 16.10.2012.



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Keywords: overview; wax; phase change; materials

The properties and classification of wax phase change materials (WPCMs) such as melting point, fusion heat, density, thermal conductivity and specific heat capacity have been reviewed in the present article. Three types of packaging wax methods have also been discussed such as the direct mixing method, the soaking and absorption method and the container packing method. The complete development of WPCMS has been resulted in good economic and social benefits.

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INTRODUCTION

Wax is one of the important chemical products in an oil refinery. It is a white to yellowish-white in colour, gelatinous, crystalline, water-insoluble substance. Its main content includes n-paraffin. Its carbon number, molecular weight, distillation range and density are 16-32, 300-540, 350°C-500°C and 0.880-0.915, respectively.¹ As a phase change material, wax plays an important role in the global industrial processes such as construction, air conditioning and textitles, etc. WPCM not only changes their phase but also absorbs or releases a lot of latent heat with the change of the reaction temperature. The advantages of WPCM are that it has a high temperature thermal storage capacity, high thermal efficiency and also maintains energy at a constant temerature.²

In the present paper, the properties, classification and three kinds of packaging wax have been discussed, in comparison to the properties and classification of WPCM.

DISCUSSION

Classification of wax phase change material

Phase change material (PCM) is classified into two kinds of materials such as organic phase change material (OPCM) and inorganic phase change material (IPCM).³ IPCM mainly includes pure salt with high melting point, base metal, alloy and mixing salt etc. IPCM has a high heat of fusion and constant melting point. However, it is strongly corrosive and super-cooling in nature and has a tendency that phase change material is separated during the phase changing process. For the investment point of view of the manufacturer, the regeneration system must use specific materials in order to avoid equipment corrosion. On the other hand, OPCM consists of wax classes with high rates of fatty acid classes, polyolefin and alcohol etc. The advantages of WPCM are to generate good moulding ability. It is very hard to separate and create super-cooling during the phase changing process. OPCM has low corrosive properties also which are proved to be stable over time. However, it has very low thermal conductivity. Moreover, its poor heat transfer is due to a poor thermal contact between the two surfaces. Its heat transfer performance will be improved by adding high heat materials such as copper or aluminium powder or graphite.

The properties of wax phase change material ⁴

Table 1 shows the heat properties of n-paraffins. The melting point of even-numbered n-paraffins increased with an increase in the molecular weight. Furthermore, even-numbered n-paraffins had higher melting heat than that of odd-numbered n-paraffins. However, odd-numbered n-paraffins did not follow any rule with the molecular weight.

Table 1. the heat properties of n-paraffin wax

Molecular	Molecular	Melting	Melting heat
formula	weight	point (°C)	$(J \cdot g^{-1})$
C ₁₆ H ₃₄	226	16.7	236.81
C17H36	240	21.4	171.54
C18H38	254	28.2	242.67
C19H40	268	32.6	-
$C_{20}H_{42}$	282	36.6	246.86
$C_{21}H_{44}$	296	40.2	200.83
$C_{22}H_{46}$	310	44.0	251.04
C23H48	324	47.5	234.30
C24H50	338	50.6	248.95
C25H52	352	53.5	-
C ₂₆ H ₅₄	366	56.3	255.22
C27H56	380	58.8	234.72

Three kinds of packaging wax

Wax is a solid-liquid phase material, which is used in the different areas due to its different types of packages, such as the direct mixing method, the soaking and absorption method and the container packing method. In the direct mixing method wax is mixed with other materials. Wang Qishan⁵ mixed wax with gypsum that was used during summer. Its advantages were to control amount of wax easily, distribute evenly and a simple process, however, it is easily separated between solid phase and liquid phase and causes leaking. In the soaking and absorption method wax is soaked and absorbed with porous materials and then packaged. Luo Qing⁶ introduced bricks those were soaked and absorbed into wax to produce the phase change material on their surface. The advantage of this method was that its construction was very simple, but wax was unevenly distributed and easily leaked from bricks. Further, the bricks' temperature was hard to control and they were easily polluted or corroded. The container packing method includes the microscopic and the macroscopic structure packaging method. Miroslaw Zukowski⁷ used the polyethylene bag to seal wax and studied on the possibility to store the energy. Nowadays the phase change material is widely used in the different areas such as air conditioner and solar energy etc. But the phase change material has less surface to touch with outside atmosphere, so its heat transfer ability is very poor. Hu Xiaofang ⁸ used porous ceramics with soft tissue to absorb wax, and produced phase-change-material particles whose diameters were between 1µm and 100µm. These were having the advantages of simple process, stable performance, high energy storage and high thermal conductivity.

CONCLUSION

Based on the above discussion and review, wax phase change materil is widely used in different areas such as construction, air conditioning and textitle, etc. *China* owns a considerable amount of paraffin base petroleum and high quality wax. It is not only used as high value product for the requirement of residents and factories, but also increase *Chinese* Government Revenue also. It is an urgent need for *Chinese* scientists to find new methods and technologies which easily transfer from wax product to wax phase change material.

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Received: 14.10.2012. Accepted: 17.10.2012.



MAGNESIUM SUPPLEMENTATION AND MICROELEMENT HOMEOSTASIS

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Paper was presented at the 4th International Symposium on Trace Elements in the Food Chain, Friends or Foes, 15-17 November, 2012, Visegrád, Hungary

Keywords: magnesium supplementation, rat, essential elements, metabolic alteration, hyperlipidemy.

Magnesium participates in numerous enzymatic reactions in the human body and it has an essential role in maintaining the antioxidant system. Our purpose was to investigate the effect of magnesium on element content in blood. Male Wistar rats were divided into four groups. The animals in group I. were fed with normal diet, the animals in group II. were fed with normal diet and treated with magnesium polygalacturonate (200 mg Mg/kg body weight ad libitum daily). The animals in group III. were fed with fat rich diet containing cholesterol (2.0%), sunflower oil (20%) and cholic acid (0.5%) added to the control diet. The animals of group IV. were fed with fat-rich diet and magnesium polygalacturonate. The rats were kept on the diets for 9 days. The element concentration (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Ni, P, Pb, S, Si, Sn, Sr, Ti, V, Zn) of blood samples was determined with an ICP-OES after digestion with a mixture of nitric acid and hydrogen peroxide. The results show that the concentration of several elements changed significantly in both magnesium-treated groups, nevertheless the alteration was different in the control and hyperlipidemic groups. It has been concluded that high amount of magnesium supplementation alters the metal ion homeostasis in short-term experiment. Although some favourable effects were found in the hyperlipidemic group by magnesium polygalacturonate treatment, it is worth to note that supplementation with magnesium should be carried out carefully especially in metabolic diseases.

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Introduction

Magnesium is essential for the function of living organisms. It has structural roles in bone, cell membranes and chromosomes. Active transport of several ions as potassium and calcium through cell membranes needs magnesium. Magnesium is required for muscle contraction, the function of the heart and nerve cells and for the metabolism of carbohydrates and fats to produce energy in magnesium-dependent biochemical reactions. Magnesium plays a key role in more than 300 enzymatic reactions in the body. ^{1, 2}

Metabolic pathways, which consume energy, require magnesium in a complex form with adenosine triphosphate (MgATP), and MgATP stores the energy in phosphate bonds. Magnesium is essential in the synthesis and metabolism of carbohydrates, lipids, proteins, and nucleic acids, for example, for synthesizing DNA and RNA in mitochondria. ^{2, 3} Magnesium is also required for the synthesis and maintenance of the antioxidant defence system, including enzymes and antioxidant molecules. ^{4, 5}

Low magnesium intake is a risk factor in the development of several diseases e.g., diabetes, ischemic heart disease, severe retinopathy and causes reduced magnesium content in cells.^{6,7,8} Magnesium supplementation may have protective effect on the development of different diseases and may increase magnesium concentration and insulin sensitivity.^{9,10}

Hypomagnesemia is one of the common features of obesity, liver diseases as fatty liver, alcoholic and other cirrhosis. In these diseases decrease in the magnesium level in serum, erythrocyte, lymphocyte, liver tissues, heart muscle, skeleton muscle and bone is a well-known symptom. 11, 12, 13

The absorption of magnesium depends on several factors. In general 30-40% of the daily dietary intake of magnesium is absorbed in the small intestine. In case of low magnesium intake, absorption rate may be as high as 75%, and if the intake is high, the absorption rate may be reduced to 25%. The presence of calcium and other divalent cations, as well as phosphorus, fat, lactose, influences also the rate of magnesium absorption.¹⁴

The low magnesium absorption in jejunum and ileum causes low magnesium status in several diseases. Increased urinary magnesium excretion also contributes to latent magnesium deficiency. The first sign of magnesium deficiency is the low level of serum Mg (hypomagnesemia). ^{15, 16}

Alimentary induced hyperlipidemy and consecutive development of fatty liver is a suitable experimental model for studying liver damage and metal element homeostasis, therefore our aim was to study the effect of supplementation of Mg in polygalacturonate form on metal element homeostasis in hyperlipidemic rats.

	Control		Control+		Hyperlipid	lemic	Hyperlipidemic +		Significance at
			Mg-treate	Mg-treated				d	<i>P</i> <0.05 by
	Main	SD	Main	SD	Main	SD	Main	SD	ANOVA
Liver (g)	11.71	1.44	11.76	1.03	14.38	1.06	13.84	1.16	Sign.
Heart (g)**	0.89	0.12	0.93	0.15	0.90	0.08	0.78	0.10	Sign.
Lung (g)	1.28	0.37	1.55	0.49	1.13	0.09	1.13	0.11	Sign.
Spleen (g)	0.70	0.13	0.61	0.11	0.66	0.14	0.61	0.13	Not sign.
Thymus (g)**	0.46	0.15	0.52	0.12	0.50	0.09	0.94	0.07	Sign.
Kidney (g)	0.99	0.10	1.05	0.13	1.00	0.08	0.94	0.10	Not sign.
Body weight (g)**	314.5	18.36	322.4	12.38	294.0	11.2	269.9	14.6	Sign.

** significant difference between hyperlipidemic and hyperlipidemic+Mg-treated group at P<0.05 (Student-t test)

Table 2. Rutin parameters in sera of rats (n=10)

	Control		Control	Control Hyperlipidemic		lemic	Hyperlipid	lemic +	Significance at
		+Mg-treat		ed			Mg-treated	1	<i>P</i> <0.05 by
	Main	SD	Main	SD	Main	SD	Main	SD	ANOVA
UA (µmol/L)	114.6	20.4	115.6	34.0	131.0	31.4	113.6	18.5	Not sign.
GGT (U/L)	0.125	0.820	0.600	1.260	0	1.050	1.20	1.750	Not sign.
Triglicerid (mmol/L)**	1.22	0.42	1.47	0.44	0.57	0.28	0.86	0.30	Sign.
GPT (U/L)	65.43	18.60	62.00	22.83	76.20	19.75	54.67	21.00	Not sign.
GLUC (mmol/L)	7.63	0.98	8.44	0.75	8.57	0.66	7.87	0.68	Sign.
T-bilirubin (mmol/L)	1.25	0.63	1.22	0.67	1.11	0.60	0.89	0.93	Not sign.
Albumin (g/L)*	28.25	1.06	31.00	1.05	32.50	1.51	32.50	1.09	Sign.
BUN (mmol/L)	5.01	0.68	5.57	0.72	4.09	0.66	4.26	0.72	Sign.
ALP (U/L)**	584.9	102.0	561.8	50.1	1458	43.2	1217	166	Sign.
Total protein (g/L)	50.75	2.75	52.38	1.41	54.10	2.42	55.70	2.21	Sign.
Creatinin (µmol/L)	35.38	1.51	36.70	3.12	43.10	2.06	41.00	3.02	Sign.
GOT (U/L)	123.4	45.9	133.4	22.1	145.8	43.2	126.5	38.5	Not sign.
Cholesterol (mmol/L)*	1.67	0.38	2.11	0.34	5.48	1.83	4.49	1.38	Sign.
Amylase (U/L)**	2520	512	2771	175	4094	1082	3234	284	Sign.

* significant difference between control and control+Mg-treated group at P<0.05 (Student-t test); ** significant difference between hyperlipidemic and hyperlipidemic+Mg-treated group at P<0.05 (Student-t test)

Experimental

Materials

Basic magnesium-polygalacturonate from pectin (a component of higher order plants) was produced by In Vitro Kft according to a patent and the permission of OÉTI. ^{1, 17, 18} Several methods were applied for the characterization of the magnesium polygalacturonate, e.g. elemental analysis, infrared spectroscopy, thermogravimetry. ¹⁸ The magnesium content of magnesium poligalacturonate was 7.2%.

Animal experiment

Male Wistar rats (n=40; 150-200 g bw) were divided into four groups. The animals in group I were fed with normal diet from BIOFARM FARM PROMT Kft (BFP, Gödöllő, Hungary). The animals in group II were fed with normal diet and treated with magnesium polygalacturonate (200 mg Mg/kg body weight ad libitum). The animals in group III were fed with diet rich in fat contained cholesterol (2.0%), sunflower oil (20%) and cholic acid (0.5%) added to the control BFP. The animals of the IVth group were fed with fat rich diet and magnesium polygalacturonate (200 mg Mg/kg body weight ad libitum). The rats were kept on the above diets for 9 days. All experiments were performed with the permission of the Animal Health and Food Control Station (MÁB 1.81.4/2006).

The rats were anaesthetized with Nembuthal (35 mg/kg) and were exsanguinated from the abdominal vein. The liver was removed and washed. The rat bodyweight and the different organs were measured by gravimetry.

Hyperlipidemy was proved by elevated serum lipid parameters.

Rutin laboratory parameters

The next routine laboratory parameters were obtained with the use of a Hitachi 717 analyser: alkaline phosphatase (ALP), amylase, glucose, total bilirubin (T-bilirubin), albumin, total protein, blood urea nitrogen (BUN), serum triglycerides (TG), cholesterol (CHOL), uric acid (UA), creatinine, gamma glutamyl transferase (GGT), glutamateoxaloacetate transaminase (GOT), glutamate-pyruvate aminotransferase (GPT).

Measurement of elements

Element concentration (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Ni, P, Pb, S, Si, Sn, Sr, Ti, V, Zn) of the

Lable 0 . Element content ($\mu_{\rm E}$) \equiv) in blood of fats (n =10)	Table 3	. Element	content	$(\mu g/g)$	in	blood	of rats	(n=10))
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	Control		Control+	Control+Mg-treated		Hyperlipidemic		demic + Mg-	Significance at P<0.05 by	
	Main	SD	Main	SD	Main	SD	Main	SD	ANOVA	
Al**	11.73	6.76	12.63	5.10	14.00	4.25	23.25	7.48	Sign.	
As	1.96	0.47	2.10	0.34	1.94	0.32	2.15	0.38	Not sign.	
B**	28.89	16.38	21.52	6.19	25.30	8.96	59.48	17.48	Sign.	
Ba**	0.0690	0.019	0.0638	0.02	0.0744	0.0298	0.161	0.118	Sign.	
Ca*	144.7	17.08	53.78	4.78	60.30	8.31	57.63	15.39	Sign.	
Cd*,**	0.0061	0.0004	0.0139	0.0019	0.0121	0.0051	0.0052	0.0015	Sign.	
Co	0.011	0.008	0.007	0.0007	0.016	0.016	0.015	0.007	Not sign.	
Cr*	0.0641	0.0706	0.120	0.018	0.144	0.089	0.093	0.036	Sign.	
Cu*,**	0.704	0.104	0.830	0.093	0.915	0.177	0.777	0.087	Sign.	
Fe*	521.6	53.5	422.8	133.9	473.2	73.7	488.2	172.7	Not sign.	
K*,**	1873	99	1587	123	1716	278	2005	301	Sign.	
Li	2.01	0.32	2.07	0.25	2.00	0.33	1.66	0.54	Sign.	
Mg	44.03	4.03	43.50	3.63	42.04	6.97	43.84	5.69	Not sign.	
Mn	0.0116	0.0081	0.0094	0.0121	0.0065	0.0048	0.0476	0.1175	Sign.	
Ni*	0.142	0.061	0.035	0.011	0.121	0.186	0.125	0.215	Not sign.	
P*	596.8	72.4	477.8	55.4	481.9	88.4	458.1	99.1	Sign.	
Pb*	0.259	0.085	1.16	1.08	0.447	0.340	0.225	0.109	Sign.	
S	1498	347	1728	242	1638	235	1614	336	Not sign.	
Si*,**	78.12	37.60	127.9	25.89	140.4	25.60	42.97	33.63	Sign.	
Sn	0.181	0.129	0.211	0.125	0.212	0.111	0.135	0.123	Not sign.	
Sr*	0.074	0.0168	0.0476	0.0079	0.073	0.0179	0.0906	0.0793	Not sign.	
Ti	0.302	0.244	0.174	0.113	0.217	0.08	0.184	0.120	Not sign.	
v	0.0298	0.0102	0.026	0.0062	0.0237	0.007	0.0228	0.0024	Not sign.	
Zn	4.14	0.48	4.95	0.58	5.15	1.00	4.78	0.69	Sign.	

* significant difference between control and control+Mg-treated group at P < 0.05 (Student-t test); ** significant difference between hyperlipidemic and hyperlipidemic+Mg-treated group at P < 0.05 (Student-t test).

blood samples was determined with an ICP-OES (inductively coupled plasma optical emission spectrometer). Type of instrument: Spectro Genesis ICP-OES (Kleve, Germany). After digestion of the samples with a mixture of nitric acid and hydrogen peroxide (10 + 5 mL) and dilution with double distilled water to 25 mL, concentration of elements was determined.¹⁹

Statistical analysis

Means and standard deviations (SD) were calculated from the results. For comparison of the means of the four groups, one way analysis of variance (ANOVA) was used and for determination of the difference between two groups, the Student *t*-test was used by GraphPAD software version 1.14 (1990). Significance was determined as P < 0.05.

Results

The magnesium supplementation affects the body weight of rats and the weight of different organs (Table 1). The measured weights are significantly different in the four groups (ANOVA, P<0.005) instead of spleen and kidney. The weights in control groups did not change, while in the hyperlipidemic groups significant changes were observed for heart, thymus and bodyweight. Nevertheless the difference was larger between the control and hyperlipidemic groups than between the control and controltreated or hyperlipidemic and hyperlipidemic-treated groups.

The routine laboratory parameters showed that significant changes were observed in triglyceride, glucose, albumin, BUN, total protein, creatinine, GOT, cholesterol, ALP and amylase content between the four groups calculated by ANOVA test (Table 2). The magnesium supplementation hardly changed the routine parameters of rats in the control group, significant elevation was only seen in albumin and cholesterol levels, while in the hyperlipidemic group the level of triglyceride, ALP and amylase changed significantly. Similarly to the weights of organs, the difference was larger between control and hyperlipidemic groups than between the control and control-treated or hyperlipidemic and hyperlipidemic-treated groups.

The element concentration changes in the whole blood were significant in the four groups for Al, B, Ba, Ca, Cd, Cr, Cu, K, Li, Mn, P, Pb, Si and Zn by the method of ANOVA. Significant changes in the concentration of Ca, Cd, Cr, Cu, Fe, K, Ni, P, Pb, Si and Sr were also observed between the control group and control-treated group (Student's *t* probe), while the concentration of Al, B, Ba, Cd, Cu, K and Si showed significant alteration between the hyperlipidemic and hyperlipidemic-treated group (Table 3). In this sort time experiment high amount of magnesium changed the metal ion homeostasis, whilst the magnesium concentration in the blood did not change significantly.

Discussion

For magnesium supplementation several magnesium products are available in the market. For the animal experiment magnesium polygalacturonate was selected because of its favourable absorption property proved by human studies. ²⁰ The most important benefit of magnesium polygalacturonate is that the carrier is of natural origin. According to acute oral toxicological investigation, these complexes are nontoxic even in high concentration ($LD_{50} > 5000$ mg/kg body weight). By oral application of the complexes, no side effects have been observed so far. ²⁰ This natural origin may be the cause of results that magnesium concentration in blood did not increase. The concentration of several elements changed significantly in both magnesium-treated groups, nevertheless the alterations were different in the control and hyperlipidemic groups.

It has been concluded that high amount of magnesium supplementation changes the metal ion homeostasis in short-term experiment. Although some favourable effects were found in the hyperlipidemic group by magnesium-treatment, it is worth to note that supplementation with magnesium should be carried out carefully especially in metabolic diseases. Similar results were found for magnesium supplementation with magnesium malate in rat experiment. ^{21, 22} The cause of this may be that both magnesium compounds have natural origin and the uptake occurs similar absorption in the intestine. ²³

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Received: 15.10.2012. Accepted: 17.10.2012.



ISOLATION AND IDENTIFICATION OF MARINE PHYTOPLANKTONS FOR PRODUCTION OF CARBOHYDRATE TYPE BIOMASS

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Keywords: Types of sea phytoplankton, Biomass production, Carbohydrate content, Phytoplankton culture, Arschat medium

The primary aim of the present study was to isolate and identify a number of sea phytoplanktons for biomass production and determination of carbohydrate content. Sea phytoplankton was cultivated in cultured media "Ares-chat" to multiply seeds and cultivated stocks. In the mass media cultivation, isolation and identification of sea plankton was done based on size and some specific characteristics. The measurement of temperature, salinity and pH was also done in the media. The biomass weight of the density of selected phytoplankton was done by gravimetric method and the carbohydrate content was determined by glucose with Luff School method. The isolation results indicate six different types of sea phytoplanktons: *Chlorella sp., Dunaliella sp., Tetraselmis chuii, Chaetoceros calcitrans, Chaetoceros gracilis*, and *Chaetoceros Isocrysis galbana*. The highest biomass content 0.34 gL⁻¹ was on *Chlorella sp.* and the lowest 4.70% on *Chaetoceros gracilis*.

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Introduction

Microsize water organisms floating with the water movement are known as plankton.¹ Plankton concentration at the surface of sea water varies from 500 cells/mL to 10 cells m/L.² Plankton plays an important role and sometimes dominates material cycle in sea.³ Planktons are divided into two groups: phytoplankton and zooplankton.^{4,5}

Most phytoplankton are very small to see by the naked eye, but large in number. They appear as green in color in water due to chlorophyl in their cells, although the real color is varied for each species due to the presence of an extra pigment such as phycobiliprotein.^{6,7} Phythoplankton usually gathers at the euphotic zone where light intensity that makes photosynthesis possible (Arinardi et al., 1997 and Richtel, M., 2007). Phytoplankton gets energy by photosynthesis,^{8,9} for which they must be on the sea surface (called as euphotic zone), lake or other source of water. Through photosynthesis, phytoplankton produces a lot of oxygen into the earth's atmosphere.¹⁰ Because of the photosynthesis, the organism lives on the surface of water, and are also able to produce carbohydrate (glucose).^{11,12} The ability of phytoplankton to synthesise its organic material, make them to be the main source of food chain in the sea ecosystem and fresh water $(Fig.1)^{12}$

This planktonic organism is usually colleted by using a net. Based on the size of mesh of the net, phytoplankton is classified as megaplankton (bigger than 0.2 mm;) and macro lankton (0.2-2.0 mm).

Microplankton is sizes 20-0.2 mm.¹³ A plankton which is captured by filter milipore is known nanoplankton, whereas



a very small plankton sizes 2-20 $\mu m,~$ ultraplankton, a smaller plankton less than 2 $\mu m.^{14}$

Indonesia has the longest coastal line in the world which is about \pm 80.791.42 km. Phytoplankton consists of 30.000 species.¹⁵ Its habitat is on the surface of different types of water bodies. It is a large perspectives of phytoplankton utilization for production of carbohydrate as biofuel (bioethanol and biobutanol) and raw material to substitute the food grade corn or cereal raw materials.¹⁶ The other benefit of phytoplankton is that they are able to absorb carbon dioxyde and converse it to oxygen. As much as 90% of dry weight of phytoplankton adsorbe carbon dioxyde so that it is able to reduce gas up to 1.000 tons/ha/year.¹⁷

	Macro Nutrients											
							A	dded				
No.	Mineral Salt	c, 10 ⁻³ mol L ⁻¹	g L ⁻¹	Note	Note		g	mL L ⁻¹)				
1.	NaCl	300	25.38	direct addi	ition							
2.	MgSO ₄ .7H ₂ O	10	4.730	direct addi	ition							
3.	KNO3	4	0.503	stock 1 M	/100 mL		10.1	3				
4.	KH ₂ PO ₄	2	0.236	stock 1 M	/100 mL		13.6	1				
5.	CaCl ₂ .6H ₂ O	15	1.210	stock 1 M	/1000 mL		110.99	10				
	Micronutrients											
			Ad	lded	Stock 2	Ade	ded, mL					
No.	Mineral salt	c, 10 ⁻⁶ mol.L ⁻¹	M mL ⁻¹	g	mL L ⁻¹	M mL ⁻¹	Stock1 *	Stock 2 ⁺				
6.	H ₃ BO ₃	300	0.4/100	2.5724	1	-						
7.	ZnSO ₄ .7H ₂ O	1	0.2/100	3.7274		0.02/100	1	1				
8.	MnSO ₄ .4H ₂ O	1	0.4/100									
9.	CuSO ₄ .5H ₂ O	0.2	0.01/100	0.3495		0.01/100	1	1				
10.	CoCl ₂ .6H ₂ O	0.2	0.01/100	0.3738		0.01/100	1	1				
11.	(NH4)2M0O4.4H2O	0.2	0.01/100	0.8016		0.01/100	1	1				
12.	NaFeEDTA	25										
13.	Na2SiO3.9H2O**	15	0.1/100	2.6909	1	-						
14.	Tris mix (7.8):	0.023% (w/w); m	ean: 0.025 g Tris	s mix in 100 g v	water (MJ wa	tter = 1 g.mL^{-1}	⁻¹)					
	TRIS-HCl			0.01722								
	TRIS-base			0.00778								
15	Vitamin mix:				1							
	Biotin			0.2								
	Vitamin B1			0.15								
	Vitamin B12			0.2								

Table 1. Macronutrients (A) and micronutrients (B) for marine alga production

Notes: * Use 1 mL of stock solution to make a stock solution of 2; + Use 1 mL of stock solution 2 to make 1 L medium; ** Use for diatom

Experimentals

Materials and methods

Seeds extracted from pure cultures Pitoplankton Research Institute of Fisheries and Marine Maros, South Sulawesi.

Instrument and Apparatus

Equipment cups: Consists of the culture vessel, covering 1000 mL bottle size, tank size of 60 liters and a set of glassware. Salinity was measured salinity meter.

Identification of types of sea plankton with high carbohydrate content

Isolation and identification of phytoplanktons

Isolation of phytoplankton in the present study was done by taking samples of mass culture result for shrimp feed which contains bacteria and/or other microorganism such as Protozoa. In order to get pure phytoplankton strain, washing the cell at the new culture media and planted in medium to be selected for study. The culture medium used was modification of several culture media with artifial sea water which is known as "Ars-chat" which stands for Arifin-

Eur. Chem. Bull. 2012, 1(8), 311-316

Syahrul-Syahruddin-Henk Schat. Whereas the jelly medium was made by mixing the gelatin in medium solution of Arschat as much as 1% (10 grams). After autoclaved, it was poured into a gelatin plate each about 20 ml. When the gelatin plate is cool, 3 drops are spread over the surface of gelitin plate by a sterile pipette. After a span of 3 to 5 days the growth of phytoplankton cell colony was observed and found that phytoplankton did not associate with colony of bacteria. Further, 2-5 cells of phytoplankton were implanted in a test tube containg Ars-chat for phytoplankton culture of about 5-10 mL. After a span of 8 - 15 days the phytoplankton cell would grow with high density $(10^3 - 10^6)$ cells/mL). Then the seed of this phytoplankton cell was planted in the medium Ars-chat of which the volume was more (in Erlenmeyer glass of 50 mL, 250 mL, and 500 mL) then in culture bottle 1000 mL.

Further culture was done to multiply the seed aside from being kept for culture stock.

Physico-chemical parameters of water samples

In order to find out the growth condition of phytoplankton to be isolated, measurement of several physico-chemical parameters was done, such as temperature, salinity, and pH in situ in mass culture (in the field).



Figure 2. Research method

Pure Culture of Phytoplankton

Pure culture of phytoplankton was initiated by innoculating seed of phytoplankton cell into a culture tube with density of low phytoplankton cell in Erlenmeyer flask of 500 mL. After observing for 8 days, the culture condition was seen to be old enough (density ranges from 105-106 sel/mL) the culture was divided into 3 parts. The first and second parts each 200 mL was put into a culture bottle volume 1 liter. Whereas the rest 100 mL was added with medium Ars-chat as much as 400 mL, to make it to 500 mL culture volume in erlenmeyer flask as culture stock again kept for 8 days in the future. Whereas the 1 Liter volume culture after 8 days was shifted to aquarium volume of 60 liters. For both culture bottles of 1 liter, each of its growth pattern was observed daily for ten days by using Haemositometer through microscope.. At this culture the flow of its specific growth was observed using the formula:

$$\mu = \frac{\ln N_t - \ln N_0}{t} \tag{1}$$

where

- N_t is the density of the cell population at the time *t* (cells mL⁻¹)
- N_0 is the density of the cell population at baseline (cells mL⁻¹)
- μ is the specific growth rate constant (hr-1)
- t is the time (hours)

The amount of bomass in each liter culture volume was observed by filtering culture medium during the optimum growth by using a suitable filter paper as per the size of phytoplankton. The weight of phytoplankton was set by weiging the filter paper used before and after.

Biomass culture of selected phytoplankton types and Its weight determination.

Referring to physico-chemical parameter, the growth condition of phytoplankton in field measured in situ, selected phytoplankton was cultured in large amount at aquarium of 60 liters. After the density of optimal phytoplankton, 1 liter was taken out for the mass culture to determine its biomass gravimetrically. Then harvesting process was done by stopping the light and aeration for about 3 days for the separation between water and phytoplankton by sedimentation.

Analyzing carbohydrate contents of selected phytoplankton.

Carbohydrate analysis was done by using glucose reduction determination method of Luff Schoorl.

Results and Discussion

Isolation and Identification of sea phytoflankton

This study has been carried out for the isolation and identification of a number of marine phytoplanktons from both, dinoflagellate and diatom groups: Dinoflagellate consists of *Chlorella sp., Dunaliella sp.,* and *Tetraselmis chuii,* diatom species of *Chaetoceros calcitrans* consist of, *Chaetoceros gracilis* and *Chaetoceros Isocrysis Galbana* (Table 2).

Observation result on the growth of flagellate types: *Chlorella sp., Dunaliella sp.,* and *Tetraselmis chuii,* in artificial water medium (Fig.3). Observation result of growth pattern of diatom *Chaetoceros calcitrans* and *chaetoceros gracilis* in artificial water medium (Fig. 4).

The growth pattern of the three phytoplanktons viz. *Chlorella sp., Dunaliella sp.* and *Tetraselmis chuii* cultured at experimental environmental conditions, such as culture temperature, continuous light, nutrient used, salinity of sea water for each species of phytoplankton. Water pH applied and aeration CO₂, show growth pattern similar to one which underwent 3 stages of growth, namely adjustment, splitting and growth-dead. Optimum density was attained on the seventh day for pythoplankton type *Chlorella sp.* and for *Tetraselmis chuii* it was attained on the sixth day as 1.238.333 x 10⁴ cell mL⁻¹ and 173.250 x 10⁴ cell mL⁻¹. (Table 4), respectively.

Table 2. Results of isolation and identification of phytoplanktons

No	Types of	Size (um)	Information
110.		Size (µm)	mormation
	Phytoplankton		
1.	Chlorella sp.	3-4	Green, not motile and no flagella. Spherical cell with cup-shaped chloroplas
2.	Dunaliella	Width 5-8	Green motile with two flagella, near the back of the cells, The cells move quickly in
		Length 7-12	the water with shaking behaviour while swimming. Cells are spherical to cylindrical and usually have a red-eye point.
3.	Tetraselmiks chuii	width 9-10	Motile green, with a four flagella grew out of a groove in the back of the anterior
		Length 12-15	cells. The cells move rapidly in the water and looked shaken while swimming.
			There are four lobes are elongated and have a point reddish eyes.
4.	Isochrysis galbana	4 - 8	Motile cells with two flagella that grow near the rear part of the cell. Cells move
			faster in the water and turning while swimming. These algae are spherical shaped,
			gold-colored and usually have a red-eye point.
5.	Chaetoceros gracilis	0,5–2	These organisms are single cells and may form an interconnected chain using a hook
			of the adjacent cell. The main body is like a petri dish shape. Side view of square-
			shaped organisms gives an impression of spines from the corner.
6.	Chaetoceros	4	Cylindrical and reddish brown in colour
	calcitrans		•



Figure 3. Growth pattern of dinoflagellate species *Chlorella sp.*, *Dunaliella sp.*, and *Tetraselmis chuii*.





Figure 4: The pattern of growth of Diatoms *Chaetoceros* calcitrans and *Chaetoceros* gricilis.

Specific growth rate (μ) of phytoplankton types *Chlorella sp., Dunaliella sp.,* and *Tetraselmis chuii* (Table 5).

The pattern of specific growth rate (μ) of diatom group for types *Chaetoceros calcitrans* and *Chaetoceros gracilis* cultured at experimental environmental conditions as stated earlier in the present paper. Optimum density of both phytoplanktons was attained on the sixth day for phytoplankton types *Chaetocero calcitrans, Chaetoceros gracilis,* 713.333 x 10⁴ cells per mL and 223.667 x 10⁴ cell per mL respectively (Table 6).

Table 4. Phytoplankton density of *Chlorella sp., Dunaliella sp., Tetraselmis chuii*, at the 8th day of culture

Time	Types of Phytoplankton density, cells mL ⁻¹									
(days)	Chlorella sp.	Dunaliella sp. (10^4)	<i>T. chuii</i> (10 ⁴)							
-	(10^{5})	(10*)								
0	10,000	25,000	10.000							
1	19,583	69,333	13.167							
2	92,000	412,667	32.333							
3	257.000	844,333	80.333							
4	453,833	1.126,500	130.667							
5	627,333	1.204,667	161.333							
6	654,000	1.238,333	173.250							
7	656,333	1.158,667	150.667							
8	634,000	1.089,333	131.255							

Table 6. Density and Chaetoceros calcitrans phytoplanktonChaetoceros gracilis cultures on 8th day

	Types of phytoplan	kton density, cells mL ⁻¹
Time, days	Chaetoceros	Chaetoceros gracilis
	calcitrans (10 ⁴)	(10 ⁴)
0	10,000	2,500
1	42,167	10,333
2	206,667	51,667
3	331,667	112,000
4	533,333	174,667
5	660,000	198,333
6	713,333	223,667
7	650,000	216,667
8	538,333	214,333

Specific growth rate (μ) of pythoplankton types *Chaetoceros calcitrans* and *Chaetoceros gracilis* can be seen in Table 7.

Table 5. Phytoplankton cell density and specific growth rate (μ)

Species	Size µm	t, days	Observations, cells mL ⁻¹		μ, d ⁻¹)
			No	Nt	
Chlorella sp.	3–4	6	1.000.000	66.000.000	0.0318
Dunaliella sp.	8	6	250.000	13.500.000	0.0302
Tetrasel mis chuii	10–15	7	100.000	1.725.000	0.0198

Table 7. Phytoplankton cell density and specific growth rate $(\boldsymbol{\mu})$

Species	Size (µm)	t, days	Observation cells mL ⁻¹		μ, d ⁻¹
			Noa	Nt	
Chaetoceros calci p trans	4	6	100.000	7.133.333	0.0291
Chaetoceros gracilis	0,5–2	6	25.000	2.236.667	0.441

Biomass culture and determination of dry weight of selected phytoplankton

Determination of the relationship between biomass dry weight of phytoplankton and culture volume in optimum phase (Table 8).

Table 8. Relationships of phytoplankton biomass dry weight and 1

 liter of culture volume in the optimum phase

No.	Types of	Biomass dry weight,
	phytoplankton	mg L ⁻¹
1.	Chlorella sp.	0,34
2.	Dunaliella sp.	0,28
3.	Tetraselmis chuii	0,33
4.	Chaetoceros calcitrans	0,27
5.	Chaetoceros gracilis	0,24
6.	C. Isocrysis galbana	0,14

To predict the biomass obtained from mass culture of phytoplankton, dry weight test was done. Based on dry weight test of biomass of phytoplankton cultured with Arschat medium, it was observed that for phytoplankton of dinoflagellata type was having higher dry weight as compared to phytoplankton of diatom type. From the data it can be concluded that to obtain biomass in large amount, it is suggested to culture the type of dinoflagellata with dry weight as much as 0.34 mg/L, 0.33mg/L, and 0.28 mg/L mass culture medium respectively for phytoplanktons *Chlorella sp., Tetraselmis chuii*, and *Dunaliella sp.*

Carbohydrate analysis of selected phytoplankton

The results of carbohydrate test contained in each sea phytoplankton are recorded in Table 9.

 Table 9. Carbohydrate levels on various types of species of phytoplankton biomass in the culture.

No.	Types of	Carbohydrate levels (%)
	phytoplankton	
1.	Chlorella sp.	30,75
2.	Dunaliella sp.	31.99
3.	Tetraselmis chuii	26,68
4.	Chaetoceros	6,02
	calcitrans	
5.	Chaetoceros gracilis	4,70
6.	C. Isocrysis galbana	12,00

On the basis of the type of cultured phytoplankton, it is apparent to note that phytoplankton which has higher percentage of carbohydrate content is from dinoflagelata group, and that are of phytoplankton types *Dunaliella sp.*, *Chlorella sp.* and *Tetraselmis chuii*, which have carbohydrate content up to 31.99%, 30.75% and 26.68% respectively.

Conclusions

Isolation results for six types of phytoplanktons are obtained. They are *Chlorella sp., Dunaliella sp., Tetraselmis chuii,*. *Chaetoceros calcitrans, Chaetoceros gracilis* and *Chaetoceros Isocrysis galbana*. The highest biomass 0.34 g/L is of *Chlorella sp.* of dinoflagellata type and the lowest is 0.14 g/L of *Isocrysis galbana* of diatom type, whereas the highest carbohydrate content is in Dunaliella sp. i.e. 31.99% of dinoflagellata type and the lowest is in *Chaetoceros gracilis* i.e. 4.70% of diatom type. Phytoplankton with high carbohydrate content is suggested to be processed further to become vegetable fuel.

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Received: 15. Sept. 2012. Accepted: 09. Oct. 2012



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Keywords: corrosion, FTIR, SEM, AFM, inhibitor, sea water.

An accepted practice is the use of inhibitors in the corrosion control of metals and its alloys which are in contact with any aggressive medium such as sea water. Inorganic and organic compounds have been studied for their corrosion control potential; these studies reveal that the inhibitors especially with the polar atoms such as P, N, S and O showed excellent inhibition efficiency (IE). The inhibitors adsorbed on the metal surface through the polar atoms; protective films are formed. The protective films have been analyzed by surface characterization studies such as UV, fluorescence spectra, FTIR, SEM, EDX, Raman spectroscopy, Auger electron spectroscopy, XRD, XPS and AFM. Adsorption of the inhibitors obeys various adsorption isotherms. The IE has been investigated by electrochemical studies such as polarization, impedance spectroscopy, open circuit potential and cyclic voltammetry, etc. The conclusion of this article gives vivid account of both inorganic and organic compounds which are used as corrosion inhibitors for various metals and its alloys in natural/artificial sea water medium.

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Introduction

Corrosion is a natural, spontaneous and thermodynamically favourable process. It can be controlled, but it cannot be prevented completely. It means corrosion mitigation and control methods shall be properly selected to meet the specific environment and operational condition. Depending upon the metal/environment combinations, different types of inhibitors are used in suitable concentrations. The use of inhibitors is an important method of protecting materials against corrosion.

Sea water is the well known aggressive medium containing high chloride ions causing severe corrosion problems. Various inorganic and organic compounds have been tried and reported as inhibitors for metals and its alloys in neutral chloride medium. The inhibitors contain heteroatoms such as P, N, S and O coordinate with the corroding metal ions, through their electrons and hence protective films are formed on the metal surface so that corrosion is prevented.1-116

Inhibitors

Both inorganic compounds^{14, 16, 17, 21, 24, 32, 38, 55, 60, 63, 74, 76, 80,} ^{81, 95, 100, 101, 110}, and organic compounds – naturally available 5, 22, 62, 88, 89, 113, 116 and synthesized compounds¹⁻⁴, 6-13, 15, 18-20, 23, 25-31, 33-37, 39-54, 56-59, 61, 64-73, 75, 77-79, 82-87, 90-94, 96-99, 102-109, 111, 112, ^{114, 115} have been used to control the corrosion of various metals and its alloys in natural/artificial sea water medium.

Metals

The inhibitors have been used to control the corrosion of various metals such as Fe, ¹², ¹⁸, ²⁴, ²⁷, ³⁸, ⁷¹, ⁷³, ⁹⁸, ¹⁰⁰ carbon steel, ², ³, ⁵, ⁸, ¹³, ¹⁵, ²³, ²³, ²⁴, ⁴³, ⁵⁴, ⁵⁵, ⁵⁸, ⁶², ⁶³, ⁶⁷, ⁷⁰, ⁷⁴⁻⁷⁶, ⁸⁶, ⁹⁶, ⁹⁹, ¹¹⁰, ¹¹², ¹¹³, ¹¹⁵ mild steel, ^{1, 4, 35, 44, 45, 57, 61, 72, 106} stainless steel^{79, 80, 83, 85}, Al and its alloys,^{9, 10, 14, 16, 21, 37, 56, 60, 66, 69, 95, 101, 103, 107, 111} Zn and its alloys,^{17, 77} Cu and its alloys^{6, 7, 11, 19, 20, 22, 24-26, 28-30, 33, 34, 36, 39, 46-53, 59, 64, 65, 68, 73, 78, 81, 82, 84, 87-94, 97, 102, 104, 105, 108, 109, 114, 116} and Ni and its alloys24, 31 in natural/artificial sea water medium.

Medium

The inhibition efficiency (IE) of various inhibitors, in controlling corrosion of metals and its alloys in natural sea water medium^{1, 2, 5, 6, 21, 27, 34, 35, 62, 67, 69, 70, 77, 80, 81, 88-90, 101, 103,} ¹⁰⁴ and artificial sea water medium^{3, 4, 7-20, 22-33, 36-61, 63-66, 68, 71-} 76, 78, 79, 82-87, 91-100, 102, 105-116 have been studied.

Additives

Along with the inhibitors, substances like EDTA ¹, Al³⁺ and Mg^{2+ 3}, Ca^{2+ 3, 42}, Zn^{2+ 4, 13, 15, 23 58, 71, 72}, thiosulphate ⁸, docosanol ³⁴, KI ⁴¹, sodium benzoate ⁴⁴, oxalic acid ⁴⁵, sulphides ⁵¹, carbon black ⁵⁴, Ni^{2+ 58}, cysteine ¹⁰⁹ and SiO₂ ¹¹⁰ have been used to enhance the corrosion inhibition process. Moreover, ammonia,^{26,105} ethanol,^{28, 53, 75, 88} dilute NaOH,³² toluene⁵³ and acetic acid⁶³ have been employed as solvent for the dissolution of inhibitors.

Temperature

The IE of various inhibitors have been evaluated at room temperature, 1-38, 40, 41, 43-62, 64-71, 73-87, 89-98, 100-116 and also at higher temperatures ^{39, 42, 63, 72, 81, 88, 95, 99}.

	Ref	1	7	ю	4	s	6	7	×	6	10	11	12	13
	Findings	EPS is a strong corrosion inhibitor, protective film consists of metal- polysaccharide complex and EPS served as a structural matrix polymer.	IE increases with inhibitor concentration, obeys Langmuir isotherm and the order of inhibition is $SDS < HTABr < Pa EO$.	Cathodie inhibitor, IE in presence of Al ³⁺ ion is about 90% and interpretation of corrosion inhibition mechanism and cathodic control.	Mixed-type inhibitor, IE decreases as the immersion period increases and IE of CEPA is better than CPA.	IE increases with inhibitor concentration, but decreases due to the growth of fungi and obeys Langmuir adsorption isotherm.	Mixed-type inhibitor and the inhibition film do not lose efficiency even at anodic polarization.	Mixed-type inhibitor, excellent inhibitor for Cu corrosion and IE from cathodic Tafel plots and polarization were in good agreement.	IE of the inhibitor ranging between 74 and 96% and IE of DDQB, DDPC and IMI were almost same.	IE increases with inhibitors concentration and the order of inhibition is SDBS $> \rm LAPACI > \rm DPh(EO)_9$	Mixed-type inhibitor and obeys Langmuir adsorption isotherm.	BTA shows excellent corrosion inhibition in both media than the others, PP is not shows effective inhibition and GASS shows maximum inhibition at the concentration of 0.01 M.	Obeys Langmuir adsorption isotherm and thermodynamic theory, ΔG° = 30.4 kJ / mol, pendant functional group of IM plays key role in the inhibition and the increase of temperature and chloride ion decreases the adsorption potential.	Mixed-type inhibitors, synergistic effect, IE of CEPA better than CMPA and the protective film consists of ${\rm Fe}^{24}$ -phosphonate complex and Zn(OH) ₂ .
	Method	Weight loss, capillary gas chroma- tography and growth curve experiments.	Weight loss study and X-ray diffraction analysis.	Potentiodynamic polarization study.	Polarization study and fluorescense spectra.	Weight loss and potentiostatic polarization technique.	Weight loss, polarization measurements, EIS and Auger electron spectroscopy (AES) studies.	Electrochemical polarization, impedance spectra, cyclic voltammetry and IR spectra techniques.	Weight loss and polarization studies.	Potentiodynamic polarization and cyclic voltammetric studies.	Weight loss, potentiodynamic polarization and impedance measurements, UV, XRD and SEM studies.	Electrochemical impedance spectroscopy (EIS) and electroche- mical noise analysis (ENA).	Electrochemical impedance spectrum, polarization curves, scanning tunneling microscopy (STM) and XPS studies.	Weight loss, XRD, FTIR and luminescence spectral studies.
	Additive	10-mM EDTA, 2N HCl		$A1^{3+}, Ca^{2+}$ and Mg^{2+} .	Zn ²⁺				$S_2O_3^{2-}$					Zn^{2+}
awater	Inhibitor	Exopolysaecharide (EPS)	Non-ionic polyoxy- ethylene monopalmitate (PaEO), cationic hexadecyltrimethyl- ammonium bromide (HTABr) and anionic sodium dodecyl-sulphate (SDS).	Thiourea (TU)	2-carboxyethyl phosphonic acid (CEPA) and ethyl phosphonic acid (EPA)	Natural honey (NH)	Sodium-diethyl-dithiocarbamate (NaDDTC)	2-mercapto-1-methylimidazole (McMIm)	n-dodecylquinolinium bromide (DDQB), n- dodecylpyridinium chloride (DDPC), benzyl- stearyldimethylammonium chloride (BSDMAC), 1-(2-amminoethyl)-2-n-tridecyl- 3-imidazoline (IMI-13), 2-n-hexyl-3-imidazo- line (IMI-6), 2-n-tridecyl-3-imidazoline (IMI) and N-phenyl-cinnamylidenimine (PH-ATC).	Anionic sodium dodecylbenzene sulphonate (SDBS), nonionic dodecyl phenol ethoxylated with 9 units of ethyleneoxide (DPh(EO) ₉) and cationic 1,1-laurylamidopropyl ammonium chloride (LAPACI)	1,2,4,5 tetrazo spiro (5,4) decane-3 thione	Benzotriazole (BTA), glueonic acid sodium salt (GASS) and polyphosphoric acid sodium salt (PP)	Imidazoline amide (IM)	Carboxymethyl phosphonic acid (CMPA) and 2-carboxyethyl phosphonic acid (2-CEPA)
on inhibitors for se	Medium	Sea water (Dona Paula Bay, Arabian Sea)	Sea water	3.5% NaCl and sea water	Chloride medium	High saline water	Sea water	Aerated 3% NaCl solution	5% NaCl + 0.5% acetic acid	3.5% NaCl solution and sea water	3.5% NaCl solution	3% NaCl and artificial sea water	3.0 mol / L NaCl solution saturated with 0.1 MPa CO ₂	Neutral aqueous environment containing 60 ppm CI ⁻
1. Corrosic	Metal	Mild steel	Carbon steel	Steel	Mild steel	Carbon steel	CuNi ₁₀ Fe	Cu	Carbon steel	Al – Brass	Arsenical Al brass	Brass	Fe	Carbon steel
Table	S.No.	1	3	e	4	s	6	7	×	6	10	11	12	13

0	nt.). Con	osion inhibitor	s for seawater		_		-
tal Me	<u> </u>	dium	Inhibitor	Additive	Method	Findings	Ref
5083 3.5 Mg sol	(A) (T)	% NaCl lutions	CeCl ₃ and LaCl ₃		Weight loss, electrochemical techniques, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) studies.	Cathodic inhibitor, 250 ppm CeCl ₃ and 250 ppm LaCl ₃ shows highest IE and interpretation of inhibition mechanism.	14
bon 60 1 me	- v	ppm chloride edia	Sodium dodecylsulphate (SDS)	Zn ²⁺	Weight loss study, FTIR and fluorescence spectra.	Mixed-type inhibitor, IE 93%, Synergistic effect exists between SDS and Zn^{2+} , and protective film consists of Fe ²⁺ -SDS complex.	15
Mg 3.5 y 5083 sol	- v -	% NaCl ution	CeCl ₃		Electrochemical noise measurements.	The usefulness of robust statistical parameters, wavelet transform and transient shapes were illustrated.	16
Aé	1 10 10 10 10 10 10 10 10 10 10 10 10 10	erated 0.5 M aCl solution	CeCl ₃ and sodium octylthiopropionate (NaOTP)		Potentiostatic measurements, XPS and electron-probe microanalysis techniques.	Synergistic effect exists between the inhibitors and combined IE is 95%.	17
Z		aCl solution	Piperidin-1-yl-phosphonic acid (PPA) and (4- phosphono-piperazin-1-yl) phosphonic acid (PPPA)		Potentiodynamic polarization study.	Shifting of pitting potential in the positive direction and the decrease of corrosion current illustrates the inhibitive effect of the inhibitors and PPPA has better IE than PPA due to the adsorption of NCH ₂ PO ₃ H group on the metal surface.	18
N		aCl solution	Imidazole derivative		Weight loss and electrochemical polarization studies.	Inhibitors with a phenyl ring have better IE and obeys Freundlich adsorption isotherm.	19
Z Z ss		eutral aqueous aCl solution	N-[1-(benzotriazol-1-yl) methyl] aniline (BIMA) and 1-hydroxy methyl benzotriazole (HBTA)		Weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) and FTIR studies.	Mixed-type inhibitor, dezincification factor calculated and characterization of protective film.	50
29	. . ()	arine water Jochin estuary)	Cerium		Weight loss, linear sweep voltammetry, and potentiostatic polarization techniques.	Cathodic inhibitor, protective layer consists of CeO_2 , Ce treatment on pure Al has significant corrosion inhibition.	21
0 2		1 M NaCl Jution	Tannin (extracted from Tamarix articulate)		Polarization curves, impedance measurements and SEM studies.	Anodic inhibitor, IE is 93.2% at concentration of $2g/l$, protective film formation and explanation for the inhibition process.	22
bon N i sc		eutral chloride Jution	N-phosphonomethyl-glycine (NPMG)	Zn ²⁺	Electrochemical impedance measurements, polarization curves, XPS and AES techniques.	Mixed-type inhibitor, IE increases from 85 to 95% when inhibitor concentration increased from 10 to 100 mg/L and formation of protective film.	23
Ni and 3.	~ 0	% NaCl Iution	Calcium monofluorophosphate (CM)		Potentiodynamic polarization, open circuit potential, XPS and SEM techniques.	Anodic inhibitor, Increasing concentration of inhibitor shifts corrosion potential in positive direction and formation of protective layer.	24
то	10 1	% NaCl and 5 M HCl	Bis(1-benzotriazolyl-methylene)(2,5- thiadiazolyl)-disulfide (BBTD)		Potentiodynamic polarization and FTIR techniques.	Mixed-type inhibitor, BBTD behaves better in 3% NaCl than in 0.5 M HCl and protective layer consists of Cu(I).	25
30Ni 3 y s	I 0 0	% NaCl Jution	3-amino-1,2,4-triazole (ATA)	Amnonia	Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) and non-linear regression methods.	Mixed-type inhibitor, IE is 98% which is enhanced in presence of ammoniac and kinetic parameters were evaluated from Levich-Koutecky relation.	26
ZËR		aCl-bicarbo- ite solution id sea water	Phthalic acid and salicylic acid		Kinetic model experiment.	Phthalate ion decreases the Fe(II) oxidation rate where as salicylate ion increases oxidation due to the formation of Fe(II)-salicylate complex.	27
ωø	. ~ 0	0% NaCl Jution	N-Phenyl-1, 4-phenylenediamine	1% EtOH	Weight loss, potentiodynamic pola- rization, electrochemical impedance spectroscopy, FTIR and UV-visible, SEM and EDAX studies.	Mixed-type inhibitor, protective film formation and the order of corrosion of Cu is oxygenated > aerated > deaerated solutions.	28

Tab	le 1 (cont.). (Corrosion inhibitor	rs for seawater			
S.No.	Metal	Medium	Inhibitor Add	itive Method	Findings	Ref
29	Brass	Artiff-cial sea water	N,N-dibenzotriazol-1-ylmethylaminomethane (DBMM) and 3-hydroxypropyl benzotriazole (HPBT)	Weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), cyclic voltammetry and current transient techniques.	Mixed-type inhibitor, formation of protective film and inhibition of anodic dissolution of brass in artificial sea water effectively.	29
30	Cu-Ni alloy	0.2 M NaCl solution	Dodecylamine	Potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and AFM studies.	Cathodic inhibitor, IE increases with inhibitors concentration increased from 0.0005 M to 0.005 M and adsorption of dodecylamine on Cu-Ni alloy surface.	30
31	Nickel plated copper	3.5% NaCl solution	Polyaniline (PANI)	Cyclic voltammetry, AC impedance spectroscopy (EIS) and polarization curves.	PANI modified nickel plating provided much better barrier property to copper for longer periods.	31
32	Carbon steel	3% NaCl solution	TiO ₂ dilu	e Electrochemical impedance spectroscopy (EIS), coupling test, H XRD and SEM techniques.	Decrease of film resistance, film formed at 120 V can serve as photoanode and film accelerates the corrosion in the dark.	32
33	Brass	0.10 M NaCl solution	2-[(E)-pyridin-2-ylimino)]phenol (L ₁) and 2-[(pyridin-2-yl-amino)methyl]phenol (L ₂)	Potentiostatic polarization and AC impedance methods.	IE increases with inhibitors concentration and protective film formation.	33
34	Cu	Sea water	Poly(N-hexadecylaniline) Doc	Weight loss, potentiodynamic osanol polarization and SEM studies.	IE is 95%, stable and strong film formation over metal surface and obeys Langmuir-Blodgett adsorption isotherm.	34
35	Mild steel	Sea water	Polyhydric alcohol phosphate ester (PAPE)	Polarization curves, electrochemical impedance spectroscopy (EIS) and scanning tunneling microscopy (STM) studies.	Mixed-type inhibitor, obeys Langmuir adsorption isotherm and complex film formation due to the interaction of R ₁ function of PAPE and Fe ²⁺ , Mg^{2+} , Ca^{2+} , etc	35
36	Cu	3.0% NaCl	2-amino-5-ethyl-1,3,4-thiadiazole (AETDA)	Weight loss, pH, potentiodynamic polarization, potentiostatic current- time and electrochemical impedance spectroscopy (EIS), SEM and EDX studies.	Mixed-type inhibitor, maximum IE is 97% at 5 x 10 ⁻³ M AETDA, protective film is formed due to strong adsorption of AETDA molecules and the order of IE is oxygenated > aerated > de-aerated solutions.	36
37	Ы	0.50 M NaCl solution	1,4-naphthoquinone (NQ)	Potentiodynamic polarization, chronoamprometry (CA), open- circuit potential (OCP), EIS, SEM, cyclic voltammetric, and quartz crystal analyzer (QCA) techniques.	NQ shows maximum inhibition at 1.0×10^{-3} M and protecting the pits on Al surface.	37
38	Fe	0.1M NaCl solution	Zine chromate and zine phosphate	EIS, scanning vibrating electrode technique (SVET) and open circuit potential (OCP) measurements.	Both inhibitors show lower inhibition efficiency.	38
39	Cu	Aerated NaCl solution	Sodium oleate (OA)	Weight loss, potentiodyamic polari- zation and impedance measure- ments, SEM and EDX studies. Temperature: $15 - 65^{\circ}$ C	"Green" - Mixed-type inhibitor, formation of an adsorbed film on the metal surface, IE increases with inhibitor concentration and time of immersion and adsorption obeys Frumkin's equation.	36
40	Galvanic electrode (N80 carb. steel (CS) + S31803 stainless steel (SS))	1% NaCl solution	Dodecanoic acid and its sodium salt (DDAS)	Electrochemical methods, FTIR and AFM studies. pH = 4.0	Anodic inhibitor, protective layer formed on the metal surface due to the strong adsorption of the inhibitor and protective layer formed on the single CS electrode is less compact than that of on coupled CS.	40

1 (c	ont.). C	orrosion inhibito	rs for seawater				-
Metal		Medium	Inhibitor	Additive	Method	Findings	Ref
Galvanic electrode (GE) (N80 carb. steel + S31803 stainless steel)		NaCl solution	Imidazoline derivative (MAD)	KI	Electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, AFM and FTIR studies.	Cathodic inhibitors, synergistic effect exists between MAD and KI, and IE of MAD is higher in presence of KI due to the distribution of excess charge on the GE surface.	41
N80 steel		NaCl solution	Quaternary alkynoxymethyl amine (IMC-80-Q)	Ca ²⁺	Electrochemical impedance spectroscopy (EIS) and polarization resistance techniques. Temperature: 57°C	IMC-80-Q shows optimum inhibitor concentration significantly increased with the increase of Cl ⁻ concentration from 3% NaCl to 4.6% NaCl solution.	42
Steel		NaCl solution	Cerium and lanthanum cinnamate		Attenuated Total Reflectance- Fourier Transform Infrared (ATR- FTIR) spectroscopy.	The corrosion protection mechanism involves adsorption of the rare earth metal-cinnamate complex and oxide film on the steel surface.	43
Mild steel		3% NaCl solution	Polyaniline (PANI)	Sodium benzoate	Electrochemical impedance spectroscopy (EIS) and TGA.	PANI/epoxy coating shows better IE than epoxy coating.	44
Mild steel	· · · · · · · · · · · · · · · · · · ·	3% NaCl solution	Poly(N-methylaniline) (PNMA) and poly(N- ethylaniline) (PNEA)	Oxalic acid	Electrochemical impedance spect- roscopy (EIS) and DC polarization techniques.	PNMA and PNEA exihibits effective anti-corrosive properties.	45
Cu		3% NaCl solution	2-amino-5-(ethylthio)-1,3,4-thiadiazole (ATD)		Weight loss and pH measurements, potentiodynamic polarization, potentiostatic current-time, EIS, SEM and EDX studies.	Mixed-type inhibitor, IE is 94% at 5.0 mM of ATD, strong adsorption of ATD molecules on copper surface and the order of IE is oxygenated > aerated > de-aerated media.	46
Cu-Ni alloys		Neutral chloride solution	Cysteine		Polarization and impedance techniques.	2.0 mM cysteine shows 1E of 96%, strong physical adsorption of cysteine molecules on the alloy surface involves $\Delta G \sim -37.81$ kJ/mol.	47
Cu, Zn, and Brass (Cu-10Zn and Cu-40Zn)	-	0.5 M NaCl solution	Benzotriazole (BTAH)		Electrochemical techniques, atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) studies.	BTAH shows efficient inhibition, surface film (Cu ₂ O, ZnO, Cu(J)-BTA and Zn(II)-BTA) provides effective barrier against corrosion.	48
Cu		3.5% NaCl solution	5-(Phenyl)-4H-1,2,4-triazole-3-thiol (PTAT)		Weight loss, potentiodynamic polarization, potentiostatic current time and pH measurements, and FTIR specta.	Mixed-type inhibitor, IE of 500 ppm PTAT is 13% only and that of 1500 ppm PTAT is 90%, pH values decreases with concentration of PTAT and protective film formed on copper surface due to the strong adsorption of PTAT molecules.	49
Cu		Aerated synthetic sea water (3.5% NaCl solution)	3-amino-1,2,4-triazole (ATA)		Weight loss, electrochemical, gravimetric, pH measurements and Raman spectroscopy.	IE increases with inhibitors concentration and a protective film is achieved by strong adsorption of ATA molecules on the metal surface.	50
Cu-10Ni alloy		3.4% NaCl salt water	Benzotriazole (BTAH)	S ²⁻ ion	Optical and scanning electron microscopy (SEM) and X-ray diffraction (XRD) studies.	BTAH has very high IE at the concentration above 5 x 10 4 M and at lower concentration pitting corrosion occur.	51
Cu		1.0 M NaCl solution	Purine (PU)		Weight loss, electrochemical polarization, electrochemical quartz crystal microbalance (EQCM) and SEM techniques. pH = 6.8	IE increases with inhibitors concentration, adherent layer of inhibitor on metal surface account for the protective effect and chemical adsorption follows Langmuir isotherm.	52

1 (cont.). Corrosion inhibitors for seawater Metal Medium Inhibitor	Corrosion inhibitors for seawater	rs for seawater		Additive	Method	Findines	Ref
Cu 0.5 M NaCl solution	0.5 M NaCl solution		1-decanthiol (DT), 1,9-nonanedithiol (NDT) and 1,4-benzendimethanethiol (BDMT)	Absolute EtOH, toluene, DMF, and acetonitrile.	Polarization, electrochemical impedance spectroscopy (EIS), cyclic voltammetry, FTIR and AFM studies.	The order of IE is NDT > DT > BMDT and the solvent used for dissolving thiols have only a marginal effect on the IE.	33
Steel NaCl solution	NaCl solution		Polyvinyl alcohol	Carbon black (CB)	Electrochemical impedance spectroscopy (EIS), polarization curves, immersion measurements and salt fog tests.	Composites coatings with CB nanoparticles reduced drastically the corrosion rate of steel.	54
Carbon Alkaline Cl-ion steel contg. water	Alkaline Cl-ion contg. water		Tungstate (WO ₄) ² , molybdate (MoO ₄) ² , and nitrite (NO ₂) ⁷ ions		Cyclic voltammetry, potentiostatic current-time measurements, scanning electron microscopy (SEM), EDAX and XPS analysis.	The rate of pit initiation decreases and the pitting potential moves to more positive direction upon the addition of inorganic anions and the order of pitting inhibition is $(WO_4)^{2-} > (MO_a)^{-}$.	55
Al alloy 3.5% NaCl 2024-T3 solution	3.5% NaCl solution		8-hydroxyquinoline (8HQ) and 8-hydroxy- quinoline-5-sulfonic acid (HQS)		Open circuit potential, polarization measurements, electrochemical impedance spectroscopy (EIS) SEM and EDS studies.	Mixed-type inhibitors, adsorption of 8HQ and HQS on metal surface forms a protective layer, 8HQ has better IE than HQS.	56
Galvanize 0.5 M NaCl aqueous solution mild steel	0.5 M NaCl aqueous soluti	и	Polyurethane (PU)		Electrochemical impedance spectroscopy (EIS)	The relationship between the changes in mechanical properties and the degradation process were studied and PU coating shows higher adhesion and anticornosion behavior.	57
Carbon Neutral solutic	Neutral solutic	Ę	Pimeloyl-1,5-di-hydroxamic acid (C7)	Zn^{2+} and Ni^{2+}	Surface analytical and electrochemical techniques.	C7 offers effective corrosion inhibition in the presence of Zn^{2+} and Ni ²⁺ due to the formation of stable slightly soluble complexes with these cations.	58
Cu 0.6 M NaCl ar	0.6 M NaCl ar 1.0 M HCl	q	Cysteine		Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) studies.	Maximum IE is 90%, decrease in corrosion current, shifting of corrosion potential in the negative direction and obeys Langmuir adsorption isotherm with $\Delta G \sim -25$ kJ/mol.	59
Al alloy 3.5% NaCl AA2014 solution	3.5% NaCl solution		LaCl ₃ and CeCl ₃		Polarization and electrochemical impedance spectroscopy (EIS) and SEM studies.	1000 ppm of LaCl ₃ and CeCl ₃ shows significant corrosion inhibition, increase of double layer capacitance and film resistance, and film consists of precipitates of oxide/hydroxide of La and Ce.	60
Mild steel 0.01 M NaCl solution	0.01 M NaCl solution		Lanthanum-4 hydroxy cinnamate		Linear polarization resistance (LPR), cyclic potentiodynamic polarization (CPP) and EIS studies.	Anodic reaction strongly controlled and protective film formation.	61
Carbon Sea water steel	Sea water		Hibiscus rosa-sinensis linn flower extract (FE)		Weight loss, polarization and AC impedance, UV-visible and FTIR spectra and AFM studies.	Mixed-type inhibitor and protective film consists of ${\rm Fe}^{2+}$ -quercetin-3-O-glucoside complex.	62
St37 Carbon Aerated Na steel solution	Aerated Na solution	G	Mixture of Cerium and Lanthanum oxides (2:1)	AcOH	Weight loss, potentiodynamic pola- nization, open circuit potential and constant potential measurements. Temperature: $25 - 70^{\circ}$ C	The inhibitor is suitable for carbon steel in low to chloride media and 500 ppm of inhibitor concentration has maximum IE of 76%.	63
Cu 3% NaCl solution	3% NaCl solution		N-(5,6-diphenyl-4,5-dihydro-[1,2,4]triazin-3- yl)-guanidine (NTG)		Weight loss, potentiodynamic polarization measurements, EIS and electrochemical frequency modulation (EFM) studies.	IE is 99% and obeys Langmuir adsorption isotherm.	64
Brass 0.2 M NaCl	0.2 M NaCl		2-mercaptobenzo-thiazole (MBT) and polyoxyethylene sorbitan monooleate (Tween-80).		Potentiodynamic polarization, X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma analysis (ICP).	Mixed-type inhibitor, MBT and Tween-80 shows IE's 79% and 62.5% and their combination shows IE 94% and synergistic effect controls dezincification of brass.	65

	Ref	66	67	68	69	70	11	72	73	74	75	76	<i>LL</i>	78	79	80
	Findings	IE increases with inhibitors concentrations, PA and SPT shows significant synergistic effect and obeys Langmuir adsorption isotherm.	The natural naphthalates are very good inhibitors.	IE increases with inhibitor concentration, adherent layer formed on the metal surface account for the protective effect, and chemical adsorption obeys Langmuir isotherm.	Mixed-type inhibitor, the decrease of current density and double layer capacitance and increase of polarization resistance confirms the corrosion inhibition and protective film formation on the metal surface.	Effective inhibitors, corrosion potential shifted in noble direction, IE is very high even at low concentration, and bonding mechanism between the metallic surface and the inhibitors.	IE of 0.005 M PPA is 76.7% where as that of 0.005 M PPA – 20% Zn ²⁺ is 90.2%, synergistic effect exists between PPA and Zn ²⁺ , and the protective film consists of Fe ²⁺ -PPA and Fe ²⁺ -PPA + Zn(OH) ₂ in the absence and presence of Zn ²⁺ .	Mixed-type inhibitors, synergistic effect exists between phosphates and Zn^{2+} , order of IE is STPP > SHMP > ATP, IE decreases with temperature, IE of STPP and SHMP increases with concentration and IE of ATP decreases with concentration.	TU adsorbs at the alloy surface by Langmuir adsorption isotherm, IE is 91% and corrosion rate is in the order Cu <cu-20%fe<fe.< td=""><td>Crevice corrosion resistance significantly improved, surface layer consists of Y_2O_3 and Cr_2O_3 and it acts as a barrier to reduce the corrosion.</td><td>PANI –coated metal have excellent protection from corrosion and the passive layer over the surface consists of $\alpha\text{-}Fe_2O_3$ and $Fe_3O_4.$</td><td>The order of IE is $ZAPP > ZP$ and formation of precipitated layer on the metal surface.</td><td>Mixed-type inhibitor and protective film formation.</td><td>Excellent inhibitor and DEIS is a relatively rapid measurement technique.</td><td>Both compounds act as anodic-type inhibitors and IE of norfloxacin is higher than ciprofloxacin.</td><td>Corrosion rate increases with time of exposure to the corrosive medium and 4% inhibitor in sea water shows optimum corrosion inhibition.</td></cu-20%fe<fe.<>	Crevice corrosion resistance significantly improved, surface layer consists of Y_2O_3 and Cr_2O_3 and it acts as a barrier to reduce the corrosion.	PANI –coated metal have excellent protection from corrosion and the passive layer over the surface consists of $\alpha\text{-}Fe_2O_3$ and $Fe_3O_4.$	The order of IE is $ZAPP > ZP$ and formation of precipitated layer on the metal surface.	Mixed-type inhibitor and protective film formation.	Excellent inhibitor and DEIS is a relatively rapid measurement technique.	Both compounds act as anodic-type inhibitors and IE of norfloxacin is higher than ciprofloxacin.	Corrosion rate increases with time of exposure to the corrosive medium and 4% inhibitor in sea water shows optimum corrosion inhibition.
	Method	Electrochemical impedance spectroscopy (EIS) and Tafel polarization techniques.	Electrochemical and stalagmometric methods.	Weight loss, electrochemical polarization, electrochemical quartz crystal microbalance (EQCM) and SEM studies.	Potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and SEM studies.	Electrochemical impedance spectroscopy (EIS), potentiodyna- mic polarization, FTIR, SEM and EDAX studies.	Weight loss, potentiodynamic polarization and FTIR studies.	Weight loss, electrochemical polarization and SEM techniques. Temperature: 30, 40, and 50 °C	Open-circuit potential measurements (OCP), polarization and electrochemical impedance spectroscopy (EIS) studies.	Electrochemical measurements, Auger electron spectroscopy (AES) and XPS studies.	Electrochemical corrosion measurements and Raman spectroscopy analysis.	EIS, linear polarization (LP), SEM and EDX studies.	Cyclic voltammetry, SEM and EDAX studies.	Dynamic electrochemical impedance spectroscopy (DEIS).	Open circuit potential (OCP) and potentiodynamic polarization techniques.	Weight loss method
	Additive						Zn ²⁺	Zn ²⁺			EtOH					
s for seawater	Inhibitor	Propargyl alcohol (PA) and Sodium potassium tartarate (SPT)	Ca^{2+} , Ni^{2+} and Co^{2+} naphthalates	Adenine (AD)	Sodium benzoate	Thiomorpholin-4-ylmethyl-phosphonic acid (TMPA) and morpholin-4-methyl-phosphonic acid (MPA)	Piperidin-1-y1-phosphonic acid (PPA)	Sodium tripolyphosphate (STPP), sodium hexametaphosphate (SHMP) and adenosine triphosphate (ATP)	Thiourea (TU)	Yttrium (Y) and chromium (Cr)	Polyaniline (PANI)	Zinc aluminium polyphosphate (ZAPP) and zinc phosphate (ZP)	2-mercaptotriazole	Benzotriazole	Ciprofloxacin and norfloxacin	Sodium nitrite
orrosion inhibitor	Medium	0.5% NaCl solution	Sea water	1.0 M NaCl solution	Sea water	Sea water	3% NaCl solution	3% NaCl solution	1.0 M NaCl solution	NaCl solution	5% NaCl aqueous solution	3.5% NaCl solution	Red sea water	Artificial sea water	1.5% NaCl solution	Sea water
e 1 (cont.). C	Metal	3003 Al alloy	Steel	Cu	Al alloy	Carbon steel	Armco Fe	Mild steel	Cu, Fe and Cu- 20%Fe alloy	Carbon steel	Carbon steel	Steel	Zn	Brass- MM55 alloy	304 stainless steel	AISI/SAE Steel
Table	S.No.	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80

βľ	e 1 (cont.). C	Corrosion inhibito	rs for seawater		-		
	Metal	Medium	Inhibitor	Additive	Method	Findings	Ref
	90-10 Cu-Ni Alloy	Sea water	Thiosulphate		Potentiodynamic polarization study. Temperature range: 25 and 50 – 80 °C	At 25 °C, the corrosion rate increases with inhibitor concentration and at 50 or 80° C inhibitor forms a protective film that effectively decreases the corrosion rate.	81
	Brass-118	Artificial sea water	Benzotriazole (BTA)		Dynamic electrochemical impedance spectroscopy (DEIS).	Excellent inhibitor and DEIS is a very useful technique in the field of inhibitor research.	82
	AISI 430 stainless steel	3% NaCl solution	Polyethyleneimines (PEI)		Weight loss, polarization and cyclic polarization measurements and XPS technique.	PEI provides the best protection against localized corrosion and acts as a diffusion barrier which follows physical adsorption.	83
	Cu	NaCl solution	Benzotriazole, phenyl derivatives of tetrazole, bypyrazoles and 2-methyl-5-mercapto-1,3,4- thiadiazole.		Scanning electron microscopy (SEM).	The corrosion inhibition is due to the adsorption of inhibitor molecule on copper surface.	84
	ASTM 420 stainless steel	3% aqueous NaCl solution	Polyethyleneimine (PEI)		Linear polarization, cyclic polarization, immersion tests and XPS studies.	Very good inhibitor against pitting corrosion and a dense layer of PEI prevents the diffusion of ionic species from the film by chlorine from the salt water.	85
	Carbon steel	3% NaCl solution	Poly (aniline-co-o-toluidine)		Potentiodynamic polarization and EIS techniques and FTIR, UV- visible, TGA and XRD studies.	Mixed-type inhibitor, IE is 70% at 100 ppm of inhibitor and obeys Temkin adsorption isotherm.	86
	Brass	0.6 M NaCl solution	2(β-benzenesulphon-amido)ethylbenz-oxazole (I), 2(β-ben-zenesulphonamido)-ethylbenzimi- dazole (II), 2(β-benzene-sulphonamido)ethyl- imidazoline(III), 2(β-benzenesulphonamido) ethyl-1,4,5,6-tetra-hydropyndimine (IV)		Gravimetric, Potentiodynamic polarization, AC impedance and EDS methods. pH: 6.0	Very good mixed-type inhibitors, the order of IE is $I < II < IIV$, the best IE is 77.6% and the inhibition is due to the formation of mixed ligand complex on the brass surface and blocking the active site.	87
	Cu and brass	Sea water	Vitis vinifera (Extract prepared from seed and skin part of grapes)	EtOH	UV, FTIR and XRD studies. Temperature: 303 K, 313 K and 333 K respectively	IE increases with inhibitor concentration but decreases with temperature and time, complex film formation, obeys Langmuir and Temkin adsorption isotherms.	88
	Cu and its alloy (Cu-27Zn)	Sea water	Emblica officinalis leaves extract		UV and IR studies. Temperature: 303 and 333 K, respectively	Physical adsorption obeys Langmuir and Temkin isotherms, which are exothermic and spontaneous.	89
	Brass alloy	Mediterranean sea water (MSW) and oil field water	Benzotriazole (BTAH)		Weight loss, potentiodynamic polarization, X-ray diffraction (XRD) and SEM studies.	Mixed-type inhibitor, formation water is more corrosive for brass alloy than sea water, excellent control of dezincification of brass and IE \sim 98.13% for formation water at optimum concentration.	06
	Cu	3.5% NaCl solution	2-mercapto-4-(p-meth-oxyphenyl)-6-oxo-1,6- dihydropyrimidine-5-carbonitrile (MPD)		Electrochemical frequency modula- tion (EFM), electrochemical impe- dance spectroscopy (EIS), potentio- dynamic polarization and molecular stimulation (MS) techniques	Mixed-type inhibitor, IE increases with inhibitor concentration and the number of electrons transferred from MPD to metal surface calculated by semi-empirical quantum chemical calculations.	16
	Cu	3.5% NaCl solution	1-phenyl-2,4-dithiobiuret (Inh I), 1-p- methoxyphenyl-2,4-dithiobiuret (Inh II) and 1- p-chlorophenyl-2,4-dithiobiuret (Inh III).		Weight loss, electrochemical impedance spectroscopy, polarization curves, SEM and ESCA studies.	The order of IE is $\ln h II > \ln h II > \ln h III$ and the inhibition is due to the formation of protective film consist of Cu(1)-inhibitor complex, CuCl or CuCl ₂ ⁻¹ complex ions.	92
	Cu	Aerated 0.1 M NaCl solution	8-aminoquinoline (8-AQ)		Open circuit potential (OCP), poten- tiodynamic polarization and electro- chemical impedance spectroscopy (EIS) measurements, and atomic force microscopy (AFM) study.	Mixed-type inhibitor at concentration higher than 10^{-3} M, a film formed of thickness 10 μ m and the interaction between 8-AQ and copper surface is most probable.	93

Tabl	e 1 (cont.). (Corrosion inhibitor	s for seawater				
0.	Metal	Medium	Inhibitor	Additive	Method	Findings	Ref
	Cu	3.5% NaCl solution	2,5-dimercapto-1,3,4-thiadiazole		Weight loss, potentiostatic polarization, AC-impedance, UV- visible, FTIR, ESCA and SEM studies. pH = 6.5, 7.0 and 9.0	Mixed-type inhibitor, IE at pH 7.0 is 94.5% and formation of protective film consist of $Cu(J)$ -inhibitor complex, $CuCl$ or $CuCl_2$ -complex ions or both and no oxide on metal surface.	94
	Al-Si alloy	3.5% NaCl solution	Alumina		Potentiostatic polarization, EIS, SEM and XRD studies. Temperature: 25°C and 300°C pH = 4.0	Non-porous protective coating of thickness around 7µm, higher corrosion resistance and a significant decrease in diffusion of chloride ion through metal.	95
5	Carbon steel	200 mg L ⁻¹ NaCl solution	Activated starch (AS) and carboxymethylated starch (CMS)		¹³ C NMR, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and AFM studies.	Modified starches have corrosion inhibitive properties, AS shows better IE than CMS, IE depends on degree of substitution, strong ionic interation between AS and Fe^{2+t} ions, and higher protection is due to the densification of the inhibitive layer.	96
N	Brass	0.6 M NaCl solution	Glycine (D), L (-)-aspartic acid (II), glutarnic acid (III), N-benzenesulphonyl glycine (IV), N-ben-zenesulphonyl-L (-)-aspartic acid (V) and N-benzenesulphonyl-L (-)-glutarnic acid (VI)		Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. pH = 6.0	Mixed-type inhibitors, order of IE is I <ii<iv<v<vi, 4="" <math="" at="" ie="" is="" maximum="" x="">10^{-5} M concentration, IE increases due to the π electron contribution of the benzene ring and presence of more adsorption sites,</ii<iv<v<vi,>	97
~	Fe	$\begin{array}{c} 30 \text{ mg } \mathrm{L}^{-1} \mathrm{NaCl} \\ + 70 \mathrm{mgL}^{-1} \\ \mathrm{Na_2SO_4} \end{array}$	Sodium benzoate (SB)		Tafel polarization curves, electro- chemical impedance spectroscopy (EIS), XRD and SEM studies.	IE of SB increases as the grain size decreased from microorystalline to nanocrystalline and it is associated with the increase of the surface energy.	98
6	Steel	Salt water saturated with CO ₂	Hydroxyethyl imidazoline		Polarization curves, linear polarization curves, EIS and electrochemical noise studies. Temperature: 50°C	Anodic inhibitor, best IE at 25 ppm and protective film formation.	66
00	Mild steel	8.6 mM NaCl solution	Molybdate (Mo O_4) ²⁻ and nitrite (N O_2) ² ions		X-ray photoelectron spectroscopy (XPS) technique. pH = 8.0	Anion films are ~ 5 nm deep, film consists of ferric molybdate and nitrite respectively.	100
01	3003 Al alloys	Sea water	Calcium nitrite		Cyclic polarization testing and SEM studies.	Formation of protective oxide layer and increase in the amount of inhibitor leads to pitting corrosion.	101
02	Cu	3% NaCl solution	N-decyl-3-amino-1,2,4-triazole		Potentiodynamic measurements, electrochemical impedance spectroscopy (EIS), SEM and EDAX studies.	Mixed-type inhibitor and IE increases with inhibitor concentration.	102
03	AI	Arabian Gulf Sea water (AGS) and 3.5% NaCl solution.	3-amino-5-mercapto-1,2,4-triazole (AMTA)		Cyclic potentiodynamic polarization (CPP), Chronoamperometric current-time and electrochemical impedance spectroscopy (EIS) measurements.	AGS is more corrosive than 3.5% NaCl solution and IE of AMTA is higher for AGS than 3.5% NaCl solution.	103
04	Brass	Sea water (Eliot beach-southern coast of Chermai, India)	2-amino-5-ethyl-1,3,4-thiadiazole (AETD), 2- amino-5-ethylthio-1,3,4-thiadiazole (AETTD) and 2-amino-5-tert-butyl-1,3,4-thiadiazole (ATBTD)		Potentiodynamic polarization, EIS, inductively coupled plasma atomic emission spectroscopy (ICP-AES) and SEM, EDAX and FTIR studies.	Mixed-type inhibitors, IE% increases with inhibitor concentration, obeys Langmuir adsorption isotherm, control of cathodic reaction and dezincification of brass.	104
35	Cu70- 30Ni alloy	Aerated 3% NaCl solution	3-amino-1,2,4-triazole (ATA), 3-4'-bitriazole- 1,2,4 (BiTA) and 2-mercaptobenzimidazole (MBI)	$\rm NH_3$	Potentiodynamic measurements, electrochemical impedance spectroscopy (EIS) and SEM studies.	Mixed-type inhibitor controls both anodic and cathodic reactions and IE increases with inhibitors concentrations and corrosion rate decreases.	105

Metal Medium Inhibitor	Medium	Inhibitor		Additive	Aethod	Findings	Ref
Mild steel 3.5% NaCl Zine acetate (ZA), zine acetylacetonate (acetate (ZA)) and zine gluconate (ZG)	3.5% NaCl Zinc acetate (ZA), zinc acetylacetonate (acetylacetonate (acetylacetonate (zd)) and zinc gluconate (ZG) and zinc gluconate (ZG)	Zine acetate (ZA), zine acetylacetonate (and zine glueonate (ZG)	(ZAA)	S H	lectrochemcial impedance pectroscopy (EIS), pH, XRD and EM techniques.	ZG shows better IE than the others and it forms insoluble protective film over metal surface	106
Al-Cu Chloride Cerium diphenyl phosphate (Ce(dpp) ₃) alloy solution	Chloride Cerium diphenyl phosphate (Ce(dpp) ₃) solution	Cerium diphenyl phosphate (Ce(dpp) ₃)		S. el	EM and ToF-SIMS coupled with lectrochemical impedance pectroscopy (EIS) measurements.	Strong corrosion inhibitor and formation of a protective complex oxide film of Al and Ce .	107
Cu 3% NaCl N,N-bis (3-carbomethoxy-5-methylpyrazol- solution 1-ylmethyl) cyclohexylamine (BiPyA)	3% NaCl N,N-bis (3-carbomethoxy-5-methylpyrazol-solution 1-ylmethyl) cyclohexylamine (BiPyA)	N,N-bis (3-carbomethoxy-5-methylpyrazol- 1-ylmethyl) cyclohexylamine (BiPyA)		te III P	otentiodynamic polarization and inear polarization (LRP) schniques.	Efficient mixed-type inhibitor, IE's from Tafel plots and LRP method are in good agreement and BiPyA adsorbed on the copper surface according to Langmuir isotherm.	10
Brass 0.6 M NaCl tynyl)ethanoic acid (R _m H) and 1-benzene- solution solution sulphonamido-1,2-bis(2-imidazolynyl)-etha	ac-benzenesulphon-amido-β-(2-imidazo- lynyl)ethanoic acid (R _m H) and 1-benzene- solution solution sulphonamido-1,2-bis(2-imidazolynyl)-etha	$\label{eq:absolution} \begin{array}{l} \alpha \mbox{-benzenesulphon-amido-}\beta-(2-imidazo-lynyl) \mbox{-lipsolution} \\ lynyl) \mbox{-lipsolution} \\ sulphonamido-l,2-bis(2-imidazolynyl) \mbox{-etha} \\ (R_{\circ}H) \end{array}$	ne	P Cysteine el st pj	otentiodynamic polarization and lectrochemical AC impedance tudies. H = 6.0	Very good mixed-type inhibitors and antifouling agents, IE of the two inhibitors is higher than 80%, order of IE is $R_{b}H > R_{m}H$ and IE of $R_{m}H$ is increased due to synergistic effect of cysteine and this effect was not observed in case of $R_{b}H$.	=
Galvanize 0.1 M NaCl Cerium (IV) oxide solution	e 0.1 <i>M</i> NaCl Cerium (IV) oxide solution	Cerium (IV) oxide		Pi SiO ₂ el si	otentiodynamic polarization and lectrochemical impedance pectroscopy (EIS).	Cathodic inhibitor and mechanical treatment performed on the CeO_2 and SiO_2 particles promote the formation of an effective corrosion pigment.	
Al alloy 0.05 M NaCl Cerium cinnamate (CC) solution	0.05 M NaCl Cerium cinnamate (CC) solution	Cerium cinnamate (CC)		P III	olarization measurements, mmersion tests, XPS and electron- robe microanalysis (EPM).	Anodic inhibition is due to the deposition film and protection mechanism involves deposition of CC and then hydrolysis of cerium ions to form Cerium oxide/hydroxide.	
Carbon Alkaline 1-butyl-3-methyl-imidazolium steel chloride solution tetrafluoroborate ([BMIM]BF_a)	Alkaline1-butyl-3-methyl-imidazoliumchloride solutiontetrafluoroborate ([BMIM]BF4)	1-butyl-3-methyl-imidazolium tetrafluoroborate ([BMIM]BFa)		ΥË	lectrochemical measurements, AFM and XPS studies.	Mixed-type inhibitor, obeys Langmuir adsorption isotherm, inhibitor controls anodic and cathodic processes effectively and blocks the access of chloride ions to the metal surface.	
Carbon NaCl solution Mussel adhesive protein (Mefp-1) (derived from marine mussel <i>Mytilus edulis</i>)	NaCl solution Mussel adhesive protein (Mefp-1) (derived from marine mussel <i>Mytilus edulis</i>)	Mussel adhesive protein (Mefp-1) (derived from marine mussel <i>Mynitus edulis</i>)		E SI A A D	Lectrochemical impedance pectroscopy (EIS), otentiodynamic polarization and AFM studies. H = 4,6	Mefp-1 confers significant corrosion inhibition, within a short exposure time, the IE is increases with chloride concentration, but for longer exposure the IE is increases with lower chloride concentration and the protective film consists of bovine serum albumin (BSA).	
Cu 3.5% NaCl 2-carboxymethylthio-4-(p-methoxyphenyl)-6 oxo-1,6-dihydro-pyrimidine-5-carbo-nitrile (CPD)	3.5% NaCl 2-carboxymethylthio-4-(p-methoxyphenyl)-6 oxo-1,6-dihydro-pyrimidine-5-carbo-nitrile oxo-1,6-dihydro-pyrimidine-5-carbo-nitrile (CPD)	2-carboxymethylthio-4-(p-methoxyphenyl)-6 oxo-1,6-dihydro-pyrimidine-5-carbo-nitrile (CPD)	1	st d II E	Electrochemical frequency nodulation (EFM), EIS, potentio- lynamic polarization and molecular timulation (MS) techniques.	Mixed-type inhibitor, IE increases with inhibitor concentration and adsorption obeys Langmuir isotherm.	
Carbon 0.5 M NaCl Thiadiazole derivatives steel	0.5 M NaCl Thiadiazole derivatives solution	Thiadiazole derivatives		S B. 5 O	pen circuit potential (OCP), Tafel olarization, electrochemical mpedance spectroscopy (EIS) and iEM techniques.	Anodic inhibitor, IE increases with inhibitor concentration and decreases with temperature, obeys follows Langmuir isotherm and inhibitor acts as retarding catalyst for pitting corrosion.	
Cu 3.5% NaCl Fungicides (myclobutanil and hexaconazol solution	3.5% NaCl Fungicides (myclobutanil and hexaconazol solution	Fungicides (myclobutanil and hexaconazol	Ô	st III	Veight loss, electrochemical neasurements, SEM and EDX tudies.	Mixed-type inhibitors, obeys Langmuir adsorption isotherm and good performance at different temperatures.	-

pН

The IE of various inhibitors have been evaluated at neutral pH, $^{1-39, 41, 53-86, 88-93, 96, 98, 99, 101-108, 110-112, 114-116}$ and also at pH 4.0, $^{40, 95}$ 6.8, 52 6.0, $^{87, 97, 109}$ 6.5, 7.0 and 9.0, 94 8.0¹⁰⁰ and 4.6¹¹³.

Methods

Various methods have been used to evaluate the IE of inhibitors. Usually, weight loss method, ^{1, 2, 5, 6, 8, 10, 13-15, 19-21, 28, 29, 34, 39, 46, 49, 50, 52, 54, 62-64, 68, 71, 72, 80, 83, 85, 90, 92, 94, 111, 116 pH variation, ^{36, 46, 49, 106} potentiodynamic polarization, ^{3-10, 12, 14, 17-26, 28-31, 33-37, 39-42, 45-50, 52-56, 58-76, 79, 81, 83, 85-87, 91-99, 101-105, 108-116 electrochemical impedance spectroscopy, ^{6, 7, 10-12, 14, 20, 22, 23, 26, 28-33, 35-38, 40-42, 44-48, 50, 52, 54, 56-62, 64, 66, 67, 69, 70, 73, 74-76, 78, 82, 86, 87, 91-99, 102-107, 109, 110, 112-116 open circuit potential, ^{24, 37, 38, 56, 63, 73, ^{79, 93, 115} chronoamperometry, ^{37, 103} inductively coupled plasma atomic emission spectroscopy, ^{65,104} cyclic voltammetry, ^{7, 9, 21, 29, 31, 37, 53, 55, 77 electrochemical frequency modulation, ^{64, 91, 114} quartz crystal analysis, ^{37, 52, 68} molecular stimulation, ^{91, 114} gravimetry, ⁸⁷ thermogravimetric analysis, ^{44, 86} stalagmometry, ⁶⁷ electrochemical noise analysis, ^{11, 16, 99} electron probe microanalysis, ^{17, 111} coupling test, ³², kinetic model technique, ²⁷ capillary gas chromatography, ¹ growth curve method, ¹ and scanning vibrating electrode technique³⁸ have been employed.}}}}}

Adsorption isotherms

The adsorption behaviour of the atoms/ingredients present in the inhibitor over the metal surface has been investigated and the type of adsorption isotherm such as Langmuir adsorption isotherm,^{2, 5, 10, 12, 34, 35, 52, 59, 64, 66, 68, 73, 88, 89, 104} Freundlich adsorption isotherm,¹⁹ Frumkin adsorption isotherm,³⁹ and Temkin adsorption isotherm,^{86, 89} have been proposed, and it is supported by various thermodynamic parameters such as changes in free energy, enthalpy and entropy.

Surface analysis

The protective films formed on metal surface, during the process of corrosion protection of metals by inhibitors, have been analyzed by various surface morphological studies such as UV-visible spectroscopy,^{10, 28, 62, 86, 88, 89, 94} fluorescence spectroscopy,^{4, 13, 15} Raman spectroscopy,^{50, 75}, FTIR, 7, 13, 15, 20, 25, 28, 41, 43, 49, 53, 62, 70, 71, 86, 88, 89, 94, 104 EDX, 14, 28, 39, 46, 55, 56, 70, 76, 77, 87, 102, 104, 116 XRD, 2, 10, 13, 32, 51, 86, 88, 90, 95, 98, ¹⁰⁶ Auger electron spectroscopy,^{6, 23, 74} XPS, ¹², 17, 23, 24, 48, 55, 65, 74, 83, 85, 100, 112 ESCA, 92, 94 STM, ¹², 35 SEM, ¹⁰, 14, 22, 24, 28, 32, 34, 39, 46, 51, 52, 55, 56, 60, 68-70, 72, 76, 77, 84, 90, 92, 94, 95, 98, 101, 102, 104-107, 115 and AFM.^{30, 41, 48, 53, 62, 93, 96, 112, 113} It has been observed that the protective film consists of the metal-inhibitor complex at the anodic sites of metal surface and in some cases, Zn(OH)₂ is deposited on the cathodic sites of the metal surface, if Zn²⁺ is used along with the inhibitor.

Plant and animal materials

Extracts of various parts of the plants such as leaves,⁸⁹ flowers⁶² and seeds,^{22, 88} and animal products such as honey,⁵ protein¹¹³ and fungicides¹¹⁶ have been used as

corrosion inhibitors since they are eco-friendly, non-toxic, bio-degradable and cost effective.

Solvents

Solvents such as water^{5, 22, 62, 89} and ethanol,⁸⁸ have been used to extract the ingredients present in plant and animal products.

A list of various inhibitors that have been used as corrosion inhibitors for sea water is given in Table 1.

Conclusion

This review paper will be useful to a researcher who would like to select inhibitors to control corrosion of metals and its alloys in sea water. Especially this will be useful, when sea water is used in cooling water system.

Acknowledgement

The authors are thankful to DRDO India and to their respective managements for their help and encouragements.

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Received: 05.09.2012. Accepted: 18.10.2012.



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Keywords: Thorium doping; Perovskite; Th-doped 212-vanadate ceramics;

The compounds with general formula $Bi_2SrV_{2-x}Th_xO_9$, where (x=0.05, 0.1, 0.2, 0.3, 0.6) were carefully synthesized and processed by using mixed techniques solid state reaction and solution routes with sintering temperature at 880 °C for 20 h. XRD – analysis of the prepared samples proved that thorium(IV)-dopant can substitute successfully until x=0.55 mole on the Bi-layered perovskite crystal structure without damaging the original perovskite structure . It was observed that Th-dopings have slight to moderate effects on both ESR-signals and conduction mechanism of Th-doped Bi-Sr-V-O regime. Electrical measurements indicated that the energy gap E_g and number of electrons in conduction band N_{cb} increase as the ratio of Th doping increases from x=0.05 till x=0.6 mole respectively due to the increasing of paramagnetic character of thorium than vanadium .

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Introduction

The multi-layered perovskite structural materials such as Bi-Sr-V-O have attracted increasing attention in the research community because they are fatigue – free and lead free¹⁻³. The wide spread application and commercialization of bismuth-layered perovskite ferroelectrics have been limited due to drawbacks, as high processing temperature and relatively low remanent polarization⁴⁻⁵. Recently, efforts have been made to enhance the properties of layered perovskite ferroelectrics by addition or substitution of alternative cations⁶⁻⁸. It's now well established that the variation of oxygen content and distribution of oxygen atoms on the lattice site strongly influences the physical and structural properties (e.g. electrical conductivity) at high-temperature, as superconductors and many other metallic oxides⁹.

The discovery of high temperature superconductors has drawn much attention for their technological application such as superconducting quantum interference devices (SQUID), the high Tc ceramic super-conductor, the Bibased system has been studied because of its high critical temperature especially with the partial substitution of Pb in Bi and Sr sites since it promotes the stabilization of 2223 phase when grown from 2212 phase¹⁰⁻¹¹.

Many published reports¹²⁻¹⁴ are explaining the discovery of mixed metal oxides having bismuth layer alternating with perovskite structure layers, because of their ionic structural framework, Aurivillius phases exhibit great flexibility with respect to metal cation substitution. Therefore, these phases have high potential for systematic control of their properties¹⁵.

There are various studies showing the chemical substitution such as Pb doping on Bi-O layers that can be used to improve conduction in the blocking layers and so as to large decrease in the resistivity anisotropy. The reduced anisotropy leads to improvement of the critical current in the heavy Pb-doped¹⁶⁻²¹.

Das et al.²² reported the improved remanent polarization of SBN and $SrBi_2Ta_2O_9$ this films, when a small amount of Ca cations were incorporated into A sites: Bismuth layered perovskite materials have high fatigue resistance^{23,24}.

The crystal structure and chemical composition of these layered perovskites were systematically studied²⁵ with the general formula of $(Bi_2O_2)^{2+}$ $(Am^{-1}BmO^3m^{+1})^{3-}$, consisting of m-perovskite unites sandwiched between bismuth oxide layers called the family of bismuth layered structured ferroelectrics²⁶, where A and B two types of cations that enter the perovskite unite A is Bi³⁺, Ba²⁺, Sr²⁺, and B is Ti⁴⁺,Ta⁵⁺, and *m*=1-6 layered perovskite strontium tantalite is a member of bismuth layer- structured ferroelectrics.

The crystal structure of Sr $Bi_2Ta_2O_9$ comprises pseudoperovskite blocks $(SrTa_2O_7)^{2-}$ that are sandwiched between $(Bi_2O_2)^{2+}$ layers. Sr occupies the A site of the perovskite block and Ta occupies the B-site²⁷.

The essential objective of the present study is to investigate effects of wide range of Th - dopings on vanadium-sites on the main structural, electrical and spectroscopic features of 212-perovskite vanadate ceramics.

Experimental

The pure perovskite compound $Bi_2SrV_2O_9$ and different Th-doped samples with the general formula $Bi_2SrV_{2-x}Th_xO_9$, where x=0.05, 0.1, 0.2, 0.3, 0.6 mole were prepared by conventional solid state reaction and solution routes with sintering procedure using the appropriate amounts of $Bi_2(CO_3)_3$, $SrCO_3$, $(NH_4)_2VO_3$ and ThO_2 (each purity > 99%).

Thorium oxide is tested by Geiger counter of radioactivity, it was radioactive oxide with low emission. The mixture was grounded in an agate mortar for one hour then dissolved in few drops of concentrated nitric acid then dilution process was made with adjusting pH-value by 30% ammonia solution. The obtained solution was divided into two portions out of which one portion was treated by 0.4 M oxalic acid and the other one by ammonium carbonate of 0.4 M respectively.

$$M(NO_3)_n + (n/2)H_2C_2O_4 \rightarrow M(C_2O_4)_{n/2} \downarrow + n/2HNO_3$$
(1)

$$M^{1}(NO_{3})_{n} + n/2(NH_{4})_{2}CO_{3} + xH_{2}O \rightarrow NH_{4}NO_{3}$$

+(n-x)/2CO₂M(OH)x(CO3)_(n/2-2x) (2)

where M=Bi, Sr, V and Th(IV) ions, respectively .

The result metals precipitates (as oxalates, basic carbonates and hydroxylated oxides) were collected and dried in oven at 80 °C .Then the finely grounded powder was subjected to heat at 800 °C for 10 hours, regrounded and finally pressed into pellets with thickness 0.2 cm and 1.2 cm diameter and sintered at 880 °C for 20 hours. Then the furnace is cooled down slowly to room temperature. Finally the materials are kept in vacuum desiccator over silica gel dryer.

Structural Measurements

X-Ray diffraction (XRD)

The X-ray diffraction measurements (XRD) were carried out at room temperature on the fine grounded $Bi_2SrV_2O_9$ and Bi_2SrV_{2-x} Th_xO₉ systems in the range ($2\theta = 10-80^\circ$) using Cu-K α radiation source and a computerized [Bruker Axs-D8 advance] X-ray diffractometer with two theta scan technique.

Conductivity Measurements

The DC-electrical conductivity of the samples was measured using the two terminals DC-method. The pellets were inserted between spring loaded copper electrodes, A KEITHLEY 175 multimeter (ASA) was employed from room temperature up to 500K. The temperature was measured by a calibrated chromel-alumel thermocouple placed firmly at the sample. Measurements were conducted in such a way that at each temperature, sufficient time was allowed to attain thermal equilibration.

Solid infrared absorption spectral measurements

The IR absorption spectra of the prepared samples were recorded using "Nexus 670 FT IR spectrometer in the range 500-2500 cm-¹ using pure KBr matrix".

Electron paramagnetic resonance measurements

The electron spin resonance spectra (ESR) were recorded at room temperature for the prepared samples using at xband frequencies on a "Bruker- ELEXSYS E 500 Germany" spectrometer.

Results and Discussion

X-Ray Diffraction

The X-ray diffraction patterns of pure and variant Thdoped samples with the general formula Bi2SrV2-x ThxO9, where x= 0.05, 0.1, 0.2, 0.3, 0.6 mole are shown in Fig. 1.a-f. Analysis of the corresponding 2θ values and the interplanar spacing d (A°) by using computerized program proved that the compound is mainly belongs to distorted perovskite type with hexagonal crystal form, that expressed by assigned peaks in major. The unit cell dimensions were calculated using parameters of the most intense X-ray reflection peaks and found to be a = b = 5.7984 Å and c = 7.2124 Å for the pure 212Bi-Sr-V-O. Single phase of the layered perovskite structure appeared when M^{4+} is up to or equal to $0.05.^{28}$ The substitution of Th^{4+} for V^{5+} in BSV would induce A-site cation vacancies in perovskite layers, which leads to an increase of internal stress for the shrinkage of unite cell volume as reported.²⁹ The increasing number of tetravalent thorium ions in the crystal lattice of BSV will result in strong stress, which will expel other Th-ions from the crystal lattice of BSV(212-Bi-V-O) causing some extent of distortion on the perovskite layers .



Fig (1a-f): XRD patterns recorded for (a) pure $Bi_2SrV_2O_9$ and Thdoped samples (b): $Bi_2SrV_{1.95}Th_{0.05} O_9$, (c): $Bi_2SrV_{1.9}Th_{0.1} O_9$, (d): $Bi_2SrV_{1.8}Th_{0.2} O_9$, (e): $Bi_2SrV_{1.4}Th_{0.6}O_9$

The layered perovskite structure would be more restrictive since $(Bi_2O_2)^{2+}$ interlayeres impose a great constraint for structural relaxation. Such a structural constraint induced from $(Bi_2O_2)^{2+}$ interlayeres may well explain the lack of an appreciable decrease in lattice parameters with an increased amount of vanadium dopping³⁰.



Figure 2. Variation of *c*-axis as a function of Th-content.

From Fig.2 it is clear that *c*-axis increases as a result of substitution Th-dopant. On the bases of ionic radius it is expected that *c*-axis increases as Th⁴⁺ doping ratio increases. Furthermore, Th⁴⁺ is lower in charge than V⁵⁺ and as a result of which it is expected to decrease stress inside lattice and consequently the shrinkage factor of lattice will be increased. From Fig.1a-f, it is clear that the Th-substitutions are successful in the most of investigated range even at high concentration x=0.6 mole since there is no evidence noticeable at X-ray diffractogram referring to Th-impurity phase which reflects that all doping ratios are within the internal lattice structure. This confirms that Th-dopant can substitute in the V-sites successfully in the whole investigated range.



Electron paramagnetic resonance measurements

Fig. 3a, 3c and 3e explain the electron spin resonance (ESR) signals recorded for pure Bi-212-vanadates and some selected thorium doped samples with x=0.1 and 0.3 mol.

It was shown that the effective g-values (g_{iso}) exhibit an increase from x=0.0 mole to x=0.3 mol due to strong interaction of coupling between Th⁴⁺ ion that substitutes V⁵⁺ ion successfully at low dopant concentration as shown in Fig. 4.

These results of ESR-spectra proved that the anisotropy occurred as a result of increasing of Th doping is due to the increasing of paramagnetic character of substituted vanadates where g_{eff} varies as function of x value.^{31,32,33}



Figure 4. Variation of G_{iso} versus Th-content.

DC-Electrical conductivity measurements

Fig.5a-f displays the variation of DC-electrical conductivity as a function of reciprocal of absolute temperature for various Th⁴⁺ dopings. The data from Fig.5a-f exhibit conducting and semi-conducting behavior since the conductivity increases with an increase in temperature in case of conductor and conductivity decrease with an increase in temperature in case of semiconductor.³³

Fig. 6a and 6b show the relation between the energy gap (E_g) , number of e⁻ in conduction band (N_{cb}) for Th-doped samples, in which both of E_g and N_{cb} increase as the ratio of Th-doping increases from x = 0.05 to x = 0.6 mole, which may attributable to the numbers of unpaired electrons in the thorium outer shell which is higher than those of existed in the vanadium ions .

$$\rho = \rho_0 e^{\frac{\Delta E_g}{kT}} \tag{3}$$

Figure 3a, 3c and 3e. ESR spectra at room temperature for pure and some selected Th-doped 212-Bi-Sr-V-O system where (a): Bi₂SrV₂O₉, (c): Bi₂SrV_{1,9}Th_{0,1}O₉ and (e): Bi₂SrV_{1,7}Th_{0,3}O₉

$$N_{cb} = AT^{3/2} e^{\frac{\Delta E_g}{2kT}}$$
(4)

where A = constant, $E_g = \text{energy gap in eV}$, k = Boltzmann constant and finally $N_c = \text{numbers of electrons in the conduction band in electrons unit}$.

Furthermore, the energy gab in the thorium band structure is lower than that of vanadiun and as result of it a number of electrons evaluated in the conduction band Nc are increasing as thorium dopings increase.



Figure 5a. Variation of DC- electrical conductivity as a function of temperature for pure 212-Bi-Sr-V-O system .



Figure 5b. Variation of DC- electrical conductivity as a function of temperature for (b) $Bi_2SrV_{1.95}$ Th_{0.05}O₉.

Solid infrared absorption spectral measurements

The infrared absorption spectra of pure $Bi_2SrV_2O_9$ and their thorium doped samples in the range of 500-2500 cm⁻¹ are shown in Fig. 7.

It is well known fact that 212-Bi-Sr-V-O₉ $\pm \delta$ system is mainly belongs to deficient perovskite structures and an extra oxygen atom(O₉ $\pm \delta$). Oxygen nine converts it to distorted perovskite structure and consequently the common vibrational modes of IR-spectra of perovskite are clearly appeared.



Figure 5c. Variation of DC- electrical conductivity as a function of temperature for (c) $Bi_2SrV_{1.9}Th_{0.1}O_9$



Figure 5d. Variation of DC- electrical conductivity as a function of temperature for (d) $Bi_2SrV_{1.8}$ Th_{0.2}O₉.



Figure 5e. Variation of DC- electrical conductivity as a function of temperature for (e) $Bi_2SrV_{1.7}Th_{0.3}O_9$.

From Fig.7 we can summarize the different vibrational modes and their reasons as follows;



Figure 5f. The variation of DC- electrical conductivity as a function of temperature for (f) $Bi_2SrV_{1.6}Th_{0.4}O_9$



Figure 6a. Variation of Egab versus Th-content.

(a) The range from 390-620 cm⁻¹ includes the most of infrared active phonons involving stretching modes of vibrating Bi-O, Sr-O and V-O/Th-O plus bending modes of Bi-O-V, Bi-O-Sr, respectively.



Figure 6b. Variation of N_{cb} versus Th –content.

(b) The broad band around 800 cm⁻¹ is mainly due to an increase in the free carrier scattering as reported in many previously published papers as reported in ³⁴⁻³⁵.



Figure 7. The room temperature solid infrared absorption spectra recorded for ; (a): Pure $Bi_2SrV_2O_9$, (b): $Bi_2SrV_{1.95}$ Th_{0.05}O₉, (c): $Bi_2SrV_{1.9}$ Th_{0.1}O₉, (d): $Bi_2SrV_{1.8}$ Th_{0.2}O₉, (e): $Bi_2SrV_{1.7}$ Th_{0.3}O₉, (f): $Bi_2SrV_{1.4}$ Th_{0.6}O₉

(c) The vibrational modes at $\approx 690-820$ cm⁻¹ is due to the effect of charge exchanging of V⁺⁵/Th⁺⁴ carriers which is enhanced by increasing paramagnetic character caused by Th-dopings.

Conclusions

In summary, 212-Bi-Sr-V-O ceramics with various Thdoping ratios were successfully synthesized by mixed solid state/solution routes. X-ray diffraction proved that the compounds have distorted perovskite structure with hexagonal crystal form and the Th-ions can substitute successfully even at high concentration as x=0.6 mole. The ferroelectric properties of the layered perovskite have been significantly enhanced with Th-doping. The DC-electrical studies show conducting and semi-conducting behavior. IR spectra indicated that the system is mainly belongs to deficient perovskite structure with an extra oxygen atom (O₉± δ where δ less than 1).

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Received: 03.10.2012. Accepted: 22.10.2012.



AN OVERVIEW ON SYNTHETIC METHODS OF N-BUTYL ACETATE

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Keywords: overview; synthetic study; n-butyl acetate; catalysts

Nowadays a few synthetic methods of n-butyl acetate using different catalysts such as inorganic salt like ($Ce(S_2O_8)_2$, FeNH₄(SO₄)₂·12H₂O, LaSO₄/SiO₂, KHSO₄ and SnCl₄/C), HZSM-5, oxide (MoO₃/SiO₂), I₂, heteropolyacid (H₂(PW₁₂O₄₀)·nH₂O), quaternary ammonium salt ionic liquid and nanometer ZnO have been reviewed. The yields of n-butyl acetate are improved by the addition of above catalysts. These methods are having the advantages of simple process and low investment costs.

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Introduction

n-Butyl acetate is one of the colourless flammable liquids. It is used as a synthetic flavour agent in food products and/or as a solvent in the production of lacquers, plastic or artificial leather.¹ n-Butyl acetate and other organic solvent such as alcohol, aldehyde, ester, etc. are completely miscible in all proportions. Natural n-butyl acetate exists in apple, banana, cherry and grape fruits, etc. It is easily evaporated and hard to dissolve in water. Furthermore, it can dissolve brain grease, gum and rosin. It has anaesthetic and pungent in character. Its specific gravity $d4^{20}$, refractive index np^{20} and boiling point are 0.8825, 1.3941 and 126.1 °C, respectively.²

In the present paper, different catalysts such as inorganic salt (Ce(S_2O_8)₂, NH₄Fe (SO₄)₂·12H₂O, LaSO₄/SiO₂, KHSO₄ and SnCl₄/C), HZSM-5, oxide (MoO₃/SiO₂), I₂, heteropolyacid (H₃(PW₁₂O₄₀)·nH₂O), quaternary ammonium salt ionic liquid and nanometer ZnO have been discussed.

DISCUSSION

$Ce(S_2O_8)_2$ -SBA-15 as a catalyst to produce n-butyl acetate

Yin Yanlei ³ introduced the preparation of n-butyl acetate and the effect of the reaction conditions on its yield. $Ce(S_2O_8)_2$ and SBA-15 as catalysts were ground and roasted to produce n-butyl acetate. The optimum conditions were the reaction time (2 hours) and molar ratio of acetic acid to n-butanol (1.0:1.2), amount of catalyst (0.0375g) respectively. The maximum yield of n-butyl acetate was 95.13%. The experimental results showed that $Ce(S_2O_8)_2$ and SBA-15 had good catalytic performance and were reused several times.

$NH4Fe(SO_4)_2\label{eq:source}12H_2O$ as a catalyst to generate n-butyl acetate

Kong Xiangwen⁴ explained why NH₄Fe(SO₄)₂·12H₂O as a catalyst took the place of concentrated sulfuric acid to generate

n-butyl acetate. The effect of the reaction conditions such as the reaction time, molar ratio of acetic acid to n-butanol and amount of catalyst had been discussed. The experimental results represented that the best conditions were that the reaction time, molar ratio of acetic acid to n-butanol and amount of catalyst were 0.75 hours, 1.0:1.2 and 1.1 g, respectively. The maximum yield of n-butyl acetate was 98.5%.

LaSO₄/SiO₂ as a catalyst to produce n-butyl acetate

Song Jianguo⁵ described the synthetic method of n-butyl acetate by using LaSO₄/SiO₂ as catalysts. The effect of the reaction conditions such as the reaction time, molar ratio of acetic acid to n-butanol, amount of catalyst and number of reusable catalyst had been discussed. The best conditions were that the reaction time, molar ratio of acetic acid to n-butanol and amount of catalyst were 2 hours, 1.0:1.3 and 0.06 g, respectively. The maximum yield of n-butyl acetate was 95.2%. After recovery and reuse of LaSO₄/SiO₂ as a catalyst it was noticed that its catalytic performance was very poor. For example, when LaSO₄/SiO₂ were reused 5 times, the yield of n-butyl acetate only reached 56.3%.

KHSO₄ as a catalyst to generate n-butyl acetate

Cai Xin'an⁶ used KHSO₄ as a catalyst to produce n-butyl acetate. The effect of the reaction conditions such as amount of n-butanol, molar ratio of acetic acid to n-butanol and amount of catalyst had been discussed. The best conditions were that amount of n-butanol, molar ratio of acetic acid to n-butanol and amount of catalyst were 0.25 mol, 1.0:1.3 and 1.15 g, respectively. The maximum yield of n-butyl acetate was 86.83%.

SnCl₄/C as a catalyst to produce n-butyl acetate

Li Jiagui⁷ described the synthetic method of n-butyl acetate by using SnCl₄/C as catalysts. The effect of the reaction conditions such as amount of acetic acid, molar ratio of acetic acid to n-butanol, amount of catalyst and number of reusable catalyst had been discussed. The best conditions were that amount of acetic acid, molar ratio of acetic acid to n-butanol and amount of catalyst were 0.1mol, 1.0:2.2 and 0.15 g, respectively. The maximum yield of n-butyl acetate was 94.8%. When SnCl₄/C as catalysts were recovered and reused, their catalytic performance was found to be very good. For example, when $SnCl_4/C$ were reused 5 times, the yield of n-butyle acetate still reached 90.1%.

HZSM-5 as a catalyst to generate n-butyl acetate

Li Minghui⁸ introduced the preparation of HZSM-5 and the effect of the reaction conditions such as the reaction time, molar ratio of acetic acid to n-butanol and amount of catalyst on the yield of n-butyl acetate. The best conditions were that the reaction time, molar ratio of acetic acid to n-butanol and amount of catalyst were 1 hour, 1.0:1.1 and 0.5 g, respectively. The maximum yield of n-butyl acetate was 94.0%.

MoO₃/SiO₂ as a catalyst to produce n-butyl acetate

Li Shuchang⁹ described the preparation of MoO₃/SiO₂ and the effect of the reaction conditions such as the reaction time, molar ratio of acetic acid to n-butanol, amount of catalyst and number of reusable catalyst on the yield of n-butyl acetate. The best conditions were that the reaction time, molar ratio of acetic acid to n-butanol and amount of catalyst were 3 hours, 1.0:4.0 and 1.0 g, respectively. The maximum yield of n-butyl acetate was 95.6%. When MoO₃/SiO₂ as catalysts were recovered and reused, their catalytic performance was perfect. For example, when MoO₃/SiO₂ were reused 5 times, the yield of n-butyle acetate still arrived at 95.2%.

I2 as a catalyst to generate n-butyl acetate

Jiang Hongbo ¹⁰ used I₂ as a catalyst to generate n-butyl acetate. The effect of the reaction conditions such as the reaction time, molar ratio of acetic acid to n-butanol and amount of catalyst had been discussed. The best conditions were that the reaction time, molar ratio of acetic acid to n-butanol and amount of catalyst were 4.0 hours, 1.5:1.0 and 0.6 g, respectively. The maximum yield of n-butyl acetate was 67.52%.

H2(PW12O40) nH2O as a catalyst to produce n-butyl acetate

Guixian¹¹ Li introduced of the preparation H₃(PW₁₂O₄₀)·nH₂O with attapulgite and the effect of the reaction conditions such as the reaction time, molar ratio of acetic acid to n-butanol, amount of catalyst and number of usable catalyst on the yield of n-butyl acetate. The best conditions were that the reaction time, molar ratio of acetic acid to n-butanol and amount of catalyst were 2.5 hours, 1.0:2.5 and 0.1580 g, respectively. The maximum yield of n-butyl acetate was 94.0%. When $H_3(PW_{12}O_{40})$ nH₂O as a catalyst was recovered and reused, its catalytic performance was poor. For example, after used 5 times as catalyst, H₃(PW₁₂O₄₀)·nH₂O, the yield of n-butyl acetate reached only to 77.98%.

Quaternary ammonium salt ionic liquid as a catalyst to generate n-butyl acetate

Li Wenjun¹² described the preparation of four types of quaternary ammonium salt ionic liquids such as $[Et_2NH_2][HSO_4]$, $[Et_3NH][HSO_4]$, $[n-Pro_3NH][HSO_4]$ and $[n-Pro_3NH][HSO_4]$ and $[n-Pro_3NH][HSO_4]$.

But_3NH][HSO_4] . He used [Et_3NH][HSO_4] as a catalyst to generate n-butyl acetate. The effect of the reaction conditions such as the reaction time, molar ratio of acetic acid to n-butanol and molar ratio of [Et_3NH][HSO_4] to n-butanol had been discussed. The best conditions were that the reaction time, molar ratio of acetic acid to n-butanol and molar ratio of [Et_3NH][HSO_4] to n-butanol and molar ratio of [Et_3NH][HSO_4] to n-butanol and molar ratio of [Et_3NH][HSO_4] to n-butanol were 8.0 hours, 2.0:1.0 and 1.0:4.0, respectively. The maximum yield of n-butyl acetate was 81.94%.

Nanometer ZnO as a catalyst to produce n-butyl acetate

Lai Wenzhong¹³ used nanometer Zno as a catalyst and acetic acid to n-butanol as feedstocks to produce n-butyl acetate. The effect of the reaction conditions such as the reaction time, molar ratio of acetic acid to n-butanol and amount of catalyst on the yield of n-butyl acetate had been discussed. The best conditions were that the reaction time, molar ratio of acetic acid to n-butanol and amount of catalyst were 3.0 hours, 1.0:2.0 and 0.80 g, respectively. The maximum yield of n-butyl acetate was 86.72%.

CONCLUSION

Based on the above discussion and review, NH₄Fe(SO₄)₂·12H₂O that is one of the best catalysts is used to produce n-butyl acetate because it is very cheap, stable and insoluble in organic acids and organic alcohol. After the reaction is done, NH₄Fe(SO₄)₂·12H₂O becomes insoluble material and is easily separated from the reaction system. It has high performance catalytic and selectivity and non-corrosive. However, I₂ is one of the worst catalysts and its maximum yield of n-butyl acetate only reaches 67.52%.

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Received:	22.10.2012.
Accepted:	24.10.2012.



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Paper was presented at the 4th International Symposium on Trace Elements in the Food Chain, Friends or Foes, 15-17 November, 2012, Visegrád, Hungary

Keywords:, element mobility, soil contamination, heavy metal

The Cd and Cr fractions (mobile: 1M NH₄NO₃-soluble, mobilisable: ammonium acetate + EDTA-soluble, "total": cc. HNO₃ + cc. H₂O₂soluble) of the experimental soils and the Cd and Cr contents of spring barley grain and straw were examined in a pot experiment to investigate the effect of applying industrial-communal sewage sludge with metal contents exceeding the permissible limit. The four experimental soils were acidic sand, calcareous sandy, calcareous chernozem loamy and brown forest soil or acidic loam. The sludge was applied at rates of 0, 2.5, 5, 10 and 20 g sludge D.M. /kg air-dry soil in four replications. The mobile fraction of both elements changed only on sandy soils significantly. Regression analysis on the soil Cr and Cd fractions and the barley grain and straw element contents revealed that in the case of Cd the soil mobile fraction is the most suitable to predict the plant concentration. The changes in plant Cr concentrations were not coherent, thus the regression with soil Cr concentration did not give reliable results. Only a negligible proportion of the elements added with the sludge appeared in mobile form in the soil. This ratio is smaller in the case of Cr where only 0.02 % of the sludge Cr content can be found in the soil mobile Cr fraction. Since Cd is more mobile element therefore, 2.5 % of the added Cd can be found in the mobile fraction. Our results indicated that in case of sewage sludge application on field it is important to consider not only the element contents, but also other parameters (pH, texture, organic matter), as these may influence the dissolution of contaminants. The Cd and Cr content of the investigated sludge may cause adverse effects mainly on light textured soils.

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Introduction

The sewage sludge volume is supposed to be grown up very high with increasing drainage and capacity of wastewater treatment. In Hungary, the amount of sewage sludge dry matter is 150-160 thousand tons per year at present. This value is supposed to be increased to 350-400 thousand tons by 2015.¹

The most cost effective treatment of sludge is agricultural utilisation.² However, the sewage sludge may contain high concentrations of potentially toxic elements in it. The contamination of soils with these elements continues to be a matter of great concern because of their persistence in soils and increased uptake by crop plants even many years after sludge applications.^{3,4,5,6}

The sorption of these elements in soil depends on the chemical properties of the elements and the composition of the soil. In the three characteristic elements fractions in soil – total (cc. $HNO_3 + H_2O_2$ extracted), mobilisable ($NH_4OAc + EDTA$ soluble) and mobile (NH_4NO_3 soluble) – the last two have important role from the environment protection point of view. These fractions significantly influence the plant element uptake (thus the contamination in food chain) and the element concentration of soil irrigated water and groundwater despite its concentration may be only negligible as compared to the total fraction. The ratio between the differently soluble fractions depends on the soil and element properties either.^{7,8,9,10,11}

The effect of sewage sludge loads on soil composition and plant element uptake was investigated by various authors^{12,13,14} in a pot experiment. In these experiments the relations between the total and mobile element contents and barley element composition were investigated. This work focuses on the effects of industrial-communal sewage sludge on mobile Cr, Cd fractions, mobility in soil and its uptake by barley.

Methods

Experimental design

A pot experiment was set up for determining the effect of sewage sludge loads on soils and plants.^{13,14} Four soils were used from the plough layer (0-20 cm) of the field experimental stations of Institute for Soil Sciences and Agricultural Chemistry. Parameters of the investigated soils are shown in Table 1. The four experimental soils were brown forest soil with alternating thin layers of clay, or acidic sand (Nyírlugos), calcareous sandy soil (Örbottyán), calcareous chernozem loamy soil (Nagyhörcsök) and brown forest soil, or acidic loam (Gyöngyös/Tasspuszta).

The soils were treated with industrial-communal sludge. The pre-treatment of the sludge compost was as follows: the compost was dried then sieved 3 times for homogenisation.

The mixture of air-dried soil (< 5 mm particle size) and the air-dry compost was dispensed into 10-liter pots (10 kg soil). To take soil water supply under control the pots were in field situation, but under a shed. Soils were irrigated by deionised water as per the plants need. Applied sewage sludge loads were the following: 0, 5, 10, 20 g sludge D.M./kg air-dry soil. Number of treatments was: 4 soil x 4 load level = 16, with 4 replications.

		S	oils	
Parameter	Acid	Calcare-	Calcare-	Acid
	sand	ous sand	ous loam	loam
pH (H ₂ O)	5.4-5.8	7.8-8.3	7.8-8.1	6.6-6.8
pH (KCl)	3.9-4.8	7.3-7.6	7.5-7.6	5.8-6.3
CaCO ₃ %	-	10-13	8-10	-
Clay (<0.002 mm, %)	3-4	4-5	20-24	40-45
Organic matter %	0.5-0.8	0.6-0.8	2.6-3.0	3.0-3.5

Table 1. Selected properties of soil samples¹²

The soil and sludge mixing was followed by 1-month incubation, then spring barley (30 seeds per pot on 3th May 1999) and after its harvest and removal of the roots (26^{th} July 1999) peas (7 seeds per pot) were sown. The barley had 3 months growing period. Soil sampling was taken after pea harvest on the 20^{th} October. Composite soil samples consisted of 20 cores/pot and all above-ground total plant mass was used for analysis and yield assessment. Before sampling of the soil it was sieved so as the plant residues would be removed. In this paper only the results about barley are shown.

Chemical analysis

Determination of plant, soil and sewage sludge pseudo total element concentrations was carried out with ICP-AES method after microwave teflon bomb digestion with cc. $HNO_3 + H_2O_2$.¹⁵

From the soil samples the pseudo total, the mobilisable: 0.5 M NH₄-acetate + 0.02 M EDTA extractable¹⁶ and the mobile: 1 M NH₄NO₃ extractable¹⁷ element concentrations were measured by ICP-AES method.

Measurement of pH was carried out in 1:2.5 soil 1 M KCl solution after 24 hours of mixing. The soil organic matter content was measured by oxidation with $K_2Cr_2O_7$ according to the method of Tyurin.¹⁸ The total N content was measured after cc. $H_2SO_4 + H_2O_2$ digestion according to the modified method of Kjeldahl.¹⁹ The CaCO₃ content of the soil was determined according to.²⁰

Results and discussion

The NH₄NO₃-soluble mobile fraction showed significant changes in function of sludge loads only in the case of B, Cd, Co, Cr, Cu, Mn, Mo, Ni, Sr and Zn. The results concerning the Cu, Zn, Mn, Ni and Co elements are discussed by us.²¹ Thus in this work the results of only the Cd and Cr elements are presented.

The Cr and Cd concentration limit values for agricultural application of sewage sludge²² were exceeded 1.8 and 3.5 times respectively in the sludge treatments. Thus the sludge applied in this experiment could not be used legally in the field. Table 2 shows the element loads.

For the understanding of the changes in NH_4NO_3 -soluble mobile fraction it is necessary to investigate the changes in soil properties caused by sludge application. The sewage sludge influenced significantly the pH only in the case of the two sandy soils. The pH of acidic sandy soil increased from 5.9 to 6.2 (Table 3). While the pH of calcareous sand decreased from 7.8 to 7.4. The pH increasing effect of sludge has also been observed in the experiment of earlier workers.²³

Table 2. Cd and Cr content of sludge loads (kg ha⁻¹)

Flowert	Limit	Load leve	el (g sludg	e D.M./kg	soil)
Element	value*	2.5	5	10	20
Cr	10	13	26	53	106
Cd	0.15	0.26	0.53	1.05	2.1

*limit values for sewage sludge agricultural application, total fraction $^{\rm 22}$ (kg/ha/year)

A contradictory result like in the case of calcareous soils in this experiment was revealed by other workers²⁴ that sludge with higher pH than soil may decrease soil pH by their high Al and Fe content. The CaCO₃ concentration was affected by sludge only on calcareous sandy soil. At the same time the sludge increased the organic matter content in the sandy soils from 0.8 to 1 %. The significant increment in organic matter can be observed on the calcareous loamy soil also: the concentration reached 3.3 % in the 20 g sludge/kg soil compared to the control. The changes in organic matter content may have an influence on pH also by their functional groups.²⁵

Table 3. Effect of sludge loads on soil properties

		L	oad le	vel			
Soils	(g	sludg	e D.M	I./kg s	soil)	LSD _{5%}	Mean
	0	2.5	5	10	20		
	pH (I	H ₂ O)					
Acid sand	5.9	5.8	5.8	6.1	6.2		5.9
Calcareous sand	7.8	7.8	7.8	7.7	7.4	0.2	7.7
Calcareous loam	7.8	7.8	7.8	7.7	7.7		7.8
Acid loam	6.9	6.8	6.9	6.9	6.9		6.9
	CaC	O3 %					
Acid sand	0.0	0.0	0.0	0.0	0.0		0.0
Calcareous sand	13.1	13.3	12.7	13.1	12.5	0.6	12.9
Calcareous loam	8.3	8.5	8.4	8.7	8.5		8.5
Acid loam	0.0	0.0	0.0	0.0	0.0		0.0
	Orga	nic m	atter %	ó			
Acid sand	0.8	0.8	0.8	0.9	1.0		0.9
Calcareous sand	0.8	0.8	0.8	0.9	1.0	0.2	0.9
Calcareous loam	2.9	3.0	3.0	3.2	3.3		3.1
Acid loam	3.6	3.5	3.6	3.7	3.7		3.6

The total and mobile Cd and Cr fractions increased significantly on each investigated soil (Table 4 and 5). The mobile fractions of the two elements showed an increment only on the sandy soils. On the loamy soils no concentration change can be observed, however the control concentrations of mobile Cd and Cr are in the same magnitude of order in each soil. In the case of both elements the mobile concentrations are the highest on acidic sand.

The mobile Cd concentration changes did not follow the volume of sludge loads (Table 3). In the control treatment the soils Cd concentration was statistically the same and on sludge treated soils only the acidic sand differed significantly from the other soils. The increment in mobile

Cd concentration was significant only on the sandy soils. On acidic sand the mobile Cd concentration increased significantly after the addition of the 2.5 g sludge/kg soil load but the higher loads did not modify this value significantly. A potential explanation of this phenomenon is the increase of pH that could reduce the solubility of this element.²⁶ The NH₄NO₃ soluble Cr concentration was statistically the same on each control soil. The sludge loads increased this value on the sandy soils. However, the Cr(III) is one of the least mobile element in soil. Thus the increment may probably refer to the increased amount of Cr(VI) that can be mobile in the present conditions.¹² At the same time the lack of the toxicity of the sludge to barley is against this theory. Based on the above the Cd and Cr content of the investigated sludge may cause adverse effects principally on light textured soils but in this experiment these could not be revealed because the barley yield increased significantly as a result of sludge treatments.¹²

Table 4. Effect of industrial-communal sewage sludge loads on soil Cd fractions and barley grain and straw Cd concentration (total, mobilisable and plant concentrations are based on the data of Kádár and Morvai¹²)

	I	load l	evel (g slud	ge		
Soils		D.I	M./kg	soil)		LSD5%	Mean
	0	2.5	5	10	20		
	Cd	load	, μg C	d kg ⁻¹	soil		
	0	88	175	350	700		
Mobile (NH4NO3 s	olubl	e) Cd	conce	ntratio	on of s	oil (µg l	(g ⁻¹)
Acid sand	4	19	20	15	18	6	15
Calcareous sand	1	4	1	8	8	6	4
Calcareous loam	2	1	3	3	3	n.s.	2
Acid loam	7	4	4	4	6	n.s.	5
LSD _{5%}	12						
Total (cc. HNO ₃ +H	$_{2}O_{2}$ s	oluble	e) Cd	concer	ntratio	n of soil	l (µg kg-1)
Acid sand	68	105	153	210	355	96	178
Calcareous sand	134	169	182	310	569	178	273
Calcareous loam	234	369	410	440	659	100	419
Acid loam	510	564	706	804	1061	102	729
LSD _{5%}	95						
Mobilisable (NH4O	Ac +	EDT	A solu	ible) (Cd con	centrati	on of soil
(µg kg ⁻¹)							
Acid sand	26	60	67	158	237	59	110
Calcareous sand	80	115	109	236	394	81	187
Calcareous loam	176	187	214	330	447	51	271
Acid loam	305	364	424	496	508	64	419
LSD5%	20						
Barley grain Cd cor	ncent	ration	(µg k	g ⁻¹)			
Acid sand	38	55	65	66	82	22	61
Calcareous sand	18	31	14	24	45	16	26
Calcareous loam	18	23	21	24	44	16	26
Acid loam	38	34	37	43	46	n.s.	40
LSD _{5%}	14						
Barley straw Cd co	ncent	ration	(mg l	kg ⁻¹)			
Acid sand	0.16	0.26	0.33	0.37	0.42	0.05	0.31
Calcareous sand	0.15	0.17	0.17	0.23	0.30	0.05	0.20
Calcareous loam	0.15	0.14	0.13	0.17	0.22	0.04	0.16
Acid loam	0.24	0.26	0.26 3	0.28	0.29	n.s.	0.27
LSD5%	0.02						

n.s.: not significant

Table 5. Effect of industrial-communal sewage sludge loads on soil Cr fractions and barley grain and straw Cr concentration (total, mobilisable and plant concentrations are based on the data of Kádár and Morvai¹²)

	Load	level	(g slu	dge D.M	I. /kg	ISD.	
Soils	soil)						Mean
	0	2.5	5	10	20	%	
	Cr lo	ad, μg	g Cr/kg	g soil			
	0	4405	8810	17620	35240		
Mobile (NH4NO3	solubl	le) Cr	conce	ntration	of soil (µg/kg)	
Acid sand	5	9	12	17	18	5	12
Calcareous sand	5	6	5	8	11	2	7
Calcareous loam	8	7	5	7	6	n.s.	7
Acid loam	5	9	5	5	5	n.s.	6
LSD _{5%}	5						
Total (cc. HNO3 +	- H ₂ O ₂	2 solut	ole) Cı	concent	tration c	of soil (mg/kg)
Acid sand	11	13	15	21	27	5	17
Calcareous sand	13	16	16	22	35	11	20
Calcareous loam	36	42	47	43	58	6	45
Acid loam	50	52	65	66	77	5	62
LSD _{5%}	7						
Mobilisable (NH4	OAc +	- EDT	A solu	uble) Cr	concent	ration	of soil
(mg/kg)							
Acid sand	0.08	0.16	0.22	0.55	0.92	0.18	0.39
Calcareous sand	0.09	0.11	0.10	0.18	0.27	0.06	0.15
Calcareous loam	0.09	0.07	0.10	0.10	0.15	0.03	0.10
Acid loam	0.13	0.15	0.23	0.23	0.22	0.07	0.19
LSD _{5%}	0.09						
Barley grain Cr co	oncent	ration	(mg/k	(g)			
Acid sand	0.26	0.29	0.22	0.24	0.21	n.s.	0.24
Calcareous sand	0.35	0.26	0.34	0.21	0.27	n.s.	0.28
Calcareous loam	0.24	0.22	0.23	0.17	0.16	n.s.	0.21
Acid loam	0.17	0.15	0.17	0.18	0.21	n.s.	0.17
LSD _{5%}	0.08						
Barley straw Cr co	oncent	tration	(mg/l	kg)			
Acid sand	1.26	0.77	1.09	1.66	0.73	n.s.	1.10
Calcareous sand	0.91	0.77	1.09	1.19	1.72	0.51	1.14
Calcareous loam	1.37	0.75	0.80	0.63	0.85	0.40	0.88
Acid loam	1.06	0.80	1.06	0.76	0.84	n.s.	0.91
LSD5%	0.22						

n.s.: not significant

The regression analysis between soil element fractions and plant element concentrations involving the four soils and the five sludge loads resulted that in the case of Cd the NH_4NO_3 soluble mobile fraction is the best predictor for the plant Cd concentration. The straw Cr concentration could not be determined from the soil Cr fractions in this experiment. In the case of grain Cr concentration the total Cr fraction proved to be the best predictor. However, the grain Cr concentration did not change significantly and the equation shows negative correlation between the plant and soil Cr concentration. Thus, this connection indicates only that the total element fraction is not suitable to predict plant element content. The regression equations are the following:

 $[Cr]_{grain} = -0.002 [Cr]_{total} + 0.3 \qquad R^2 = 0.47^{**}$ (1)

 $[Cd]_{grain} = 2.51 [Cd]_{mobile} + 0.02 \qquad R^2 = 0.73^{***}$ (2)

 $[Cd]_{straw} = 9.24 [Cd]_{mobile} + 0.17$ $R^2 = 0.49^{***}$ (3)

These results reinforce the results of previous studies that showed the NH₄NO₃ soluble element fraction as a suitable predictor of plant element concentrations.^{27,28} This fact is in favour of this extraction method despite the controversies.²⁹

Comparing the concentrations in the mobile and total fraction it can be seen that only the trace of the elements added by sewage sludge appears in the mobile fraction. The ratio of two differently soluble element fractions can be defined as mobility. The mobility of an element in soil shows how soluble is the element in the soil solution ³⁰. The mobility of elements in our experiment was defined as a ratio of NH₄NO₃ extractable / pseudo total element content. The increase this value the more mobile is the given element. The mobility of an element may have a relation with the element uptake by plants. But it is necessary to consider that the plants metal content depends on plant species, physico-chemical properties of the soil, weather conditions, fertilisation, etc. Therefore plant responses to soil contamination should be always studied in a particular soil – plant system.³¹ The calculation of mobility is:

$$M = 100 \frac{\text{mobile}}{\text{pseudo total}} \tag{4}$$

where M is the mobility of a given element, "mobile" is the NH_4NO_3 extractable concentration and "pseudo total" is the result of extraction with cc. $HNO_3 + H_2O_2$ (mg kg⁻¹).

Table 6. Effect of industrial-communal sewage sludge loads on Cd and Cr mobility (Mobility = [mobile]/ [total]*100) in soil

Soils	(L g sludg	LSD5	Mean			
	0	2.5	5	10	20	%	
Mobility of Cd							
Acid sand	6.1	17.3	14.6	7.3	6.7	4.5	10.4
Calcareous sand	0.76	2.46	0.67	2.62	1.61	n.s.	1.62
Calcareous loam	0.88	0.26	0.63	0.78	0.46	n.s.	0.60
Acid loam	1.51	0.78	0.58	0.49	0.56	n.s.	0.78
LSD5%	5.04						
Mobility of Cr							
Acid sand	0.049	0.073	0.090	0.090	0.089	n.s.	0.078
Calcareous sand	0.037	0.040	0.031	0.037	0.035	n.s.	0.036
Calcareous loam	0.022	0.016	0.011	0.016	0.011	n.s.	0.015
Acid loam	0.011	0.018	0.008	0.008	0.007	n.s.	0.010
LSD _{5%}	0.024						

n.s.: not significant

Table 6 shows, that mobility of Cd is at least one order of magnitude higher than that of Cr, which is in good agreement with earlier findings also.³² The mobility has significantly maximum values in acidic sandy soil in the case of both elements. In most cases the mobility did not change in function of sludge loads. The only significant differences between treatments can be seen in the case of Cd mobility on acidic sand showing the highest mobility value at the 2.5 g sludge/kg soil load. Regarding the regression between Cd and Cr mobility and barley grain and straw concentrations only the mobility of Cd showed significant regression with the grain Cd concentration but the R^2 value

(0.40) was below that seen in the case of Eqn. 2. Based on the above facts, the mobile fraction itself proved to be a better indicator of plant Cd concentration than mobility.

Investigating the relation between the mobile fraction and the total Cd and Cr amount of the sludge loads it can be seen that in function of the increasing sludge loads the ratio of mobile fraction to the added element amount became smaller. Thus, the higher the concentration in the soil the smaller the mobile fraction compared to the total. This ratio is smaller in the case of Cr where only 0.02 % of the sludge Cr content can be found in the soil mobile Cr fraction. Since Cd is more mobile element in that case this ratio is 2.5 %.

The above results indicated that in the case of sewage sludge application on field it is important to consider not only the element contents, but also other parameters (pH, texture, organic matter), as these may influence the dissolution of contaminants.

Acknowledgement

This paper was supported by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences.

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> Received: 24.10.2012. Accepted: 26.10.2012.



EFFECT OF MICROELEMENTS ON ALFALFA ON A SANDY SOIL

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Paper was presented at the 4th International Symposium on Trace Elements in the Food Chain, Friends or Foes, 15-17 November, 2012, Visegrád, Hungary

Keywords: microelement, alfalfa, soil pollution, element composition, toxicity

The effect of 0, 30, 90 and 270 kg·ha⁻¹ rates of microelements on alfalfa was examined on a calcareous sandy soil during the year 2004 - 2008 in Őrbottyán, Hungary. The salts of the microelements were applied on a single occasion at the start of the experiment in spring 1995 in the form of $Cr_2(SO_4)_3$, $K_2Cr_2O_7$, $CuSO_4$, $Pb(NO_3)_2$, Na_2SeO_3 and $ZnSO_4$. The 24 treatments (6 elements×4 application rates) in 3 replications gave a total of 72 plots. The location was prone to drought and was poorly supplied with NPK macronutrients. The ploughed layer contained 0.7–1.0% humus and 2–3% CaCO₃, and the groundwater was located at a depth of 5–10 m. The whole experiment was given 100 kg·ha⁻¹ each of N, P₂O₅ and K₂O active ingredients as basal fertilizer each year. The favourable precipitation contributed to the advantageous development and yield of alfalfa during the 5 years period. Pb and Cu loads remained in the ploughed layer. The 0.2-0.4 mg·kg⁻¹ Pb-content of the control alfalfa hay increased to 0.5-1.4 mg·kg⁻¹ on the treated soil on average. Cu concentration rose from 5-7 mg·kg⁻¹ to 9-10 mg·kg⁻¹ due to high Cu load. Se showed an extreme 3 orders of magnitude accumulation in hay, i.e. from under 1 mg·kg⁻¹ detection limit to 200-400 mg·kg⁻¹. The hay became unsuitable for feeding. However alfalfa can be utilized in phytoremediation. During the 5 years the total yield of 45.5 t·ha⁻¹ alfalfa hay took up 6-12 kg·ha⁻¹ Se. In 2006 after the 12th year of the experiment the leaching zone of Cr(VI) exceeded 3 meters, and that of Se exceeded 4 meters in 270 kg·ha⁻¹ treatments. Vertical movement could not be verified in the case of Cr(III), Pb, Zn, Cu.

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Introduction

In a review of the health risks posed by microelements entering the food chain, the concept of the "soil-plant barrier" was introduced and microelements were classified into four groups. Group number one is comprised of the elements Ag, Cr, Sn, Y and Zr, which pose mild risks, owing to their low solubility in soil and consequently negligible uptake and translocation by plants. Elevated concentrations of these elements in foods usually indicate direct contamination by soil or dust. ^{1, 2}

Group number two includes the elements As, Hg and Pb which are strongly absorbed by plant roots, and not readily translocate to edible plant part and so pose minimum risks to human health. Group number three includes the elements B, Cu, Mn, Ni and Zn. The "soil-plant barrier" may protect the food chain from these elements, which are partly but readily taken up by plants, which are phytotoxic at concentrations that pose little risks to human health. Group number four consists of Cd, Co, Mo and Se, which pose human or animal health risks at plant tissue contents that are not generally phytotoxic.

Out of the element listed above, the elements that give most commonly risk to health concerns about food safety are the heavy metals, such as Cd, Hg and Pb together with anionic metalloids As and Se. ^{3,4}

The main sources of elevated soil As are the historically widespread use of As compounds as insecticides, herbicides and defoliants for agricultural production. These include inorganic salts and organic compounds of both arsenite As(III) and arsenate As(V). High levels of As occur naturally in some sedimentary rocks and in geothermically active areas. Feed additives for poultry and swine production can result manures with high As pool. Arsenic from phosphate fertilizers, from fossil fuel combustion and from municipal sewage sludge are considered to be significant sources of As pollution in soil. ^{5, 6, 7, 8}

When metals are added as soluble salts, they generally cause greater plant uptake and toxicity than when applied in forms such as sewage sludge or metal oxides. Metals are not in soluble forms in sludge, but fixed with organic matter binding sites or occluded in $CaCO_3$ or in other minerals. Sludge organic matter adds metal sorption capacity to the soil and raises the soil CEC and often the pH. So, the source and form of element added may strongly affect the result. This is called the "salt vs. sludge" error in experimentation for evaluating metal responses.

The 2nd error is called the "greenhouse vs. field" error. Greenhouse studies offer greater management and reproducibility, and lower cost than field studies. However, the measured element contents may be increased 2-5 fold over field measurements of the same soil and crop. In pots, the plant roots have small volume of treated soil, plants require abnormal watering. The smaller are the pots, grater are the chances of error. Plant respond differences may originate from the root distribution in the soil with depth, and can only be found correct in field studies. ^{1,4,9}

Field experiments represent the factual conditions for a given soil-plant system. They are indispensable to follow the transport of elements not only into the various crops, but also into the food chain, their downward migration, and to assess the long-term fate and effects of elements under natural circumstances.

Methods

A long-term field trial was set up at the Örbottyán Experimental Station of the Institute for Soil Science and Agricultural Chemistry (Centre for Agricultural Research, Hungarian Academy of Sciences) on calcareous sandy soil in 1994. The main characteristics of the soil are as follows: pH_(KCl) 7.0, clay content about 5%, CaCO₃ 4%, organic C 0.6%. Four levels (0, 30, 90 and 270 kg/ha) of the selected metal salts (Cr(III), Cr(VI), Cu, Pb, Se, Zn, in the form of Cr₂(SO₄)₃; K₂Cr₂O₇; CuSO₄; Pb(NO₃)₂; Na₂SeO₃; ZnSO₄, respectively) were added to the 35 m² plots once at initiation and were mixed into the 0-20 cm ploughed layer. The rates and forms of microelements applied in the experiment are shown in Table 1. The treatments were arranged in a splitplot design with triplications. The experimental plots were cultivated with commonly used agrotechnics, mineral fertilizers were added yearly (100 kg/ha N, P2O5, K2O as Ca-ammonium nitrate, superphosphate and 60% KCl) to ensure sufficient macronutrient supply. The grown crops were: carrot in 1995, pea in 1996, winter wheat in 1997, sunflower in 1998, garden sorrel in 1999, barley in 2000, rape in 2001, maize in 2002, mustard in 2003, alfalfa in 2004-2008.

Composite *soil samples* consisting of 20 subsamples were collected from the ploughed layer of each plot. Using 20-40

plants or plant parts per plot randomly, plant samples were taken from every cut of alfalfa.

 Table 1. Single rates and forms of microelements applied in the experiment in 1995 (Calcareous sandy soil, Örbottyán)

Element	Rat	es of eleme	Form of salts		
	1	2	applied		
Cr(III)	0	30	90	270	$Cr_2(SO_4)_3$
Cr(VI)	0	30	90	270	$K_2Cr_2O_7$
Cu	0	30	90	270	CuSO ₄
Pb	0	30	90	270	Pb(NO ₃) ₂
Se	0	30	90	270	Na ₂ SeO ₃
Zn	0	30	90	270	ZnSO ₄

Total number of plots: 6x4 = 24 treatment x 3 replication= 72. Size of plots: 35 m^2

The "total" amount of the elements in homogenized *soil* and plant samples were measured after microwave digestion using cc. $HNO_3+H_2O_2$. In the soil samples the so-called "mobile" fraction extracted with ammonium-acetate + EDTA ¹⁰ was also determined. The composition of prepared samples was analyzed by inductively coupled plasma spectrometry (ICP-AES) detecting 25 elements.

The sowing of alfalfa was done on 5 April 2004 with "Verkó" variety with 30 kg·ha⁻¹ seed. About the water supply of alfalfa: during the year 2004 and 2008 no extreme draught year occurred therefore the stand could thrive during 5 years. The least precipitation was a total of 466 mm in the year 2007, while highest was 619 mm in the year 2008. The average annual precipitation was 569 mm.

Number of			Yea	ars	Maan	Total	
cuts	2004	2005	2006	2007	2008	Wiean	Total
Green yield th	a ⁻¹						
1.	15	10	16	16	12	14	69
2.	7	13	12	14	10	11	56
3.	3	12	9	5	8	7	37
4.	-	10	9	-	-	4	19
Total	25	45	49	35	30	36	181
Air dry matter 9	%						
1.	22	19	20	31	32	25	-
2.	23	29	19	27	30	26	-
3.	28	25	23	34	22	27	-
4.	-	22	22	-	-	22	-
Total	24	24	21	31	28	26	-
Air dry hay yiel	d t∙ha⁻¹						
1.	3.2	1.9	3.3	4.5	3.8	3.3	16.7
2.	1.5	3.9	2.5	3.6	3.0	2.9	14.5
3.	0.8	3.1	2.3	1.7	1.8	1.9	9.7
4.	-	2.1	2.1	-	-	0.8	4.2
Total	5.5	11.0	10.2	9.8	8.6	9.0	45.1

Table 2. The average yield per cuts and years in the 10th-14th years oft he experiment (Calcareous sandy soil, Őrbottyán)

Table 3. Effect of treatments on the Cr, Pb and Cu content of the air dry hay of alfalfa in the means of the cuts (Calcareous sandy soil, Örbottyán)

Years	Rates of ele	ments in spring 1		LCD	Maan	
	0	30	90	270	LSD5%	Mean
Cr2(SO4)3 treatment, Cr mg·kg	-1					
2004	0.5	0.8	1.2	1.9	0.6	1.1
2005	0.3	0.6	0.7	0.9	0.5	0.6
2006	0.4	0.5	0.6	0.8	0.3	0.6
2007	0.3	0.4	0.6	0.7	0.3	0.5
2008	0.1	0.2	0.2	0.4	0.2	0.2
K ₂ Cr ₂ O ₇ treatment, Cr mg·kg ⁻	1					
2004	0.4	0.5	0.8	1.4	05	0.8
2005	0.6	0.6	0.8	1.0	0.4	0.8
2006	0.4	0.5	0.7	1.2	0.4	0.7
2007	0.4	0.3	0.7	1.2	0.5	0.7
2008	0.1	0.2	0.4	0.7	0.2	0.3
Pb(NO ₃) ₂ treatment, Pb mg·kg	-1					
2004	0.4	0.6	0.8	1.4	0.9	0.8
2005	0.4	0.4	0.6	0.9	0.6	0.6
2006	0.5	0.6	0.6	0.8	0.5	0.6
2007	0.2	0.3	0.5	0.5	0.4	0.4
2008	0.2	0.4	0.4	0.5	0.3	0.4
CuSO ₄ treatment, Cu mg·kg ⁻¹						
2004	5.3	7.3	8.6	9.7	2.3	7.8
2005	4.9	6.8	8.2	9.2	2.2	7.3
2006	6.7	8.6	9.4	10.4	2.8	8.8
2007	7.0	8.0	8.6	9.0	1.6	8.2
2008	6.7	7.6	8.6	9.2	1.8	8.1

Table 4. Effect of treatments on the Zn, Se and Na content of the air dry hay of alfalfa in the means of the cuts (Calcareous sandy soil, Örbottyán)

Years		Rates of element	ts in spring 1995	kg∙ha ⁻¹	LCD	Mean
	0	30	90	270	LSD5%	
ZnSO ₄ treatment, Zn mg·kg ⁻¹						
2004	19	25	28	29	8	25
2005	18	20	21	25	4	21
2006	18	20	23	29	5	23
2007	17	20	21	26	4	21
2008	21	24	28	31	5	26
Na ₂ SeO ₃ treatment, Se mg·kg	-1					
2004	<1	24	131	416	77	190
2005	<1	29	128	249	40	102
2006	<1	27	147	189	40	91
2007	<1	36	187	383	88	152
2008	<1	21	98	223	44	86
Na ₂ SeO ₃ treatment, Na mg·kg	-1					
2005	350	346	396	429	50	380
2006	386	346	451	488	56	418
2007	408	459	595	622	104	521
2008	388	532	557	706	108	546
Na ₂ SeO ₃ treatment, S %						
2004	0.36	0.45	0.59	0.66	0.10	0.52
2005	0.35	0.43	0.58	0.55	0.14	0.48
2006	0.34	0.41	0.62	0.53	0.09	0.48
2007	0.33	0.43	0.67	0.67	0.12	0.53
2008	0.24	0.30	0.44	0.43	0.08	0.35

Results and discussion

The yields of alfalfa were not affected significantly by the treatments, so data are presented only in the means of treatments by cuts and years in *Table 2*. The highest green and air dry yields were obtained in the 2^{nd} and 3^{rd} years, when the 4 cuts gave 45-49 t·ha⁻¹ green, or 10-11 t·ha⁻¹ air dry hay yield. The number of cuts, and the annual yields remained low in the 1st, 4th and 5th years. The 1st and 2nd cuts were responsible for most of the yields every year. An exceptional year was 2005, when the 2^{nd} cut gave 12 t·ha⁻¹ green mass. The air dry mass content of the alfalfa varied between 19-34% depending on the cuts and was at an average of 26%. During the 5 years the sum of the air dry hay yield was 45 t·ha⁻¹ on calcareous sandy soil.

Effect of Cr(III) treatment on the Cr content of alfalfa hay is shown in *Table 3*. The concentration of Cr rise 2-4-fold in comparison to control as an average of the years and cuts. It is well known that Cr is barely mobile in the soil-plant system. It can accumulate mainly in the root, but its transport is hindered within the plant. On calcareous chernozem soil on Cr-treated plots e.g. the shoot of the young maize contained 3 mg·kg⁻¹, while the root had 158 mg·kg⁻¹ Cr content. ¹¹

Plant samples were not washed, so external pollution cannot be excluded. The presented data series of 5 years indicate that only a small amount of Cr releases from the applied Cr(III) salt and become available for plants. The Cr accumulation of alfalfa is declining with time.

Cr accumulation of alfalfa was not significant different in Cr(VI) treatment. In this case the Cr content of the shoot is also minor. The alfalfa takes up less Cr in progress of time. However, the effect of treatment becomes relatively enhanced with the years. It is partly resulted by the fact that the water-soluble chromate form leached and accumulated in the 2-3 m soil layer in 2006. So the roots of alfalfa could reach this sphere with time.

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Table 5 Effect of frequents on the microelement	neld of alfalta in the means of the cuits l	(alcareous candy coil ()rhottyan)
Table 3. Effect of treatments on the interoclement	neid of affanta in the means of the cuts t	Calcalcous sandy son. Ononivant

Years	Rates of ele	ments in spring 1	1995, kg·ha ⁻¹		LCD	Maria
	0	30	90	270	LSD _{5%}	Mean
K ₂ Cr ₂ O ₇ treatment, Cr g·ha ⁻¹						
2004	2.8	4.4	6.6	10.4	3.3	6.0
2005	3.3	6.6	7.7	9.9	3.5	6.9
2006	4.1	5.1	6.1	8.2	3.1	5.9
2007	2.9	3.9	5.9	6.9	2.9	4.9
2008	0.9	1.7	1.7	3.4	1.7	1.9
Total:	14.0	21.7	28.0	38.8	7.9	25.6
Pb(NO ₃) ₂ treatment, Pb g·ha ⁻¹						
2004	2.2	3.3	4.4	7.7	3.0	4.4
2005	4.4	4.4	6.6	9.9	2.6	6.3
2006	5.1	6.1	6.1	8.2	2.1	6.4
2007	2.0	2.9	4.9	4.9	1.4	3.7
2008	1.7	3.4	3.4	4.3	1.2	3.2
Total:	15.4	20.1	25.4	35.0	7.4	24.0
CuSO ₄ treatment, Cu g·ha ⁻¹						
2004	29	40	47	53	13	42
2005	54	75	90	101 24	4 80	
2006	68	88	96	106	29	90
2007	69	78	84	88	16	80
2008	58	65	74	79	15	69
Total:	278	346	391	427	88	360
ZnSO ₄ treatment, Zn g·ha ⁻¹						
2004	104	138	154	160	44	139
2005	198	220	231	275	44	231
2006	184	204	235	296	51	230
2007	167	196	206	304	49	218
2008	181	206	241	267	43	224
Total:	834	964	1067	1302	174	1042
Na ₂ SeO ₃ treatment, Se kg·ha ⁻¹						
2004	<1	0.13	0.72	2.29	0.42	0.78
2005	<1	0.21	1.41	2.74	0.60	1.09
2006	<1	0.35	1.50	1.93	0.80	0.94
2007	<1	0.18	1.83	3.75	0.96	1.44
2008	<1	0.28	0.84	1.92	0.70	0.76
Total:	<1	1.15	6.30	12.63	4.40	5.01

Table 6.	Effect	of treati	nents of	n the	"total"	(cc.HNO	3+cc.H2O	2 soluble)	and	NH4 acetate+	EDTA	soluble	element	content	of th	e soil	l in
2008, mg	; kg-1 (C	Calcareo	ıs sandy	y soil,	Őrbotty	án)											

Elements	Rates of ele	ments in spring 1	1995, kg·ha ⁻¹		LSD5%	Mean
	0	30	90	270		
cc.HNO ₃ +cc.H ₂ O ₂ soluble con	itent					
Zn	22	24	28	40	6	28
¹ Cr	14	18	20	35	6	22
² Cr	11	16	18	29	6	18
Cu	4	6	13	28	5	13
Pb	10	11	14	26	5	15
Se	<1	2	3	3	2	2
NH ₄ -acetate+EDTA soluble co	ontent					
Pb	3.3	3.8	7.5	13.1	2.4	6.9
Zn	1.9	3.9	6.1	11.7	2.6	5.9
Cu	1.2	1.8	7.0	20.4	5.0	7.6
¹ Cr	< 0.1	0.1	0.2	0.4	0.2	0.2
² Cr	< 0.1	0.1	0.2	0.4	0.2	0.2
Se	< 0.1	0.1	0.2	0.4	0.2	0.2

Remark: Leaching of Cr(VI) in 2006 exceeded 3 m, while that of Se exceeded 4 m depth. In Cr(III), Pb, Zn, Cu treatments leaching could not be verifiable with NH₄-acetate+EDTA method. $^{1}Cr=Cr(III)$, $^{2}Cr=(CrVI)$

Pb is also hardly available for plants, especially on calcareous soils. Accumulation occurs mainly in roots. According to results shown in *Table 3*, concentration in shoots can increase 2-3-fold on treated plots compared to control. The average Pb content shows a decreasing trend with the years.

Table 7. NH₄-acetate+EDTA soluble element content of the 0-490 cm soil layer on the control and on the 270 kg·ha⁻¹ treated plots in 2006, in the 12th year of the experiment (Calcareous sandy soil, Örbottyán)

Sampling	Co	ntrol soil,	Trea	ted soil,
depth, cm	1	mg∙kg⁻¹	mg	·kg ⁻¹ *
	Se	Cr	Se	Cr(VI)
0-30	0.28	0.05	0.50	0.55
30-60	0.26	0.05	0.53	0.14
60-90	0.17	0.02	0.39	0.19
100-130	0.25	0.02	0.21	0.12
130-160	0.08	0.04	0.86	0.11
160-190	0.15	0.10	1.36	0.14
200-230	0.15	0.09	1.25	0.18
230-260	0.16	0.10	1.93	0.31
260-290	0.26	0.07	2.04	0.59
300-330	0.12	0.10	1.06	0.42
330-360	0.12	0.14	0.64	0.16
360-390	0.14	0.14	0.49	0.13
400-430	0.16	0.10	0.40	0.10
430-460	0.16	0.10	0.12	0.10
460-490	0.16	0.10	0.10	0.10
Mean	0.17	0.08	0.79	0.22

*The deeper soil layers were not polluted in the Pb, Cr(III), Cu, Zn treatments

In the case of copper the effects of treatments are not considerable, Cu-content of control rise usually with 40-80% due to the load. Copper is also considered as a hardly mobile element. Cu content in plant do not show extreme differences. Copper supply of 6-15 mg·kg⁻¹ in air dry alfalfa hay considered satisfactory. ¹² The applied Cu-load had a positive effect on alfalfa, as it raised its Cu content to the satisfactory level, reaching about 10 mg·kg⁻¹ values (*Table 3*). In USA, Cu-content under 10 mg·kg⁻¹ is considered as

low level, and 10-30 mg·kg⁻¹ as satisfactory level.¹³ The highest 270 kg·ha⁻¹ Zn-load resulted in only 8-10 mg·kg⁻¹ Zn-content increment on average. The minimum value was 15 mg·kg⁻¹, while the maximum was 37 mg·kg⁻¹ regarding the 1st cuts between 2004 and 2006. The other years and cuts were more settled. It is well known that Zn binds and transforms fast to less available ZnCO₃ on calcareous soil. Results shown in *Table 4* reflect this trend. Satisfactory Zn supply of alfalfa hay would be 25-70 mg·kg⁻¹ of Zn content. ¹² So the applied Zn fertilization could only ameliorate the Zn depletion of the stand, bringing it to the lower limit of the satisfactory level.

Se present extremely in hay reaching three orders of magnitude compared to control. As it is shown in *Table 4* the maximum level in plant tissue can be detected in the first year. According to deep drill soil samplings Se similarly to Cr(VI) accumulated in the 2-3 m soil layer in NH₄-acetate+EDTA soluble form. Presumably the roots of alfalfa could reach this layer and took up Se. Alfalfa is a hyper-accumulator of Se without considerable yield decrease. Se content above 1-2 mg·kg⁻¹ is physiologically undesirable in long-term. So the hay grown on treated plots cannot be utilized for feeding. Alfalfa can be suitable for phytoremediation purposes in the case of Se pollution or the pollution of deeper soil layer.

The applied Na-selenite can transform to Ca-selenate in the calcareous, well-aerated soil. Na and also the selenite form are very mobile in the soil-plant system, and cation/anion synergism can occur regarding plant uptake. According to *Table 4* Na concentration of hay rises significantly with Se load. This effect is enhanced by the years, in 2008 Na content increases with 80% on heavily Sepolluted plots compared to control. The yearly average Na content also increased with aging from 380 mg·kg⁻¹ in the 1st year to 546 mg·kg⁻¹ in the 5th year. Minimum value was 256, maximum was 883 mg·kg⁻¹ Na during the 5 years depending on the treatments and cuts. The enrichment of hay in Na could be advantageous for feeding purposes, as Na demand of animals can generally be satisfied only by grasses grown on salt-affected soils.

Se load lifted S uptake of plants. A reason for this synergistic effect could be the fact that Se together with S synthesise into amino acids. S content remains at a relatively constant 0.3% level in hay on control plots which increases to 0.6% due to high Se load, in the average of years. Extreme differences can occur as a function of cuts and years. In 2008 0.21% minimum and in 2004 0.92% maximum in the 3rd cut means more than 4-fold differences on control soil.

As a member of the oxygen group (O, S, Se, Te, Po) Se has similar characteristics to S. Se enrichment can be found at pyrite rich sites. According to Hungarian geochemical researches greater Se concentration sites are related to sulphide-mineralization. ^{14, 15} The accumulated Se in plant may cause Se toxicity in grazing animals. Se overload can be moderated by S addition in order to optimize the S/Se rate. In this case the sulphate/selenite antagonism rules and Se uptake is hindered by S-fertilization. Unfortunately Se rich soils are also well supplied by sulphate, so the ameliorative effect of S fertilization cannot develop. The satisfactory S supply of alfalfa is about 0.3-0.6%, similarly to P supply. In this experiment, Se application improved the uptake of S, therefore synergetic effect could be detected as S supply of alfalfa was moderate or poor.

Table 5 shows the microelements synthesised in the shoot of alfalfa. Uptaken volumes were Cr 14 – 39, Pb 15 – 35, Cu 278 – 427, Zn 834 – 1302 g·ha⁻¹ depending on the pollution of soils during the 5 years. Considering phytoremediation, to clean the 270 kg·ha⁻¹ load, for Pb 65 thousand years, for Cr 50 thousand years, for Cu 9060 years, for Zn 2885 years of alfalfa production would be necessary in similar conditions.

The 45 t^{-ha⁻¹} hay harvested during the 5 years contained 1.3 kg^{-ha⁻¹} Se on 30 kg^{-ha⁻¹} Se-treated plots. Thus theoretically 115 years would be necessary to clean this contamination. Similarly on 90 kg^{-ha⁻¹} Se-treated plots Se yield was 6.3 kg^{-ha⁻¹} which means 56 years of phytoremediation. So phytoremediation can be reasonable on moderately Se polluted sites.

As it is seen in *Table 6* in the year 2008, in the 14^{th} year of the experiment the effect of microelement load is strongly indicated by the "total" (cc.HNO₃+cc.H₂O₂ soluble) and the NH₄-acetate+EDTA soluble element content of the ploughed layer of the soil. A considerable part of Pb, Zn, Cu elements remained in soluble form, but Cr(VI), Cr(III), Se elements can be hardly detected in this form in the upper layer.

According to the results of 5 meters deep drill soil samplings in 2006, in the 12^{th} year of the experiment, the leaching zone of Cr(VI) exceeded the depth of 3 meters, while that of Se exceeded 4 meters. In Cr(III), Pb, Zn, Cu treatments no leaching could be detected with the NH₄-acetate+EDTA method.

The soluble contents of Se and Cr are given from every 30 cm layers on control and on 270 kg·ha⁻¹ treated plots in the examined soil profiles (*Table 7*).

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Received: 24.10. 2012. Accepted: 29.10. 2012.