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CREATIVITATEA TEHNICĂ ROMANEASCĂ LA RASCRUCE DE VÂNTURI

Ion SANDU

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1. De ce nu se mai doresc școlile de inventică?

Ca inventator cu un mare stagiou în realizarea de produse ale creației ingineresti (așa cum ne este drag nouă ieșenilor să denumim inventica), nu pot rămâne pasiv la unele acțiuni mai mult sau mai puțin conștiente ale factorilor de decizie și chiar uneori ale mass-mediei de a diminua rolul acesteia în actualul context geopolitic, oarecum nefavorabil pentru țara noastră.

Am subliniat de mai multe ori că românul s-a născut nu numai poet, ci și inventator (a se vedea interviul "*Românii sunt născuți inventatori, nu doar poeți sau artiști, mari sportivi sau olimpici*", Evenimentul de Iași, 12 Decembrie 2009). Acest "dar" dat de Bunul Dumnezeu a devenit pentru creatorii de invenții "har". Și cum spunea regretata mamă adoptivă, "ferice de cel ce dă har în dar", deci este foarte important ca inventator de profesie să fie preocupat de atragerea tinerilor spre inventică, aceasta fiind astăzi, mai mult ca oricând, o disciplină conexă, care permite neinițiaților (profanilor, dar cu gena creației în sânge), să devină inventatori. De aici ideea că inventatorii de profesie se împart în două mari grupe: inventatorii din cercetare sau producție, cu invenții aplicabile imediat, care crează prin *misiune inventivă* și respectiv inventatorii formatori din învățământ, la care scopul principal nu este atât implementarea, cât inocularea/activarea și dezvoltarea la tineri a harului de a fi creativ. Oare ce este mai prețios în viața unui profesor inventator, banii pe care îi aduce o invenție sau numărul de citări, prin care creația sa formează baza de plecare a unor noi invenții și respectiv numărul de noi inventatori formați și atrași puternic spre actul de creație. Să ne gândim, legat de ultimul aspect, cât de important este să inducem pasiune tinerilor pentru activitatea de inventică, să-i facem să descopere plăcerea de a cerceta, în actualul context al unei societăți entropice [1-4].

Foarte mulți universitari, inventatori de elită, consideră că ei au o misiune specială, și anume: aceea de a crea. "Unii creează pentru

implementare industrială, iar alții pentru știință și educația tinerilor”, consideră profesorul Dan CAȘCAVAL, decanul Facultății de Inginerie Chimică și Protecția Mediului din cadrul Universității Tehnice “Gheorghe Asachi” Iași. "Studenții inventatori sunt averea mea, pentru că la noi de pe urma invențiilor nu te poți îmbogăți, că nu are cine să îți le cumpere sau să le finanțeze pentru a intra în producție. Eu am multe medalii câștigate la Saloanele de Inventică, ceea ce reprezintă o recunoaștere a calității creațiilor mele. Cunosc mulți universitari inventatori, medaliați la marile saloane, dar puțini se pot lăuda că își aplică invențiile. Majoritatea firmelor autohtone nu privesc cu încredere invențiile românești, li se par a fi fanteziste", consideră același profesor Dan CASCVAL.

Acum vine și întrebarea: oare când să mai ai timp de implementare a unor invenții pentru industrie, când ești puternic ancorat în didactic și trebuie să elaborezi noi metode și tehnici de analiză sau de investigare, pe care trebuie să le implici în definitivarea unor cercetări sau a unor teze de doctorat. De foarte multe ori, media mă întrabă nepoliticos: care este invenția care v-a adus cei mai mulți bani și cât? Răspund retoric: câți bani poate aduce o metodă pe care o folosește doar un cercetător sau un colectiv? Răspunsul va veni după foarte mulți ani... Dinainte nu se poate spune niciodată dacă o invenție va avea sau nu succes. Ca o invenție să ajungă măcar la nivelul de prototip, este nevoie ca cercetătorul să-și aducă produsul creației sale la o anumită performanță cerută de piață.

Este cunoscut faptul că orice invenție se realizează printr-un salt inovațional și în elaborarea acestuia se parcurg de cele mai multe ori o serie de trepte care o pot duce în final la una revoluționară. Vârful scării sau a lanțului inovațional poate reprezenta o invenție performantă și, de ce nu, una revoluționară. Invenții de-a dreptul revoluționare sunt și cele generate de conexiunea lanțurilor inovaționale. Fără de acestea, anumite direcții CDI nu s-ar putea dezvolta... [5-7].

Se vorbește mult de transferul tehnologic, dar despre cum se realizează, în detrimentul cui și cât de mult este încurajat inventatorul, nu se spune nimic. De aceea scade continuu interesul pentru inventică, și dorința de a dezvolta învățământul de inventică. Sunt țări precum Japonia, Olanda, Canada, Rusia care au cursuri de Master de inventică. La noi, după 1990 nu s-au mai păstrat nici măcar cursurile opționale sau facultative de inventică, destinate anilor terminali de la facultățile de inginerie și de științe, pentru a nu mai menționa acele puține specializări de inventică, iar o propunere de acest fel este considerată în momentul actual drept neoportună și de aici întrebarea de ce?

Henri Coandă și-a dorit mult să înființeze un Centru de Gândire Românească. Alții au venit cu ideea ca România să fie gazda unei

Olimpiade Internaționale de Inventică „Henri Coandă” și solicitau ca un grup de oameni de știință și inventatori să facă lobby la Guvern pentru implementarea acestui proiect. Eu găsesc încă neoportună perioada, din cauza crizei actuale. Mai există o experiență asemănătoare, de cheltuire a banilor când nu existau prea mulți, în detrimentul altor activități mai stringente și anume: invitarea tinerilor performeri din diasporă pentru etalarea rezultatelor la București pe cheltuiala statului, care s-a finalizat fără urmări deosebite pentru cercetarea românească. Mult mai important este să se reînființeze școlile de inventică din universitățile tehnice și cele cu facultăți de științe sau măcar să activăm cercuri de inventică la nivel de liceu. Apoi, să se sprijine organizarea unor saloane de invenție de talia celor internaționale, care să stimuleze relansarea inventicii românești.

Dacă Târgul de Inventică de la Geneva este Mecca inventicii mondiale, de ce nu s-ar putea cu sprijinul statului și EUROINVENT-ul de la Iași să devină Meca inventicii europene.

2. Care este cauza scăderii numărului de invenții autohtone?

În prezent, în România foarte puține firme mari absorb invenții, doar un segment dintre firmele mici private, care au angajați cu misiune inventivă. Soluția este ca inventatorii să-și deschidă propriile firme pentru a-și materializa creațiile tehnice, dar câți inventatori reușesc?

O alternativă ar fi fondurile europene, însă accesarea acestora este îngreuiată de multă birocrație. Fondurile europene funcționează după un principiu care este greu de atins de un inventator. Acesta trebuie să facă mai întâi toate cheltuielile și apoi Uniunea Europeană să le deconteze. După un calcul aproximativ ar fi nevoie de minimum 50 de mii de Euro pentru a începe o astfel de afacere, ca apoi să faci decontările, dar de unde să iei inițial acești bani?

Statul ar trebui să ofere facilități fiscale firmelor care transformă invențiile în produse de serie, aceasta ar fi o mare încurajare a progresului tehnologic.

Producția de invenții după Revoluție a scăzut drastic. Înainte de 1989, în țara noastră existau 90.000 de cercetători și universitari care înregistrau la OSIM cca. 6500-7000 de cereri de brevete pe an. În anul 2008, OSIM-ul a eliberat mai puțin de 600 de brevete, deci numărul lor a scăzut de peste zece ori. Prin amendarea în timp a Legii protecției invențiilor [8, 9] și reducerea cuantumului taxelor de brevetare și protecție, după 2008, s-a resimțit o învioreare a numărului de înregistrări.

Dacă cererile de înregistrare de mărci s-au triplat în ultimii zece ani, solicitările de brevetare de invenții au scăzut foarte mult, atingând un minim

inacceptabil pentru potențialul României între anii 1994-2005, după care în ultimii trei ani s-a resimțit o revigorare. Cauza principală o regăsim în regresul tuturor activităților de cercetare-dezvoltare-inovare. Directorul general al OSIM, Gabor VARGA, spunea într-un interviu online: „Acest fapt este o oglindă fidelă a industriei autohtone, care ține de evoluția economiei, ce este strâns legată de cea a cercetării“. El a explicat că institutele de cercetare din partea cărora trebuie să vină cererile de brevetare și-au redus activitatea, în timp ce spiritul comerciant, reflectat de „explozia“ mărcilor românești, care ies pe piață, este în plin avânt.

În ultimii 20 de ani, firmele din industria autohtonă nu au acordat importanța cuvenită activităților CDI, în contextul în care, în alte țări cu o economie în ascensiune, concurența pe inventică în zona privată este foarte puternică. Un alt paradox este că, în România, majoritatea cererilor pentru brevete de invenții aparțin persoanelor fizice care nu au resurse financiare sau tehnice pentru a le aplica. Din cele 1.100 de cereri de brevete din 2010, doar 25% vin din partea firmelor și instituțiilor de cercetare. Conducerea OSIM-ului estimează că, la ora actuală, potențialul real al economiei românești este de 1.500-1.600 cereri de brevetare pe an. În schimb, numărul cererilor de protejare a mărcilor noi a crescut exponențial în ultimii 20 de ani, acesta ajungând la aproape 23.000 în 2005. „Aderarea României la UE este un moment în care marca trebuie să-și depășească funcția economică la nivel național și să capete putere pe piața comunitară“, sublinia în același interviu Ștefan COCOȘ, șeful Serviciului Mărci de la OSIM, adăugând că legislația românească în domeniu va fi schimbată, pentru a corespunde celei din UE. Dezavantajele sistemului național actual în privința protecției mărcilor ar fi posibilitatea înregistrării așa-ziselor „mărci de blocaj“, sau a indisponibilizării unor mărci de către firme care nu mai există în Registrul Comertului și care sunt trecute în evidențele OSIM-ului ca mărci în vigoare. În legislația comunitară, dacă titularul mărcii nu o folosește vreme de 5 ani de la data înregistrării, decade din dreptul de proprietate asupra acesteia. Mai mult, la OSIM acum nu se pot înregistra mărci olfactive, holograme sau alte semne distinctive neconvenționale folosite în UE.

Dacă certificatul de înregistrare a unei mărci durează 7 luni, brevetarea unei invenții durează între 2 ani la urgență și 4 ani normal, iar din propria mea experiență, această perioadă era prelungită de multe ori nejustificat la 5 și chiar 6 ani. În majoritatea țărilor, brevetarea durează între un an și un an și jumătate. Ce valoare mai are o invenție brevetată după 4 ani? Mai mult, în cei patru ani de analiză se percepe taxă de protecție, pentru ce? [1-4].

La întrebarea: "Care este inventatorul contemporan cu cele mai multe brevete înregistrate la OSIM?", Florin POPA, purtător de cuvânt al OSIM-

ului, în același interviu difuzat online, a răspuns: „Din datele conținute în bazele noastre, numele cel mai des întâlnit în calitate de inventator este al prof. univ. dr. ing. Dorel CERNOMAZU, de la Universitatea „Ștefan cel Mare” din Suceava, care are brevetate în calitate de autor și coautor un număr de peste 200 de invenții, dar mai sunt încă trei inventatori români care au depășit de mult numărul de 100 de brevete de invenție acordate de OSIM”. Dintre aceștia, doi aparțin Iașului, centrul invenției naționale.

Referitor la invenții, după cum am subliniat de nenumărate ori în ultimii 20 de ani, acestea ar trebui să fie apărute diferențiat pe cele două tipuri de proprietăți: *intelectuală*, al cărei drept revendică gradul absolut de nouitate prin *brevetul de invenție* sau *certificatul de autor*, cum a fost înainte de 1989 și *industrială*, reprezentată prin *patent* sau *licența de aplicare*, care apără dreptul titularului asupra utilizării invenției respective pe o perioadă și într-un areal geografic. Proprietatea intelectuală face ca invenția să nu mai poată fi re-brevetată, chiar și atunci când iese de sub protecția industrială. Se știe că, invențiile neprotejate sau cele brevetate care din lipsă de resurse financiare pentru implementare sau exploatare ies de sub protecție, intră în *fondul public* și pot oricând forma baza de plecare pentru alte invenții, rămânând potențiale generatoare de idei [1-4, 10-12].

O problemă delicată este cea legată de *protecția industrială*, când ne referim la perioada și arealul de exploatare, aici sunt multe rezerve în ceea ce privește implicațiile juridice privind utilizarea ilicită a unei invenții și modul cum se soluționează prejudiciul adus autorului. Am în minte acum povestea inginerului român Ion BASGAN, a cărei invenție, brevetată mai întâi în România (RO22789/18.05.1934) și re-brevetată (???) în Statele Unite ale Americii cu trei ani mai târziu (1937), unde a fost aplicată de către marile trusturi petroliere, până după al Doilea Război Mondial. Tot în acea perioadă, BASGAN a aflat că tehnologia realizată de el a ajuns, pe căi oculte, și la ruși, care au folosit-o gratuit în exploatarea petroliere din regiunea Baku. Conform brevetului înregistrat în SUA, dreptul de proprietate acordat lui BASGAN ar fi trebuit să fie valabil până în 1954. Pus în imposibilitatea de a beneficia de acest drept, după „confiscarea” invenției sale, inginerul BASGAN a început o luptă crâncenă pentru recuperarea banilor la care avea dreptul și care după lungi procese (118 la număr - n.a.), cu cele mai importante filiale ale Standard Oil Company, Gulf Oil Company, Shel Oil Corporation și multe altele, nu a obținut nimic. Toate aceste companii s-au folosit cu mare succes de invenția lui și ar fi trebuit să-i plătească drepturi de autor în valoare de 8,634 miliarde de dolari. Trusturile petroliere americane au folosit diverse tertipuri pentru a nu plăti, printre care și documente false (un certificat de deces al autorului, în timp ce acesta era încă în viață) sau faptul că patentul nu era

inclus pe lista bunurilor restituite în 1948 României (care la sfârșitul celui de al Doilea Război Mondial nu era considerată printre țările beligerante), brevetul lui Ion BASGAN fiind atunci considerat rechiziționat de statul american. În 1967, în cursul unei conferințe de presă care a avut loc la Londra, un petrolist din Dallas l-a avertizat pe BASGAN: „Ne vom judeca zeci de ani și apoi și cu fiii dumitale, dar nu plătim“.

La 15 octombrie 1965, Departamentul de Stat al Justiției SUA a emis „Divertising Order SA 838“, prin care s-a dispus scoaterea de sub sechestrul a brevetului și restituirea lui titularului, care era astfel repus în toate drepturile. În actul de atribuire semnat de Anthony L. MONDELOR, în numele Procurorului General al SUA, se menționa că inventatorului i se acordau „drepturile, titlurile și interesele, inclusiv drepturile de autor acumulate și toate profiturile recuperabile prin lege“. O expertiză financiară efectuată de grupul german Lomen-Reiter-Dresner Bank, în 1966, demonstra că, pentru cei 17 ani în care a fost titularul brevetului invenției sale, lui Ion Basgan i se cuveneau 8,634 miliarde de dolari. Ion Basgan a murit în 1980, fără să fi apucat să scoată vreun ban de la americani. Lupta lui a fost reluată după 1990 de urmașii săi, constituiți într-o fundație care îi poartă numele. O nouă expertiză financiară, făcută în 1998, la Zürich, a demonstrat că dobânzile acumulate în contul celor 8,6 miliarde de dolari inițiali ridică valoarea actuală a sumei datorate post-mortem inventatorului român la fabuloasa valoare de 165 miliarde de dolari. Bani pe care, evident, nu-i va mai achita nimeni, niciodată [1-4, 10-12].

Istoria noastră vine cu foarte multe exemple de genii ale românilor care nu și-au putut aplica ideile la noi. La exportul de inteligență autohtonă, România este pe primul loc în lume. NASA este plină de specialiști români, iar la Microsoft a doua limbă vorbită este româna. De ani buni, premiile de la saloanele internaționale de invenție sunt acordate românilor, în proporție de până la 25%, perioadă în care finanțarea cercetării românești s-a diminuat până spre desființare. Și din acest punct de vedere suntem unici în lume.

O întrebare foarte sugestivă pentru clasa politică, pusă de curând de Senatorul și profesorul ieșean Dumitru OPREA: câte dintre invențiile prezentate la marile saloane mondiale de invenții au fost rezultatul unor proiecte finanțate din bugetul de stat și ce programe sau linii de finanțare s-au constituit pentru a sprijini transferul acestor invenții în practică?

Mediul politic național și european trebuie să susțină mai mult inovarea, mai ales ținând cont de faptul că până în 2020 fiecare stat membru trebuie să aloce trei la sută din PIB pentru investițiile în cercetare-dezvoltare-inovare.

Deși cercetarea românească are unul dintre cele mai mici bugete la nivel european, totuși românii contribuie din plin la realizarea celui mai important obiectiv al Uniunii Europene: *creșterea economică inteligentă*, iar premiile cu care se întorc de la marele saloane și expoziții de invenție au întregit o performanță care are darul de a contura imaginea unei Româнии mai puțin cunoscută peste granițe. O imagine care vorbește despre oameni creativi, care schimbă mersul lumii și scurtează la maxim drumul spre viitor. O imagine a unor oameni tenaci la modul absolut, care resping întotdeauna ideea tentantă că există lucruri imposibile. Mai mult, la aceste manifestări se realizează o serie de întâlniri între inventatorii români, reprezentând companii private, universități, institute de cercetare și inventatori persoane fizice și diverse entități străine, interesate în preluarea ca titulari a unor invenții autohtone [20-22].

Un alt factor principal care a condus la reducerea ratei de brevetare din țara noastră o reprezintă scăderea nivelului de pregătire din școli și desființarea cursurilor de invenție.

Răspunsul la întrebarea: cum de s-a ajuns în aceasta situație? Ni-l dă profesorul Dan UNGUREANU în eseuul său prezentat online: „*În marginea fostei dezbateri despre învățământul din România*”.

Parcurgând firul principalelor etape din învățământul nostru superior de după Revoluție (1990 – apariția de noi universități și diversificarea exagerată a specializărilor, 1994 - reducerea bugetelor pentru activități didactice și de cercetare, 1995 - introducerea locurilor cu taxă în universități, 1998-2004 - suprimarea concursului de admitere etc.), se poate afla ușor principala cauză. Universitățile au dat de gustul banilor, iar studenții au devenit intangibili. De vreme ce plăteau, prezenți sau nu, trebuiau să fie promovați și să dobândească cât mai ușor diplome. După absolvire, mulți au intrat în învățământ, titulari sau suplinitori, devenind „modele”. Primii studenți pe bani, cum spune prof. Ungureanu, au absolvit prin 2000. Primii lor elevi au terminat liceul prin 2004. După implementarea programului Bologna, studenții au terminat facultatea în trei ani în loc de patru sau cinci, cu lucrări de licență de șaiszeci de pagini, nu de o sută sau două sute. În ultimii ani, lucrările de diplomă „scurte” pot fi cumpărate sau descărcate contra cost de pe Internet, de pe site-uri specializate (cu o sută de lei bucata). Așa s-a ajuns că astăzi să fie foarte mulți absolvenți care devin doar profesori suplinitori, iar elevii lor să fie tot mai prost pregătiți. Paradoxal totuși, spune prof. Ungureanu, se face mai multă școală la liceu decât în universități, la liceu, elevii care nu învață pot rămâne repetenți, fiindcă liceul e gratuit, iar profesorii nu sunt plătiți după numărul de elevi. Apoi, o mare vină o are actualul învățământ axat pe competențe. În noul sistem, elevii și studenții nu mai aprofundează noțiuni-cunoștințe, ci

dobândesc competențe. Întrădeavăr, există o serie de discipline axate pe competențe sau abilități, cum ar fi cele de creație (desenul, pictura, sculptura, muzica, inventica etc.) sau limbile străine, dar majoritatea disciplinelor sunt bazate pe cunoștințe (matematica, fizica, chimia, botanica, zoologia, anatomia, geologia, istoria, geografia, psihologia, sociologia etc.). Este adevărat că și unele dintre materiile din urmă au un oarecare grad bazat pe competențe, care sunt complementare cunoștințelor. Cultura generală e alcătuită în cea mai mare parte pe cunoștințe. Educația axată numai pe competențe reduce sau limitează nivelul de formare a unei culturi generale. Chiar și în inventică trebuie să existe o coroborare strânsă între cele două tipuri de învățare.

Pentru a stopa scăderea continuă a nivelului de pregătire a absolvenților, trebuie să se revină la învățământul superior gratuit, cu admitere și cu specializări limitate în acord cu cerințele și perspectivele locurilor de muncă. Apoi, în universități trebuie să se introducă sistemul concurențial de stimulare, prin care cadrele didactice și cercetătorii să fie periodic evaluați în baza unor grile competitive, unanim acceptate în lume. Cum s-ar putea explica de ce Israelul, țară mică, cât suprafața Moldovei, are trei universități pe locurile 102, 114 și 132 din lume sau multe alte exemple: Universitatea Carolina din Praga pe locul 230, Universitatea Jagelonă din Cracovia pe locul 302, Universitatea Ben Gurion, din deșertul Neghev pe locul 323, Universitățile din Liubliana, Eötvös-Lorand din Budapesta și cea din Szeged (oraș cu populație de numai 166 000 locuitori) pe locul 400, pe când la noi doar Universitatea din București este clasată pe locul 500, lângă Universitatea Kwazulu din Africa de Sud sau universitățile din Bangladesh, Kazahstan și Sri Lanka.

Problema universităților din România nu este să ajungă din urmă cine știe ce universități din vest ci, să se introducă norme și reguli stabile, mult folosite de cele mai performante universități din lume, iar finanțarea acestora să se facă pe baza rezultatelor obținute, să se limiteze specializările la cerințele pieții muncii, să se aplice și pentru universitățile particulare aceleași nivele minime de performanță în educație și cercetare, valabile pentru universitățile de stat și altele.

3. Profilul profesorului inventator pe care mi l-am dorit

Un inventator de profesie, aflat sub zodia performanței, abordează imediat și se înscrie rapid în lupta sa pentru nou, bine, util, pe tematici moderne solicitate de piață și de ce nu, de viață. Inventatorul, ca om, este legat de social, de piața muncii și este stimulat de recunoașterea rezultatelor sale. Pentru asta, el trebuie să fie actual, bine integrat profesional, să

stăpânească și să controleze ariile cunoașterii, să folosească optim bazele de date ale sistemelor tehnice informative, să fie flexibil, dinamic, cu o mare capacitate de aprofundare, abstractizare și concretizare. De fapt, inventatorul care se respectă este omul de știință care face cercetare fundamentală, dar care, în plus, aplică cercetarea fundamentală la noile cerințe tehnologice. Altfel spus, cum îi place marelui nostru profesor Vitalie BELOUSOV, „inventatorul cunoaște, aplică, conduce și creează tehnică”. Majoritatea invențiilor universitarilor au și o latură a cercetării fundamentale, foarte multe stând la baza unor noi efecte interdisciplinare, recunoscute în literatura de specialitate. Este adevărat că în universități se creează știința, iar în industrie și în centrele de cercetare de profil – tehnologiile, dar acest lucru nu poate fi generalizat. A rupe cercetarea fundamentală din universități de aplicația tehnologică înseamnă a nu oferi cadrul optim de formare a viitorilor specialiști.

Repet, recunoașterea stimulează continuu apetitul pentru creativitatea tehnică. Tăria sau puterea de creativitate fac parte din potențialul fiecărui individ. Inventatorul se naște cu o zestre ereditară, dar capacitatea lui de creație este și rezultatul activității lui de informare-formare, inventica fiind o disciplină care se învață, mai mult, este o știință conexă, de graniță, care dă mari șanse, mai ales celor tineri.

Format la Școala distinsului profesor emerit Vitalie BELOUSOV, de-a lungul celor peste 35 de ani de cercetare și învățământ superior, am elaborat foarte multe invenții, unele în baza unor contracte de cercetare, altele din necesități didactice sau din simpla atracție față de un domeniu. Mă mândresc cu peste 400 de inventatori formați care îmi poartă amprenta în instituții mari din lume. Din cele peste 150 de invenții, 103 sunt prezentate în baze de date internaționale - ISI Thomson prin Derwent Innovation Index, Espace@net, Academic.google etc. Interesant este că multe dintre invențiile mele sunt citate de către alte invenții străine, formând baza stadiului actual al cunoașterii, mai mult, unele sunt citate de autori străini în lucrări publicate în reviste ISI. Aceasta, pentru un profesor universitar, după cum am mai spus, este mai important decât banii pe care ar trebui să-i primescă din aplicare și chiar decât premiile. Fiind un inventator productiv, asemănător multora din școala ieșeană de inventică, aș folosi cuvântul prozaic "harnic" și înainte de '89 și după, am avut o rată de brevetare de invidiat. Bineînțeles că munca mea a fost răsplătită la marile saloane și expoziții internaționale pe măsură: peste 190 medalii de aur, 100 de argint și 60 de bronz, alături de foarte multe ordine, distincții, diplome și premii (cca. 95). În ultimii 10 ani, nu am acumulat niciodată la sfârșit de an sub 30 de medalii. Inventica mi-a dat o șansă să fiu eu însumi, inventatorul profesor, recunoscut și agreat ca membru în asociații profesionale, academii, cluburi sau jurii internaționale.

De două ori am primit înaltul titlu de Doctor Honoris Cauza (New York 1999 și Sofia 2006) și tot de două ori Oscarul Inventicii „ARCHIMEDES de Aur” la Moscova (2004 și 2006).

Foarte multe dintre invențiile mele au generat sau dezvoltat idei noi sau au permis descoperirea unor efecte interdisciplinare și, bineînțeles mi-au adus recunoașteri internaționale. Sunt purtătorul Ordinului Inventiv în grad de Cavaler (2001), Ofițer (2003), Comandor (2005) și Mare Ofițer (2007), conferit de Camera Belgiană a Inventatorului, al Ordinului Star Odin, Run și cel Reflexiv al Școlii Superioare din Sevastopol, laureat al ICEPEC și altele.

Palmaresul realizat de-a lungul anilor la marile confruntări internaționale l-am resimțit în speranțele studenților mei, în perspectiva lor de dezvoltare profesională.

Pentru un profesor inventator, conducător de doctorat, cea mai importantă invenție este cea care dă o șansă doctoranzilor săi să dezvolte o temă de cercetare. Am aplicat acest demers și la doctoranzii străini, pe care i-am condus în cadrul Școlii Doctorale Europene EPISCON (European PhD in Science for Conservation), cu sediul la Universitatea de Studii din Bologna, la care Universitatea Cuza este parteneră și unde am format doi mesageri ai științei și tehnicii românești, Mikiko HAYASHI de la Ministerul Bunurilor Culturale de la Tokio și Marta QUARANTA de la Univestitatea din Liubliana. Cu cele două am elaborat foarte multe metode și tehnici de investigare științifică a operelor de artă, utilizate în autentificare și datare. O invenție aparte am realizat-o cu doctoranda Mikiko HAYASHI, care constă într-o nouă metodă de determinare a domeniului normal de variație a echilibrului hidric pentru lemnul vechi și care i-a permis să evalueze impactul unor tratamente de preservare și restaurare a picturilor vechi pe suport de lemn, invenție care, în plus, permite stabilirea unor caracteristici arheometrice implicate în autentificare. Aceste metode noi nu aduc bani, dar contribuie la dezvoltarea activităților de cercetare și aduc imagine universității și cercetării românești.

De asemenea, ca președinte al Forumului Inventatorilor Români, am avut bucuria să cunosc și să stimulez foarte mulți tineri inventatori, pe care i-am promovat atât la saloanele naționale, cât și la cele internaționale. De fapt, aceasta este o mare dorință, ca profesor, să promovez astfel de talente.

Pentru cei pe care natura i-a înzestrat cu talentul creației, le-aș spune despre creativitate, de orice natură ar fi ea, că dă autorului o șansă unică, cea de a fi el însuși, de a atinge fericirea unei vieți aparte, după cum spunea sculptorul francez Rodin: "viața creatorului e cea mai frumoasă, pentru ca își vede evoluția creației sale". Tânărul născut sub "zodia performanței" sigur va avea șansa să-și atingă excelența și creativitatea lui să nu rămână înțepenită într-o formă amorfă. El trebuie să aibă încredere în steaua lui

norocoasă, dar să nu înceteze să-și dezvolte calitățile și să se străduiască continuu să atingă perfecțiunea în tot ceea ce face. Să-și desăvârșească o profesie, să alege calea prin care să aibă posibilitatea să fie creativ și neaparat să parcurgă toate treptele de formare, mai întâi ca specialist, apoi ca expert. Să se apropie de mentori, de marii inventatori, de marii învățați, de școlile de invenție, să învețe din experiențele lor.

Pentru inventatorul profesor universitar activitatea de creație, datorită muncii cu discipolii, este foarte tumultuoasă și deosebit de frumoasă. După cum am mai spus, recunoașterea profesorului pe plan mondial dă o șansă discipolului de a se plasa în perspectivă pe piața muncii. Pentru inventatorul de profesie, să se realizeze în România este destul greu. Este cunoscut de-a lungul istoriei că marii creatori români și-au desăvârșit opera în instituții străine. Astăzi, mai mult ca oricând, asistăm neputincioși la un exod mare de tineri creatori spre alte meleaguri. După 1990, politicul nu s-a interesat deloc de stimularea creativității, iar dacă a făcut-o, a fost formal, doar înainte de alegeri. Trebuiau să treacă mulți ani să se demonstreze că OSIM-ul a dus o politică împotriva activității de invenție și a diminuat șansele școlilor naționale de invenție. Din perspectiva guvernărilor de după 1990 s-au promis multe, dar s-au făcut foarte puține lucruri și acelea nesemnificative. De obicei, primesc onoruri sau sunt promovați spre sisteme de premiere administratorii instituțiilor, unii arondați politic, care nu respectă principiile și deontologia academică de evaluare și comensurare reală. Se dau premii pe care le împart între ei. Se dau ordine prezidențiale sau de stat doar lor (a se vedea Ordinele Naționale date în anul 2006, care le-au primit, în unele universități din România, doar rectorul, prorectorii și decanii!!!). Cei care au producție științifică și scriu cu adevărat istorie rămân cu fapta lor și de cele mai multe ori trăiesc într-un anonim impus, dar cu trecerea timpului, când nu vor mai fi, vor fi redescoperiți. Așa e la români.

De fapt, instituțiile statului mimează sprijinul acordat inventatorilor. Un exemplu, la marile saloane de la Geneva și Bruxelles, care sunt cele mai costisitoare, merg invenții selectate nu tocmai riguros de așa-zisa comisie națională de evaluare, formată din membri care nu au nimic cu invenția, dar cu echipe mari de excursioniști din ministere și cu câțiva inventatori, care merg pe banii lor.

4. Modalități de stimulare a activității de invenție din țara noastră

În prezent, asistăm la dezvoltarea unei societăți și bineînțeles a unei economii bazate pe *informație* și *comunicare*, în care gradul de implementare în practică a ideilor noi reprezintă factorul cheie. Un bun

management al cunoașterii va permite obținerea de *capital intelectual*, care își va pune amprenta asupra creației de bunuri tangibile și intangibile de mare valoare, respectiv asupra implementării acestora, astfel cunoștințele putând fi transformate în *venit*. În paralel, în activitatea de cercetare și de producție s-a impus un nou stil de conducere, prin trecerea de la atitudinea individualistă, la munca în echipă, respectiv la schimbarea *competiției* cu *coparticipația* (parteneriatul) [3-4].

Este necesar deci, ca în orice organizație economică, de stat sau privată, să se creeze o nouă mentalitate, iar la formarea acesteia, un rol important îl va juca valorificarea rezultatelor activității CDI individuale sau colective, prin recunoașterea obiectivă a valorii reale a rezultatelor și a competențelor cercetătorilor și inventatorilor.

Unul din obiectivele actuale ale politicii naționale de integrare europeană, în care România este un partener credibil, o reprezintă o rată economică în ascensiune, bazată îndeosebi pe inovare, prin valorificarea potențialului său creativ și care să devină o sursă reală de dezvoltare durabilă prin sisteme coerente de motivare a cercetării științifice și tehnologice.

Cu toate că, după anul 1992, inventatorii români s-au întors de la marile saloane și expoziții mondiale de invenții cu multe medalii, distincții, ordine, premii și diplome, care demonstrează existența în România a unui bogat potențial creativ, rata slabă a implementării invențiilor românești în industria autohtonă poate fi cauzată atât de clauzele juridice cu caracter general, referitoare la drepturile de valorificare a bunurilor tangibile și intangibile create, cât și de faptul că în rândul cercetătorilor și al inventatorilor nu s-a format încă un curent de opinie de negociator, specific unei economii de piață capitaliste [3-4].

Se simte tot mai mult nevoia elaborării unui **ghid de valorificare a rezultatelor activității creative**, care să ofere cercetătorilor, inventatorilor și tuturor creatorilor de bunuri materiale în general, posibilitatea de a cunoaște căile potențiale de implementare a noilor soluții tehnice obținute și care să prezinte strategii manageriale în domeniul protecției proprietății intelectuale și industriale în vederea punerii în valoare a capitalului intelectual. Aceste strategii trebuie să permită stabilirea unor modalități de negociere privind includerea în contractul de muncă a clauzelor care să asigure recunoașterea și stimularea reală a activităților creativ-productive și respectiv să favorizeze un climat optim de co-parteneriat în cadrul organizației.

De asemenea, în cadrul oficiilor de brevetare și patentare, în școlile și centrele de inventică, în tehnopolisuri și pe platformele de transfer tehnologic, trebuie să se uziteze des **sistemele criteriale de evaluare patrimonială** (impactul sau valoarea științifică, tehnică, economică, socială

etc.), folosind elemente de analiză *bibliometrică* și *scientometrică*. În prezent, asistăm tot mai des la evaluarea oamenilor de știință și a lucrărilor acestora prin sistemele scientometrice, tip “autor citat”. Puțini știu că invențiile sunt citate de către Institutul American de Scientometrie ISI – Thomson, prin subsistemul Derwent Innovation Index. Cu reget trebuie să subliniez faptul că invențiile românești nu figurează citate de alte invenții românești și nici auto-citate, doar un număr restrâns, cele care au trezit un interes aparte, sunt citate de invenții străine. Neajunsul îl regăsim în modul neadecvat de publicare de către OSIM în limba engleză a acestora în BOPI, unde alături de titlu, autori, număr de brevet și de cerere, cu datele înregistrării lor și a rezumatului, ar trebui să fie și referințele bibliografice (invenții, articole științifice, monografii, tratate etc.), citate de autor și separat citate de referent. Acest mod de abordare ar pune în valoare atât inventatorul, cât și exigența referentului. Pentru un autor, numărul de invenții brevetează nu spune mare lucru legat de valoare, ci numărul invențiilor implementate, care aduc capital și a celor citate, care sunt utilizate ca bază de date, generatoare de alte soluții tehnice.

Un alt sistem, care are un rol primordial în stimularea activităților CDI, îl constituie înființarea și dezvoltarea Școlilor de Inventică (Bazele creativității ingineresti), îndeosebi a școlilor interdisciplinare sau transuniversitare de Master și Doctorat, competitive la nivel european. Un rol aparte, în cadrul acestor școli, îl va juca cercetarea științifică prin aportul unor inventologi recunoscuți ca universitari de seamă sau prin parteneri cu experiențe dovedite în domeniul inventicii sau al managementului activităților CDI din cadrul unor instituții de cercetare cu o bogată tradiție și rezultate deosebite în domeniu [6 – 19].

De la înființarea Forumului Inventatorilor Români – asociație profesională de dialog și reprezentare, membri ei au ridicat o serie de aspecte menite să permită stimularea activităților de inventică din țara noastră. Dintre acestea, menționăm:

- Organizarea și dezvoltarea prin programe naționale și europene a specializărilor interdisciplinare și transuniversitare de inventică la nivel de Master, care ar reactiva și stimula școlile de inventică;

- Realizarea unui cadru adecvat privind premiarea invențiilor prin CNCISIS (actualul sistem nu permite stimularea tuturor inventatorilor români, deoarece sunt luate în discuție doar invențiile cu titulari - instituții din România și nu cele cu titulari - autori sau cele brevetează în străinătate, în baza unor colaborări, la care titular este o instituție străină, ultimul caz fiind similar cu cel al lucrărilor publicate în străinătate, la care sunt coautori și din România);

- Sistemul de evaluare a invențiilor care participă prin ANCS la saloanele și expozițiile mondiale ar trebui să implice anumite criterii de evaluare, iar în Comisia 12 (Comisia pentru Manifestări Științifice și Expoziționale a Colegiului Consultativ pentru Cercetare-Dezvoltare și Inovare al Autorității Naționale pentru Cercetare Științifică) să fie admiși pe lângă oameni de știință reprezentativi din cercetarea românească, universitari inventatori de elită și inventatori de profesie cu peste 50 de invenții brevetate și minimum 10 aplicate, care să conceapă și să stabilească normele de evaluare în urma consultării cu asociațiile profesionale ale inventatorilor din România;

- Implicarea profesorilor de inventică și a asociațiilor profesionale ale inventatorilor în comisiile de evaluare pentru premiere sau pentru participarea la manifestări științifice;

- Stimularea participării inventatorilor la confruntări internaționale prin finanțarea unor astfel de mobilități (consider nedrept ca la un mare salon mondial de invenții să lipsească inventatorii români, acestea având același suport de comuniune și emulație ca orice altă manifestare științifică, mă refer și la alte mari saloane mondiale, diferite de cele două, Geneva și Bruxelles, frecventate anual de România);

- Invențiile trebuie comensurate diferențiat, ca taxe de brevetare, pe cele trei categorii, invenții ale inventatorilor artizani (particulari), cele realizate prin contract cu misiune inventivă și cele cesionate titularului, dar și în funcție de valoarea patrimonială. Nu se pot plăti aceleași taxe pentru o metodă de laborator care rezolvă un segment dintr-o elaborare/cercetare, cu una care realizează un produs industrial foarte eficient și cu valoare mare;

- Invenția este valoroasă prin câți bani aduce, dar și prin numărul de citări, care stau la baza stadiului actual al altor invenții (aici aș aminti invenții de mare valoare conceptuală, neimplementate încă, dar care deschid noi direcții de cercetare), aceste invenții ar trebui păstrate sub protecție;

- Într-un lanț inovațional este foarte important să se breveteze toate invențiile și nu ultima, cea revoluționară, evitându-se astfel implementarea ilicită a unei trepte inferioare, studiată de autor;

- Nu este nevoie ca o invenție odată **brevetată** într-o țară să fie re-brevetată în altă țară, ci în urma unui transfer tehnologic să se acorde licența de aplicare – **Patentul**.

5. Stimularea creativității tehnice în unele universități și institute de cercetare

Există în România un grup de universități, amintesc aici în primul rând Universitatea Tehnică „Gheorghe Asachi” din Iași, Universitatea

Tehnică din Cluj și nu în ultimul rând Universitatea „Ștefan cel Mare” din Suceava, ai căror rectori sunt inventatori puternici. Este vorba de profesorii Ion GIURMA, Radu MUNTEANU și Adrian GRAUR, care anual sunt într-o competiție foarte strânsă. Dacă mulți ani Iașul era pe primul loc datorită Universității Tehnice și Institutului „Petru Poni”, în ultimii doi ani pe locul I s-a situat Universitatea din Suceava. Meritul aparține domnului profesor Adrian GRAUR și grupului numeros de inventatori de performanță de aici, din care se detașează vrednicul de laudă prof.dr.ing. Dorel CEORNOMAZU, cu peste 200 de invenții, la multe singur autor. De fapt, doresc să subliniez că domnul Rector Adrian GRAUR, după cum circulă zvonul, ar fi găsit „cheia Pandorei” și anume, la evaluarea universităților prin IC6, cota primită prin finanțare de la buget pentru invenții este mai mare decât taxele de brevetare, oferind astfel șansa multor autori să trimită dosarele OSIM spre brevetare. Acest lucru s-a discutat în ultimul timp și la alte universități, fără să se ia vreo măsură.

Stimularea creativității tehnice în universități este tot atât de utilă ca și în cazul cercetării științifice, în plus, pe lângă imagine și vizibilitate, poate aduce mari beneficii economico-sociale. Afirm aceasta deoarece brevetele de invenții sunt indexate prin Derwent Innovational Index, subsistem scientometric ISI Thomson, dar și prin alte BDI-uri, ca de exemplu, arhicunoscutul Espace@net, un instrument de neînlocuit astăzi în cercetare, dar și în analiza și evaluarea invențiilor. Sunt autori de invenții cu un număr mare de citări, atât de către alte invenții din străinătate, dar și de lucrări publicate în reviste ISI. Poate și acest lucru ar sugera ideea ca OSIM-ul să accepte dialogul la masa rotundă cu profesorii universitari de inventică, pentru a se găsi soluții în rezolvarea unor probleme prioritare ale inventicii românești. Dintre acestea, revin la scurtarea duratei de analiză a unei invenții la maximum un an și jumătate. Întrebare retorică, ce grad de noutate mai poate oferi o invenție care se brevetează după cinci sau șase ani de la înregistrare? Apoi, publicarea invențiilor în BOPI să se facă după regulile sistemului de indexare ISI Thomson (alături de limba română, ar trebui și în limba engleză titlul, rezumatul și referințele date de autor și cele date de referentul de la OSIM). În acest context, se vor evidenția mai bine citările, iar OSIM-ul își va pune mai bine în valoare profesionalismul referenților. Bineînțeles, sunt multe alte probleme importante legate de brevetare care trebuie rezolvate. Răspunsul că suntem aliniați la OMPI sau FIA este nesatisfăcător când în joc este problema demnității naționale. Instituțiile naționale sunt obligate să dea șansa devenirii și împlinirii acestei vocații. Legile, dacă ne referim la cea a invențiilor promovate de OMPI, OSIM și alte oficii naționale sau cantonale de brevetare/patentare, trebuie neapărat schimbate, sunt făcute doar de juriști, fără implicarea asociațiilor

profesionale ale inventatorilor și ale specialiștilor din domeniu (inventologi) și fără a se ține cont de specificul, de poziția geopolitică și nivelul de dezvoltare a unei țări. Consecința unei legi injuste o regăsim în rata de invenții la sută de mii de locuitori, capitol la care România se află printre ultimele țări din Europa.

Un alt aspect deja consumat și pentru care inventica ieșeană, și nu numai, a avut mult de suferit, este legat de Programul Național INVENT, dat spre gestionare Institutului de Cercetări pentru Mașini Agricole din București, când la Iași era deja bine statuat în cercetarea românească Institutul Național de Inventică. Întrebarea, câți bani s-au irosit aiurea pe teme nefinalizate, fără ca cineva să fie tras la răspundere? Este o chestiune de demnitate, să ne punem și astfel de întrebări!!! Trebuie mai multă grijă în evaluarea activităților în cadrul proiectelor și în chibzuirea banilor publici. Ca să fii membru în comisia de evaluare nu este suficient să ai doctoratul, trebuie să ai producție științifică vizibilă (de exemplu: minim 20 lucrări ISI publicate, minim 50 citări în literatura de specialitate, iar în cazul inventicii, minim 50 de invenții brevetate și măcar 10 aplicate/omologate). Evaluarea cea mai „strânsă” să fie cea post- și nu ante-. În funcție de rezultatele obținute să fie făcute finanțările ulterioare, chiar în cadrul aceleași teme, pe etape. Cu mâhnire în suflet spun că au fost finanțate teme, chiar și prin Programul IDEI, cu sume foarte mari, pentru activități de cercetare care nu solicitau bază materială și tehnică modernă, uneori cu mult peste cea oferită temelor ce necesitau experimente costisitoare. Pentru aceasta, CNCSIS-ul are nevoie de evaluatori financiar-contabili și norme specifice pentru fiecare comisie. De asemenea, evaluarea performanței în cercetare și fondurile alocate trebuie să fie diferite de la comisie la comisie.

În final, aș puncta un lucru pe care-l consider prioritar și care este prezent în toate universitățile mari din lume: competiția. Se dorește să avem universități competitive, atunci să se realizeze un climat academic concurențial, care să stimuleze creativitatea și producția științifică. Trebuie respectate grilele de evaluare, unanim acceptate de universitățile cu tradiție și ale celor care se situează pe primele locuri în activitatea de cercetare mondială.

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CREATION AND INNOVATION IN CULTURE, EDUCATION AND TRAINING

PhD. OTILIA MIRCEA

Description:

The Educational Project: **Creation and Innovation in Culture, Education and Training**, addressed to the preschool and primary and secondary school students, stimulate the receptivity of children on objects in the history museums, the desire for knowledge and simulation of restoration work, the desire to involve as small restaurateurs.

The road of an archaeological object from the site to museum was presented in three modules, from 2009 to 2011, as follows:

At the first Edition in 2009, the students learned about the role and the labor of the restorators in the muzeal laboratories and they simulated the restoration activity. In this respect, the children understood the work of specialists in museum laboratories, and the fact that most archaeological objects are often found broken in the ground, and restoring each object is like a puzzle. By sticking each fragment the children have reconstructed images from the collections of the Roman History Museum.

At the second Edition in 2010, the students learned about restoring objects with missing parts. In this stage the pupils worked with natural materials (seeds: coconut, poppy, mustard, peper, rice and other plants)

At the 2011 Edition, the pupils learned about chromatic reintegration of the fillings added to restore the archaeological objects and participated to creation workshops, where in the first stage they shaped objects in clay or plasticine, and in the second stage they highlighted the restoration process through which the discovered vessels have passed.

From the educational project the children learn about the development of the ancient people, about their ocupations, the domestic crafts, making objects of stone, bone, metals, pottery.

Practical applications by modeling or puzzle games, bring children closer to understanding the types of objects used in prehistoric times on one hand, and on the other the restorers work.

The children works are presented as small art objects on 18th May on International Day of Museums.

Partners:

**COMPLEXUL MUZEAL JUDEȚEAN NEAMȚ,
MUZEUL DE ISTORIE ROMAN,
ȘCOLI ȘI GRĂDINIȚE DIN JUDEȚELE NEAMȚ, BACĂU, GALAȚI**

PROJECT TEAM

Dr. OTILIA MIRCEA, coordonator proiect

Restorer ANA LĂCRĂMIOARA BĂCĂOANU

NEAMT County: Județul NEAMȚ:

Colegiul Național „ROMAN VODĂ” Roman, Școala de Arte și Meserii Adjudești, Școala cu clasele I –VIII Pildești – Cordon, Școala de Arte și Meserii Bălușești, Structura Bătrânești, , Structura Icușești, , Structura Rocna, Structura Mesteacă, Liceul Teoretic „VASILE ALECSANDRI” Săbăoani, Școala cu clasele I – VIII Ruginoasa, Școala cu clasele I – VIII Poienari, Școala cu clasele I –VIII „MIHAI EMINESCU” Roman/Grădinița cu Program Prolungit nr. 1, Școala cu clasele I – VIII Secuieni/Grădinița cu Program Normal Bașta, Școala cu clasele I – VIII Horia/Grădinița cu Program Normal Horia, Școala de Arte și Meserii Nisiporești, Școala cu clasele I –VIII Cordon, Grădinița cu Program Normal - Colegiul Tehnic PETRU PONI Roman, Școala cu clasele I –VIII Nr. 6 Roman/Grădinița cu Program Normal, Școala cu clasele I –VIII Nr. 8 Roman/Grădinița cu Program Normal, Școala de Arte și Meserii Valea Ursului, Structura Chiliz

BACĂU County - Județul BACĂU:

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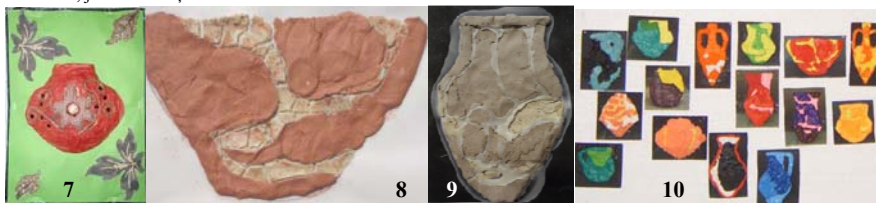
GALAȚI County - Județul GALAȚI:

Grădinița Nr. 47 Galați, Grădinița Nr. 44 Galați, Grădinița Nr. 7 „CRISTAL” Galați, Grădinița Nr. 32 Galați, Grădinița nr. 45 „Parfumul Teilor” Galați, Grădinița Nr. 9 „Sf. Nicolae” Galați, Grădinița Nr. 38 „LICURICI” Galați, Grădinița Nr. 64 „ILEANA COSÂNZEANA” Galați, Grădinița Nr. 6 „LUMEA COPIILOR” Galați, Grădinița Nr. 30 „PINOCHIO” Galați, Grădinița Nr. 56 „ANASTASIA” Galați, Grădinița Nr. 55 „OTILIA CAZIMIR” Galați, Grădinița cu Program Normal Nr. 61 „ION CREANGĂ” Galați, Grădinița nr. 15 „IOAN NENEIȚESCU” Galați, Grădinița nr. 2 Galați,, Grădinița nr. 36 MIHAI EMINESCU Galați, Școala Gimnazială Nr. 12 „MIRON COSTIN” Galați, Școala Gimnazială Nr. 15 „ELENA CUZA” Galați, Școala Gimnazială Nr. 22 „DIMITRIE CANTEMIR” Galați, Școala Gimnazială Nr. 25 „PETRU RAREȘ” Galați, Colegiul Național „COSTACHE NEGRI” Galați, Școala Gimnazială Nr. 13 „ȘTEFAN CEL MARE” Galați, Școala Gimnazială Nr. 17 „NICHITA STĂNESCU” Galați, Școala Gimnazială Nr. 29 „SFÂNTA ANA” Galați, Școala Gimnazială Nr. 16 „NICOLAE BĂLCESCU” Galați, Școala Gimnazială Nr. 34 „MIHAI VITEAZUL” Galați.

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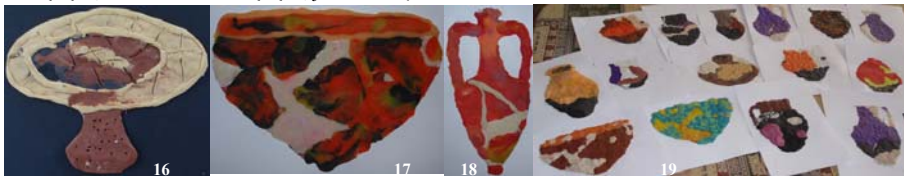


- 7 prof. **MERLOIU CĂTĂLINA GABRIELA**, ȘCOALA DE ARTE ȘI MESERII BĂLUȘEȘTI, STRUCTURA BĂTRĂNEȘTI jud. NEAMȚ
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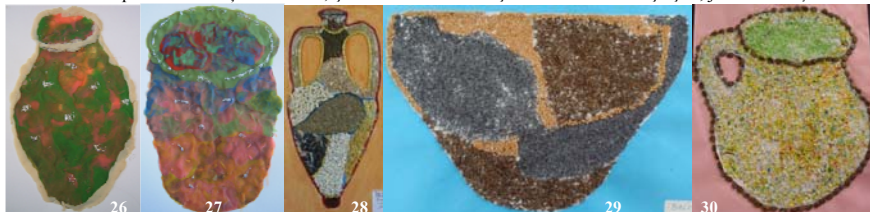
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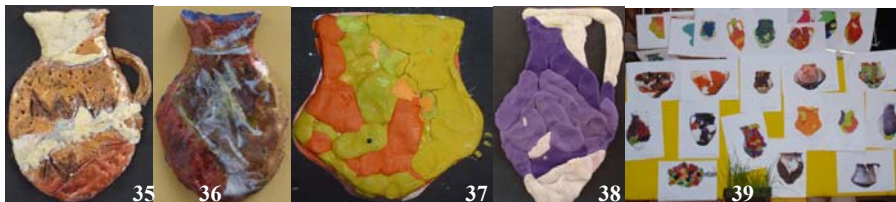


31. educatoare **BEJENARU NICOLETA**, GRĂDINIȚA CU PROGRAM NORMAL BAȘTA, ȘCOALA CU CLASELE I – VIII SECUIENI, jud. NEAMȚ

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33. educatoare **ION MIHAELA**, GRĂDINIȚA CU PROGRAM PRELUNGIT NR. 1, ȘCOALA CU CLASELE I – VIII MIHAI EMINESCU ROMAN

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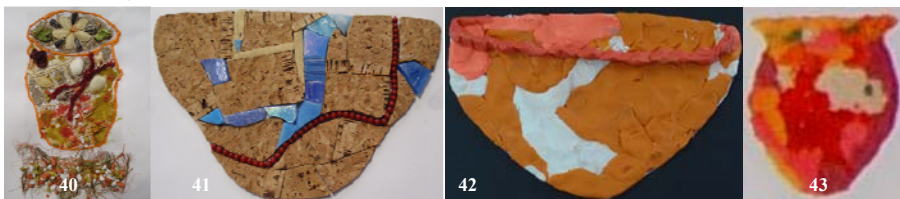
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36. educatoare **MITITELU CARMEN**, GRĂDINIȚA CU PROGRAM NORMAL HORIA, ȘCOALA CU CLASELE I – VIII HORIA, jud. NEAMȚ

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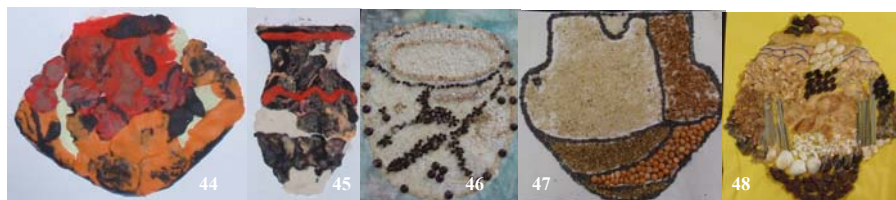


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41. educatoare **VANCEA RODICA**, BUTURĂȘ MIRELA, GRĂDINIȚA „VERONICA FILIP” PIATRA - NEAMȚ

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45. educatoare **GHEORGHESCU VIORICA**, PĂULEȚ IRINA, GRĂDINIȚA CU PROGRAM NORMAL, COLEGIUL TEHNIC „PETRU PONI” ROMAN, jud. NEAMȚ

46. educatoare **DASCĂLU LUMINIȚA**, GRĂDINIȚA CU PROGRAM NORMAL, ȘCOALA CU CLASELE I – VIII NR. 6 ROMAN, jud. NEAMȚ

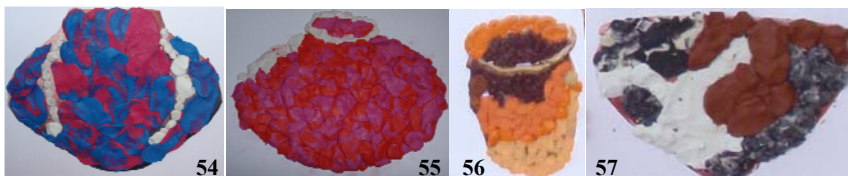
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48. educatoare **DORNESCU MARICICA**, ȘCOALA DE ARTE ȘI MESERII VALEA URSULUI, STRUCTURA CHILII, jud. NEAMȚ

II. CREAȚIE - ELEVI/CADRE DIDACTICE DE LA ȘCOLI ȘI GRĂDINIȚE DIN JUDEȚUL BACĂU



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50. educatoare **TURCU DORINA**, GRĂDINIȚA NR. 10, COLEGIUL NAȚIONAL PEDAGOGIC „ȘTEFAN CEL MARE” BACĂU
51. educatoare **PARASCAN RODICA**, GRĂDINIȚA CU PROGRAM NORMAL NR. 11, ȘCOALA CU CLASELE I – VIII „MIHAI DRĂGAN” BACĂU
52. educatoare **PARASCAN RODICA**, GRĂDINIȚA CU PROGRAM NORMAL NR. 11, ȘCOALA CU CLASELE I – VIII „MIHAI DRĂGAN” BACĂU
53. educatoare **BLANARU HARIETA**, GRĂDINIȚA CU PROGRAM NORMAL NR. 11, ȘCOALA CU CLASELE I – VIII „MIHAI DRĂGAN” BACĂU



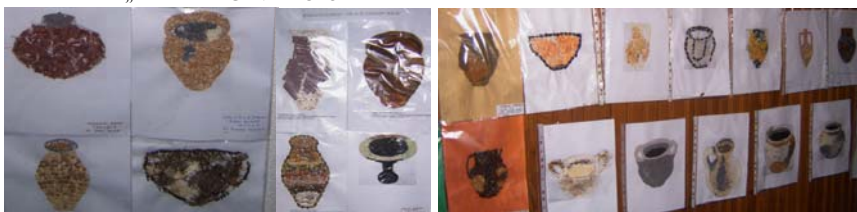
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55. educatoare **BLĂNARU HARIETA**, GRĂDINIȚA CU PROGRAM NORMAL NR. 11, ȘCOALA CU CLASELE I – VIII „MIHAI DRĂGAN” BACĂU
56. educatoare **DĂSCĂLAȘU MARICICA**, GRĂDINIȚA CU PROGRAM NORMAL NR. 11, ȘCOALA CU CLASELE I – VIII „MIHAI DRĂGAN” BACĂU
57. educatoare **DĂSCĂLAȘU MARICICA**, GRĂDINIȚA CU PROGRAM NORMAL NR. 11, ȘCOALA CU CLASELE I – VIII „MIHAI DRĂGAN” BACĂU



EXPOZIȚIA REALIZATĂ DE ȘCOALA CU CLASELE I – VIII „MIHAI DRĂGAN” BACĂU



EXPOZIȚIA REALIZATĂ DE GRĂDINIȚA CU PROGRAM NORMAL NR. 11 /ȘCOALA CU CLASELE I – VIII „MIHAI DRĂGAN” BACĂU



LUCRĂRI/EXPOZIȚIA DE LA ȘCOALA CU CLASELE I-VIII „GEORGETA MIRCEA CANCICOV” BACĂU



EXPOZIȚIA REALIZATĂ DE GRĂDINIȚA „VIOLETA” BACĂU



EXPOZIȚIA ORGANIZATĂ LA MUZEUL DE ISTORIE ROMAN COLEGIUL NAȚIONAL PEDAGOGIC „ȘTEFAN CEL MARE” BACĂU



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58. JUNCU NICOLA MARUSIA, clasa a II –a FREINET, îndrumător prof. TODIRICĂ LUMINIȚA, ȘCOALA CU CLASELE I – VIII „MIHAI DRĂGAN” BACĂU

59. LUPU ANDREEA ȘTEFANIA, clasa a II –a FREINET, îndrumător prof. TODIRICĂ LUMINIȚA, ȘCOALA CU CLASELE I – VIII „MIHAI DRĂGAN” BACĂU

60. ANDRONACHE ANDREEA ALESANDRA, clasa a II –a FREINET, îndrumător prof. TODIRICĂ LUMINIȚA, ȘCOALA CU CLASELE I – VIII „MIHAI DRĂGAN” BACĂU

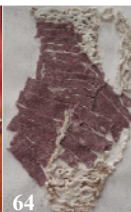
61. SOLOMON SABINA, clasa a II –a C, îndrumător prof. POPA NICOLETA, COLEGIUL NAȚIONAL PEDAGOGIC „ȘTEFAN CEL MARE” BACĂU



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65

62. VEREȘ RAFAELA, clasa a VIII –a A, îndrumător prof. SIBIȘTEANU LIVIA LILIANA, ȘCOALA CU CLASELE I – VIII „SPIRU HARET” BACĂU

63. BIBIRE RAREȘ GEORGE, clasa I A, îndrumător prof. MĂUCA CLEMANSĂ, ȘCOALA CU CLASELE I – VIII „SPIRU HARET” BACĂU

64. UNGUREANU ANA, clasa a III –a B, îndrumător prof. GABRIELA MELINCIANU, ȘCOALA CU CLASELE I-VIII „GEORGETA MIRCEA CANCICOV” BACĂU

65. prof. SCUTARU ANDRA, COLEGIUL NAȚIONAL PEDAGOGIC „ȘTEFAN CEL MARE” BACĂU



EXPOZIȚIA REALIZATĂ DE ȘCOALA CU CLASELE I – VIII „SPIRU HARET” BACĂU



EXPOZIȚIA REALIZATĂ DE MUZEUL DE ISTORIE ROMAN

III. CREAȚIE - ELEVI/CADRE DIDACTICE DE LA ȘCOLI ȘI GRĂDINIȚE DIN JUDEȚUL GALAȚI



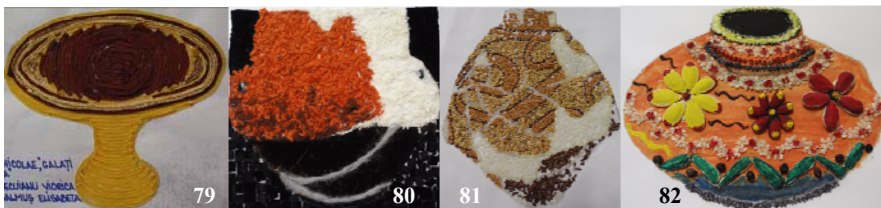
66. educatoare **ANDREȘOIU VALERICA**, GRĂDINIȚA NR. 47 GALAȚI
 67. educatoare **ION SOFIA**, GRĂDINIȚA NR. 47 GALAȚI
 68. educatoare **SAMOILĂ GABRIELA**, GRĂDINIȚA NR. 47 GALAȚI
 69. educatoare **BOUBĂTRĂN LENUȚA**, GRĂDINIȚA NR. 47 GALAȚI



70. educatoare **CHEBAC TINCUȚA**, GRĂDINIȚA NR. 47 GALAȚI
 71. educatoare **SAMOILĂ GABRIELA**, GRĂDINIȚA NR. 47 GALAȚI
 72. educatoare **ANDREȘOIU VALERICA**, GRĂDINIȚA NR. 47 GALAȚI
 73. educatoare **BERCAN MARILENA**, GRĂDINIȚA NR. 44 GALAȚI
 74. educatoare **ACĂTĂNOAIE MARILENA**, GRĂDINIȚA „PARFUMUL TEILOR” GALAȚI



75. educatoare **CĂLDĂRUȘ MĂNDIȚA**, LUPU MARIANA, GRĂDINIȚA NR. 38 „LICURICI” GALAȚI
 76. educatoare **ANA MARIA CIURARU**, GRĂDINIȚA „PARFUMUL TEILOR” GALAȚI
 77. educatoare **BUJOR AMBROZIA**, **COROPCIANU ALINA**, GRĂDINIȚA „PARFUMUL TEILOR” GALAȚI
 78. educatoare **VASILICA DRAGU**, **ANGELA GHEORGHE**, GRĂDINIȚA NR. 32 GALAȚI



79. educatoare **SECUIANU VIORICA**, **BALMUȘ ELISABETA**, GRĂDINIȚA NR. 9 „SF. NICOLAE” GALAȚI
 80. educatoare **BURIC IFTIMIA**, **ȚICĂU MARIANA**, GRĂDINIȚA NR. 9 „SF. NICOLAE” GALAȚI
 81. educatoare **DUMITRU NELUȚA**, **CĂLUIAN IULIANA**, GRĂDINIȚA NR. 9 „SF. NICOLAE” GALAȚI
 82. educatoare **TOFAN ETA MARINELA**, GRĂDINIȚA NR. 64 „ILEANA COSĂNZEANA” GALAȚI



83. educatoare **TOFAN ETA MARINELA**, GRĂDINIȚA NR. 64 „ILEANA COSÂNZEANA” GALAȚI
 84. educatoare **RARINCA SIMINA**, GRĂDINIȚA NR. 6 „LUMEA COPIILOR” GALAȚI
 85. educatoare **CHIURTU CARMEN, LAZĂR ALINA**, GRĂDINIȚA NR. 55 „OTILIA CAZIMIR” GALAȚI
 86. educatoare **PĂCURARU DANIELA**, GRĂDINIȚA NR. 6 „LUMEA COPIILOR” GALAȚI
 87. educatoare **BUJOR AMBROZIA, COROPCIANU ALINA**, GRĂDINIȚA „PARFUMUL TEILOR” GALAȚI



88. educatoare **PETICA LICA**, GRĂDINIȚA NR. 30 „PINOCHIO” GALAȚI
 89. educatoare **BUSUIOC VERGINICA**, GRĂDINIȚA NR. 56 „ANASTASIA” GALAȚI
 90. educatoare **BUSUIOC VERGINICA**, GRĂDINIȚA NR. 56 „ANASTASIA” GALAȚI
 91. educatoare **RARINCA SIMINA**, GRĂDINIȚA NR. 6 „LUMEA COPIILOR” GALAȚI
 92. educatoare **TOMA CERASELA ANY**, GRĂDINIȚA NR. 2 GALAȚI
 93. educatoare **NITU MARIA**, GRĂDINIȚA NR. 15 „IOAN NENIȚESCU” GALAȚI

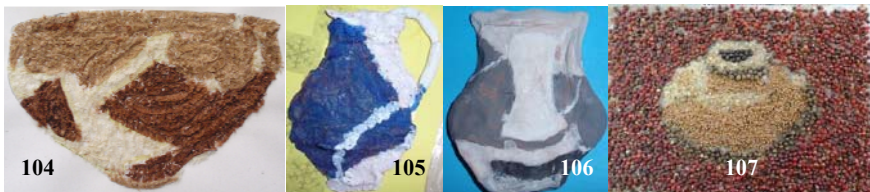


94. **ENACHE LARISA**, clasa a II – a C, îndrumător prof. GROSU ELENA, ȘCOALA GIMNAZIALĂ NR. 25 „PETRU RAREȘ” GALAȚI
 95. **DIACONIȚA BIANCA**, clasa I B, îndrumător prof. TĂNASE GABRIELA, ȘCOALA GIMNAZIALĂ NR. 34 „MIHAI VITEAZUL” GALAȚI
 96. **BRADU AURORA – ELENA**, clasa a IV –a B, îndrumător prof. PUPU VIOLETA, ȘCOALA GIMNAZIALĂ NR. 16 „NICOLAE BĂLCESCU” GALAȚI
 97. prof. **VINTILĂ IONELA**, ȘCOALA GIMNAZIALĂ NR. 15 „ELENA CUZA” GALAȚI
 98. **MOSCU TEODORA**, clasa a III –a B, prof. TACU ANIȘOARA, ȘCOALA GIMNAZIALĂ NR. 12 „MIRON COSTIN” GALAȚI



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102. **STROIA ANDREEA**, clasa a IV- a C, îndrumător prof. NEAGU MARIA, ȘCOALA GIMNAZIALĂ NR. 22 „DIMITRIE CANTEMIR” GALAȚI
103. **TOPORAȘ CRISTINA**, clasa I B, îndrumător prof. TĂNASE GABRIELA, ȘCOALA GIMNAZIALĂ NR. 34 „MIHAI VITEAZUL” GALAȚI



104. **BĂRBIERU EMANUEL**, clasa I, îndrumător inst. BURLACU CAMELIA, ȘCOALA GIMNAZIALĂ NR. 16 „NICOLAE BĂLCESCU” GALAȚI
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106. **ADRIAN ADAM**, clasa a IV –a A, îndrumător prof. ȚILEA MARIANA MIHAELA, ȘCOALA GIMNAZIALĂ NR. 29 „SFÂNTA ANA” GALAȚI
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108. **LUCA ANA**, îndrumător prof. VÎLCOV NICOLETA, ȘCOALA GIMNAZIALĂ NR. 22 „DIMITRIE CANTEMIR” GALAȚI
109. **CIURUȘNUC ALEXANDRA**, îndrumător inst. STANCIU MARIANA ȘCOALA GIMNAZIALĂ NR. 17 „NICHITA STĂNESCU” GALAȚI
110. **LIȘIȚĂ L. MIRUNA**, clasa a IV-a B, îndrumător prof. VÎLCOV NICOLETA, ȘCOALA GIMNAZIALĂ NR. 22 „DIMITRIE CANTEMIR” GALAȚI
111. **prof. ZAHARIA LILIANA, prof. TCACIUC AMALIA, prof. POPESCU AURELIA, prof. FOTACHE DANIELA**, ȘCOALA GIMNAZIALĂ NR. 15 „ELENA CUZA” GALAȚI



EXPOZIȚIA DE LA MUZEUL DE ISTORIE ROMAN
Școala Gimnazială Nr. 25 „PETRU RAREȘ” Galați

EXPOZIȚIA REALIZATĂ LA
Școala Gimnazială Nr. 15 „ELENA CUZA” GALAȚI

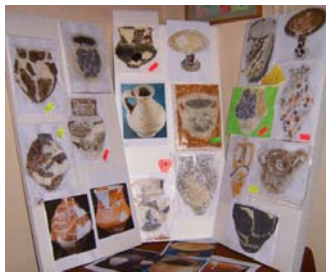
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EXPOZIȚIA REALIZATĂ LA GRĂDINIȚA NR. 47 GALAȚI



EXPOZIȚIA REALIZATĂ LA GRĂDINIȚA NR. 55 „OTILIA CAZIMIR” GALAȚI



**EXPOZIȚIA REALIZATĂ LA
COLEGIUL NAȚIONAL
„COSTACHE NEGRI” GALAȚI**

EXPOZIȚIA REALIZATĂ LA ȘCOALA GIMNAZIALĂ NR. 13 „ȘTEFAN CEL MARE” GALAȚI



EXPOZIȚIA REALIZATĂ LA GRĂDINIȚA CU PROGRAM NORMAL NR. 61 „ION CREANGĂ” GALAȚI



**Expoziția „CREAȚIE ȘI INOVAȚIE ÎN CULTURĂ, EDUCAȚIE ȘI ÎNVĂȚĂMÂNT”,
ediția a II –a, 2010, organizată la Muzeul de Istorie Roman**



Expoziția „CREAȚIE ȘI INOVAȚIE ÎN CULTURĂ, EDUCAȚIE ȘI ÎNVĂȚĂMÂNT”,
ediția a II –a, 2010, organizată la Muzeul de Istorie Roman





Expoziție realizată de elevii din clasa a V- a A,
 COLEGIUL NAȚIONAL „ROMAN VODĂ” ROMAN
 îndrumător prof. RADU CRISTINA MANUELA

ARTA PLASTICA, CREATIE SI TRAIRE

Coman Andreea Madalina

Artist plastic amator

Arta plastica este unul dintre modurile cele mai interesante de abordare a cunoasterii dincolo de aparente, reprezentand spatiul mirific prin care creatorul unei opere poate depasi limita realului, este spatiul in care sentimentele sunt traite intr-o forma pura, aproape sacra. Este aproape imposibil de definit arta insa in ochii privitorilor se contureaza o definitie a artei nu prin cuvinte ci prin sentiment. Atat pentru artist cat si pentru public, obiectul artistic creat are o poveste pe care cu placere o releva printr-un simplu contact vizual. Este foarte adevarat ca povestea aceasta nu este aceeași in ochii privitorilor, aceasta putand fi perceputa diferit de la un individ la altul si probabil tocmai aici se creaza inceputul definitiei fenomenului artistic.

In calitate de pictor amator privesc arta plastica din punct de vedere personal, intre mine si lucrarile mele formandu-se un dialog *tainic*. Lipsa profesionalismului poate se cunoaste in modul oarecum brutal de a lucra insa consider un atu faptul ca aceasta lacuna imi da libertatea de a lucra din suflet, nefiind limitata din punct de vedere creativ. Astfel in micile mele creatii se pot regasi emotii, stari de spirit, dorinta si nu in ultimul rand pasiunea pentru culoare, pentru forma si frumos. Este foarte adevarat ca tematica fiecarii lucrari poate fi intalnita si la alti pictori insa modul de abordare este unul individual. Asa cum *nudul* se regaseste in marile lucrari de arta a unor numerosi artisti consacrați, fara ca vreunul dintre ei sa-si fi insusit ideea, insa venind cu ceva inovator in realizarea operei pornind de la acea idee, asa cum divrese tematici religioase au trecut prin mainile nenumarati artisti, ficare transpunand ideea printr-o maniera personala, astfel doresc sa va aduc in fata cateva lucrari realizate nu prin stiinta ci prin pasiune.

Județul Neamț

1. prof. **CARMEN AVRAM**, ȘCOALA DE ARTE ȘI MESERII ADJUDENI, jud. NEAMȚ
2. prof. **MERLOIU CĂTĂLINA GABRIELA**, ȘCOALA DE ARTE ȘI MESERII BĂLUȘEȘTI, STRUCTURA BĂTRÂNEȘTI jud. NEAMȚ
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6. educatoare **ION MIHAELA**, GRĂDINIȚA CU PROGRAM PRELUNGIT NR. 1, ȘCOALA CU CLASELE I –VIII MIHAI EMINESCU ROMAN
7. educatoare **ADIACONIȚEI VIORICA**, GRĂDINIȚA CU PROGRAM PRELUNGIT NR. 1, ȘCOALA CU CLASELE I – VIII MIHAI EMINESCU ROMAN
8. educatoare **BIBERI MARIANA**, GRĂDINIȚA CU PROGRAM PRELUNGIT NR. 1, ȘCOALA CU CLASELE I –VIII MIHAI EMINESCU ROMAN
9. educatoare **SAMSON CRISTINA**, GRĂDINIȚA CU PROGRAM PRELUNGIT NR. 1, ȘCOALA CU CLASELE I – VIII MIHAI EMINESCU ROMAN
10. prof. **GÎRBEA TATIANA**, ȘCOALA CU CLASELE I – VIII HORIA

Județul Bacău

11. educatoare **DĂSCĂLAȘU MARICICA**, GRĂDINIȚA CU PROGRAM NORMAL NR. 11, ȘCOALA CU CLASELE I – VIII „MIHAI DRĂGAN” BACĂU
12. prof. **TODIRICĂ LUMINIȚA**, ȘCOALA CU CLASELE I – VIII „MIHAI DRĂGAN” BACĂU
13. prof. **SIBIȘTEANU LIVIA LILIANA**, ȘCOALA CU CLASELE I – VIII „SPIRU HARET” BACĂU
14. prof. **MĂUCA CLEMANSA**, ȘCOALA CU CLASELE I – VIII „SPIRU HARET” BACĂU

Județul Galați

15. educatoare **ACĂTĂNOAIE MARILENA**, GRĂDINIȚA Nr. 45 „PARFUMUL TEILOR” GALAȚI
16. educatoare **BUJOR AMBROZIA**, GRĂDINIȚA Nr. 45 „PARFUMUL TEILOR” GALAȚI
17. prof. **DUMITRIU ELENA SIMONA**, ȘCOALA GIMNAZIALĂ NR. 12 „MIRON COSTIN” GALAȚI
18. prof. **ȚILEA MARIANA MIHAELA**, ȘCOALA GIMNAZIALĂ NR. 29 „SFÂNTA ANA” GALAȚI
19. **prof. ZAHARIA LILIANA**, ȘCOALA GIMNAZIALĂ NR. 15 „ELENA CUZA” GALAȚI
20. **prof. RADU CRISTINA MANUELA**, COLEGIUL NAȚIONAL „ROMAN VODĂ” ROMAN
21. **prof. MAXIM IULIANA**, COLEGIUL NAȚIONAL „ROMAN VODĂ” ROMAN
22. **prof. PLAI MIHAELA**, ȘCOALA CU CLASELE I – VIII „MIHAI EMINESCU” ROMAN
23. **prof. TACU ANIȘOARA**, ȘCOALA GIMNAZIALĂ NR. 12 „MIRON COSTIN” GALAȚI
24. **COMAN ANDREEA MĂDĂLINA**, EXPOZIȚIE PERSONALĂ

**High School of Creativity
and Inventics "Prometheus-Prime"**

**Liceul de Creativitate
și Inventică „Prometeu-prim”**

Chișinău, Moldova

Contact:

Silvestru Aurelian - Director

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High School was founded in 1991. Theoretic support of high school was "The Concept of personality development of students in the alternative education". During 2003-2010 the creativity of the students was appreciated by over 250 awards.

Liceul a fost fondat în a. 1991. Suportul theoretic al Liceului a fost "*Concepția dezvoltării personalității elevului în condițiile învățământului de alternativă*". Pe parcursul anilor 2003-2010 creativitatea elevilor a fost apreciată cu peste 250 premii.

THERAPEUTIC ROLE OF SALINE SOLIONS IN A POLLUTED ENVIRONMENT

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Abstract: *This paper presents a number of issues relating to the use of NaCl solions in ancient times and recently in various therapies to improve human performance. Solions are hydrated solid dispersions with negative electrostatic charge. Aitken particles with sizes ranging from those on the edge of destabilization by sedimentation in gaseous systems, generated by erosion processes, resulting in nanocrystals salt on the surface of the bubble bursting or supersaturated salt solutions. They form well crystallized elements. Their positive role in the membranes of internal organs and lung is well known.*

Keywords: *NaCl solions, solion sources, halochamber, halotherapy, solion lifespan.*

1. Introduction

Ambient air quality and therapeutic environments is a current concern of scientists, because the environment has undergone a radical transformation due to climate changes caused by both internal and endogenous factors (changes that occur within the climate system, from the interactions of its components) and external or exogenous factors (change in energy emitted by the sun, volcanic eruptions, changes in Earth's orbital parameters, and anthropogenic factors, resulting from human activities, eg atmospheric composition change due to increasing greenhouse gas concentrations).

To limit the harmful effects of pollution on health, programs were developed to anticipate and prevent diseases, to increase body resistance, especially in children and the elderly. Diseases that affect the body because of its lack of natural resistance to environmental factors, are those of the respiratory tract, sinusitis, otitis, etc. as well as rheumatic diseases.

As a program of sports activities, adjusted for age and individual needs in a therapeutic environment, the saline aerosol halochamber (natural or artificial) could positively influence the functioning of the body. Among the benefits of an environmental movement salt aerosols, remember: power

increase, respiratory ventilation, enhancing functional capacity of the circulatory system by increasing blood levels and hormonal activity, accelerate metabolism, boost growth processes, muscular mass development, increase resistance to stress and the increase of overall comfort (movement will improve, creativity, concentration power, memory, emotional stability, etc.).

In order to use average solions, we need information about solion lifespan, the size distribution and concentration solions, processes for obtaining solions, artificial solions characteristics and their therapeutic applications.

2. General aspects on solions

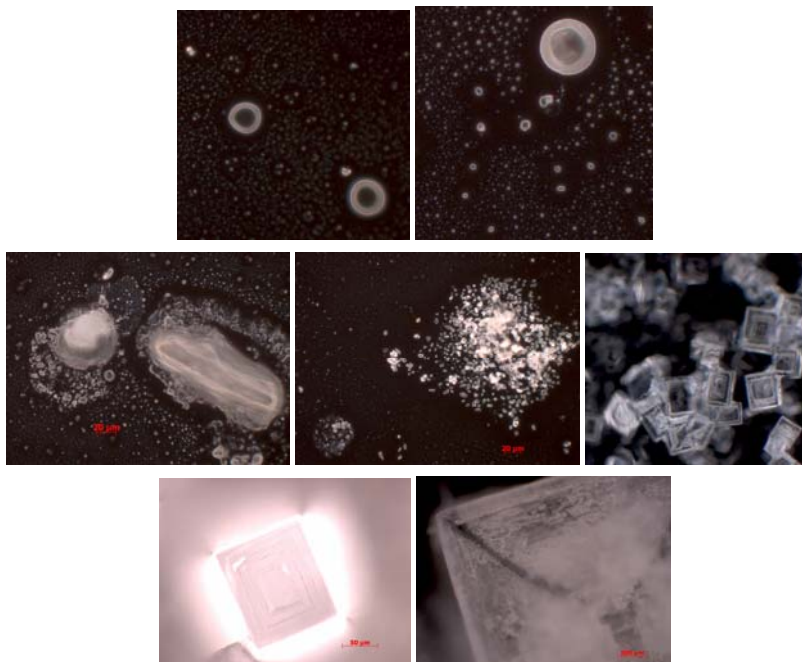
Solions polydispersion based systems, which are NaCl particles include a wide dimensional field, and microphysical properties with special nano-structure, with many practical implications (for prophylaxis and therapy of respiratory diseases, improving cardio-respiratory parameters and psycho-motor neurone In purifying and improving air quality).

Solions are mobile saline nanoparticles, with implications for prevention and therapy, ranging in size between Aitken and large particles, to sediments. They are the result of structural reform processes in the presence of water vapor in gaseous atmosphere, whose stability, as nanodisperse crystalline systems, is given by the electrostatic factor, as well as the steric [Sandu et al., 2003, 2004 a și b, 2009, 2010 a și b].

In some studies of aqueous dispersed systems in the air, it was concluded that the solions are dynamic nanostructures, spherical clusters with negative charge, which would correspond to a formula such as: $[(\text{NaCl})_n \cdot x\text{H}_2\text{O}]_{(\text{aq})}$, având $n = 8 - 64$ și $x = 0.5n - 1.5n$ [Sandu 2010 a și b].

Solions derived from natural sources (sea spray and salt from the mines) and artificial sources (halochambers, saline devices or inhalers) may be used for therapeutic purposes, leading to improvement in the life of patients, to harmonize the functioning of internal organs, to reduce admissions rate, thus reducing the number of medically inapt subjects and improving performance.

Solion lifespan varies due to varying degrees of negative charge on the surface and structural complexity of these crystal nanoclusters from a few minutes to several days [Sandu et al, 2003, Ștefan, 1998, Sandu et al, 2010].



Dimensional distribution and concentration solionilor

Various aerosol of gaseous atmospheres that are stable nanodispersions somewhat regular size and strength depending on source type, the activity of these particles and their time living and environmental conditions [Ștefan, 1998, Sandu et al, 2003, 2010c și d]. Solions vary according to the type of power generators, including only three of the groups of particles: Aitken particles (ions and higher ionic aggregates small, between 0.5 and 50 nm diameter), the mean (condensed particles, the diameter between 50 and 100 nm) and large (coagulated particle diameter of between 100 and 1000 nm).

Procedures for obtaining artificial solions

Since 1990 they have developed various methods for obtaining NaCl solions, alone or in combination with other compounds or organic inorganic with predetermined chemical compositions depending on the application. After the physical-mechanical, fluid and heat production, it is classified into four groups: mechanical splitting or erosion, followed by physical dispersion in the atmosphere halochamber with a stream of gas, solid salt systems [Clark, 1995 a, b, c; 1996; 1998; Hickey, 1994; Pascu, 2002 a, b;

2003 a, b, c; 2006; 2007; 2008; 2009]; gas bubbles break, the air bubbling processes or other inert gas through saturated salt solutions [Joutsensaari et al., 2001]; atomization of saturated salt solutions with vacuum cyclones, followed by physical dispersion with a stream of air [Katusik et al., 2000, Merchat, 1994];

Superficial particle entrainment resulting from consecutive anhydration solvolisys and surface structures, following the circulation of air through holes and grooves charged in blocks of rock salt or rectangular blocks, arranged in the form of fences, walls halochamber [Albiach, 1995; Belkin, 2005; Konovalov, 1993; Sandu et al., 2009 a, b, c, d, e, f].

Solions general characteristics of aerosols are determined by the source, but environmental factors. Among the functional characteristics that describe a source of solion are met:

- aerosol size and density;
- velocity of particle formation;
- flow source;
- gaseous environment enrichment factor;
- lifetime of aerosol particles;

NaCl solions composition can change due to interaction with atmospheric humidity and other atmospheric particles and gases, coagulation processes taking place, peptization, condensation and sedimentation. Light radiation can also influence the composition and microstructures of particle physics for systems co-assiting with other salts such as potassium chloride, calcium or magnesium and sodium or potassium iodide.

The characterization solions is with three variables, number, volume and total surface of particles are involved and other parameters such as:

- a) concentration and its variation solions while under the influence of coagulation processes, peptizare, condensation or settling etc.
- b) the size distribution of solions;
- c) the degree of surface electrostatic charge (solion measured the distance between the liquid dispersed systems);
- d) the degree of hydration;
- e) the dynamic behavior of solions, diffusion, drift mobility and their speed;
- f) environmental humidity limit at which the formation of condensation nuclei.

Solions concentration the number of particles per unit volume. Usually, numerical concentration of all aerosol particles is equivalent to the number of Aitken particles per unit volume, as the number of medium and large particles is insignificant in comparison with Aitken. Measuring the

concentration of particles can be made using the meter or particle counter laser beam.

Stringent control of concentrations and distributions of the environment solions dimensional halotherapy effect is very important for medical treatment of various respiratory and create an environment of "clean air" [Sandu et al., 2004a și b].

Depending on the concentration of solions, saline areas may have both therapeutic effect (in case of high concentrations of NaCl solions of 1-6 mg / m³ which is stationary for 1-4 hours) and a prophylactic (concentration below 1 NaCl mg / m³, but with a longer presence, 8-16 hours per day).

3. Applications of solions

Solions acting on the body by inhalation and skin absorption. Inhaling these respiratory aerosols are "cleansed" of outbreaks of infection (stafilo-strep), present in adults, especially in children, triggering and maintain numerous outbreaks of respiratory disease (mostly recurrent, with tndințe to chronic) and whose presence, the immune system, gradually decreases. Solions form the therapeutic atmosphere and act upon the body through the skin, being absorbed in the proper proportions of oxygen absorption, humidity and, of course, by hand / precipitation due to moisture and skin surface temperature difference from the atmosphere.

The beneficial effect of salt air can be increased if it is practical and physical exercises. They increase respiratory ventilation power to enhance the functional capacity of the circulatory system, increase blood levels of hormones (accelerating metabolism, boost growth processes in children, increased muscular weight, reducing the dangers of osteoporosis), slowed aging, increasing resistance state of stress and increase overall comfort (improves movement will, creativity, concentration power, memory, emotional stability, etc.).

4. Conclusions

Following synthesis of key data in the literature on the production, characteristics and applications of solions following conclusions were reached:

- irrespective of power generators, solion particles contain only three groups namely: Aitken particles (ions large and small ionic aggregates, 0.5 ... 50 nm), the average (50 ... 100 nm condensed particles) and large (coagulated particles, 100 ... 1000 nm).

- solion and aerosol characteristics are generally determined by the source, but environmental factors, so the functional characteristics that describe a source of solion remember: solion size and density, the rate of formation of particle flow source of enrichment factor gaseous atmosphere, the lifetime of solions;

- depending on the concentration of saline areas solions may have a therapeutic effect (in case of high concentrations of NaCl solions of 1-6 mg / m³ which is stationary for 1-4 hours) or prophylactic effect (concentration below 1 mg NaCl / m³, but with a longer presence, 8-16 hours per day).

- solions act on the body by inhalation and skin absorption as a remedy for many diseases, applying salt therapy since the time of Hippocrates as a complementary method and / or alternative airway protection, ancient method of healing for the body and soul, thus successfully reducing long-term drug treatment.

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IMPACT ASSESSMENT OF SALINE AEROSOLS ON EXERCISE CAPACITY OF ATHLETES

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1. Introduction

The treatment in natural salt mines (speleotherapy) was known since a very long time ago; the miners and other persons involved in these activities might have known about the great effects of the microclimate within salt mines upon human health, long before they were described in a book published by a Polish doctor in 1843. The effectiveness of speleotherapy is associated with the unique cave microclimate; the sodium chloride aerosols represent the main curative factor. The saline aerosols are formed off the salt walls by convective diffusion [1].

Halotherapy is the natural therapy method which borrows the main curative factor for speleotherapy, meaning the saline aerosol particles dispersed in the salt mine microclimate [2].

The salt room microclimate should have a constant humidity (a relative air humidity of 40-60%) and a temperature of 18-24° Celsius, as these parameters create favourable conditions for patients and they are a stable environment for aerosols [3-6]. The precinct should also ensure a stable environment, bacteria- and allergen-free; studies have shown that the microbial contamination during a halotherapy session is of 130-200 saprophyte microorganisms to 1m³ of air (the WHO standards regarding air sterility are of > 300 microorganisms/1m³ air). Thus, a 10-20 minutes break after each session is necessary to purify the air within the chamber [1, 7].

1.1. The Benefices of Halotherapy

As concerns the breathing system of the person in the precinct of the salt room, there is a permanent high concentration of dry saline aerosols. This concentration is considered therapeutic if it exceeds 1mg/m³. By inhaling these aerosols, the airways are “cleaned” of focuses of infection (staphylococci and streptococci) – present at adults and especially children – which trigger and maintain many respiratory conditions (in most cases with relapses, becoming chronic) and gradually lead to a decrease in the

body immunity. Salt is bactericide by nature, not allowing the microbial cultures to develop, behaving like a disinfectant in most cases. Through the deposition or absorption of salt ions, both for the superior and the inferior airways, mostly in case of small aerosols, conjugated with the hygroscopic property, an effect of dilution of impurity or foreign matter depositions takes place (including microorganisms). These microorganisms lead to breathing disorders or dysfunctions, starting from simple hoarseness, and up to bronchitis and asthma [1, 8-10].

The observations over time regarding the persons with breathing disorders showed that the respiratory tract mucus thickens when losing humidity and salt; the body cannot compensate the lack of necessary fluid and salt (especially Na^+ ions) [10].

Through its electro-chemical properties, salt, and mostly saline ions, once deposited on the respiratory tract, not only eliminate bacteria and microorganisms, but also determine the emollition, liquefaction and fluidization of the mucus off the airways, thus extracting the foreign matters among the cilia within the micro-cavities of the respiratory tract, determining the progressive and long-term relief of breathing, the natural and easy expectoration, the elimination of allergen or bacterial matters through the reflex phenomena of coughing, nose secretions, expectorations, etc., characteristic symptoms for the airways' relief [8-11].

1.2. Main Objective

The study concerns the adapting level of athletes' bodies and developing the effort capacity to natural saline underground factors, insufficiently valorised, or not properly used in sports, and elaborating effective halotherapy technologies

1.3. Hypothesis

We will try to extend the research referring to the effect of exposing athletes to saline aerosols, of adapting the cardiovascular system to effort and of improving the sports performances, as well as to the influence of halotherapy upon certain indices of the breathing system. Concretely, our hypothesis is that saline aerosols are effective in treating respiratory conditions, and we will try to prove that by exposing athletes' bodies to saline aerosols the respiratory and cardiovascular indices will improve, as well as athletes' performances.

2. Material and Methods

The study was carried on with a sample of 12 middle-distance runners, aged between 14 and 16. The assessment of their cardiovascular and respiratory functions will take place at the Laboratory of functional explorations, testing the effort capacity and evaluating the physical development within the Sports Clinic of Iași.

Within the research we will be monitoring the following factors:

- Respiratory indices: vital capacity (VC), maximum expiratory volume per second (MEVS), maximum ventilation (V max), peak expiratory flow (PEF) [9];
- cardiovascular indices: Blood pressure at rest (BP), heart rate at rest (HR) [8];
- cardiovascular indices during effort: the Martinet test (lab test) allows the momentary evaluation, and the evolution in time regarding the functional capacity of the cardiovascular system, being a useful means, often used in carrying on sports training [10, 11]. The test proposed by Martinet assesses the cardiovascular response to low-intensity, standard, non-specific, cabinet, short-term effort.

The investigations concerning the respiratory and cardiovascular system took place after 21 days of salt therapy. The halotherapy was carried on in an air-proof chamber, providing a precinct with saline aerosols through domestic SALINE aerosol devices, produced by Biotehnic SA Buzău. The functioning principle of the device is forcing the air to pass through the NaCl recrystallized granules, leading to alterations in the air composition and quality due to salt nanodispersion, as air ions with negative charge. The chamber was clean, well ventilated, with comfortable temperature and humidity [2].

There was a daily exposition after practices, as recovery period after the training effort. There was a gradual exposition to the saline aerosols – 20 minutes the first day, 25 minutes the second day, up to 60 minutes a day. The last four days the exposition was reduced by 5 minutes, thus avoiding the sudden interruption of the treatment. During the halotherapy session the subjects breathed normally, being relaxed, and the post-effort recovery had a total of 21 sessions per participant.

3. Results and Discussions

- Respiratory parameters

Table 2. Proportion of subjects with alterations of respiratory parameters

Respiratory parameters	Initial test				Final test			
	Increase		Decrease		Increase		Decrease	
	c.a.	%	c.a.	%	c.a.	%	c.a.	%
VC (litres)	6	50	6	50	11	91	1	9
MEVS (l/s)	9	75	3	25	12	100	–	–
V max. (l/min)	9	75	3	25	12	100	–	–
PEF (l/s)	8	67	4	33	11	87.5	1	9

Before halotherapy, half of the subjects had higher values of vital capacity, compared to the normal one, and the other half – lower values. After halotherapy the percentage of those with higher vital capacity increased (Table 2).

The same positive aspect applies to MEVS and V max.: after the treatment all the subjects presented increased values.

Of all the subjects, only one had a decrease in the VC and PEF after the treatment (possibly caused by a momentary indisposition).

Analysing the average values of the four breathing volumes, registered before and after the treatment, we see they increased after the halotherapy session attended by the subjects.

Table 3. Average values of respiratory indices

Respiratory indicators	Subjects	Initial test		Final test		P
		m	σ	m	σ	
VC (litres)	12	481.1	102.09	542.7	99.9	0,1494
MEVS (l/s)	12	425.3	68.4	484.8	74.4	0,0530
PEF (l/s)	12	8.1	1.25	10.3	1.20	0,0002
Vmax (l/min.)	12	1276.1	205.3	1454.6	223.3	0,0002

All subjects had higher values of the four respiratory volumes after halotherapy, with significant differences four three of them (Table 3). For

the VC, with no significant differences, we should mention as favourable aspect the increase tendency.

- Respiratory index

The respiratory index is calculated with the following formula [9]:

$$R = VC \text{ (cm)} / G \text{ (kg)} \times 1/10$$

It is very useful to calculate the R, because we can easily orient towards the functional lung potential of the subject, thus being a compulsory functional parameter when determining the general biologic potential. In our case, the subjects scored over 6, meaning that they have a “very good” and “excellent” respiratory index. We should also stress the fact that, after the halotherapy treatment, there was an increase in the percentage of subjects who scored over 8 – the maximum score (Table 3).

Table 4. The subjects’ scores within the respiratory index scale

Score	Initial test		Final test	
	c.a.	%	c.a.	%
Low (0-4)	–	–	–	–
Average (4-5)	–	–	–	–
Good (5-6)	–	–	–	–
Very good (6-8)	8	67	3	25
Excellent (over 8)	4	33	9	75
Total	12	100	12	100

- Cardiovascular indices

Table 5. Assessment of the cardiovascular system – initial and final test

	Heart rate at rest	Systolic BP at rest	Diastolic BP at rest
Initial test	71.30	118	67.9
Final test	69.12	116.5	66.6
Reference values	60-90 b/min	100-140 mmHg	60-90 mmHg

The assessment of the cardiovascular system at rest is very important during the medical examination because we can detect problems that would become acute during sports effort. We followed the heart rate at rest, which was within the normal rates approved by WHO. The rest bradycardia was registered at athletes with increased sports value, the average value, towards the inferior limit of heart rate, being the expression

of the bio-positive adaptation to effort, which means an economical work of the heart at rest. Bradycardia in case of athletes is secondary to the increase in the systolic volume, allowing a constant, basic heart debit [12].

WHO admits the following values of blood pressure at rest: BP max. 100-140 mmHg; BP min. 60-90 mmHg; differential BP 40-50 mmHg. and average BP of 90-100 mmHg., for both athletes and non-athletes [Muşat, 2009]. Blood pressure at rest, in case of human subjects within our research, registered values within the range approved by WHO.

- Cardiovascular indices during effort

Table 6. The martinet test– initial and final test – average values of heart rate

	Clinostatism	Orthostatism	Effort	Post effort 1 min	Post effort 3 min	Post effort 5 min	Dorgo index
Initial test	64.7	73.4	107.3	89.6	64.6	64.6	-1.66
Final test	60.3	70.5	103.8	84.71	60.3	60.3	-3.43
Reference values	60-90 b/min	+ 10-12 b/min					B (-5-0)

The initial Martinet test indicated normal values of heart rate at rest, between 60 and 90 beats/minute. There were values of 60- 80 beats/minute in clinostatim, and in orthostatism the average values of heart rate indicated an increase by 10-12 beats/minute [9-14].

The values of post-effort heart rate registered a 40-50%, increase, without exceeding 120 beats/minute. The HR values came back to normal three minutes post-effort in case of all the athletes, which shows a good functional state.

The Dorgo index of recovery was calculated at the end of the test, using the average HR values. The index had values between -2.05 and -0.01, with a -1.66 average; the GOOD qualifier [8-10].

The final Martinet test showed an improvement of heart rate at rest by 5-10 beats/minute, with values between 60 and 75 beats/minute. The average values of post-effort heart rate have also improved – 98-108 beats/minute, without exceeding 120 beats/minute.

The Dorgo index of recovery, calculated for average HR vales during the intermediary tests, was also positively altered, with values between -3.95 and 1.46, with GOOD qualifier.

The cardiovascular regulation tests are indicators of body adaptation to effort, and only indirectly of the effort capacity, allowing to assess the effectiveness of training methods used for a certain amount of time [8-13]. The quality of cardiovascular regulation is the better, the lower

the heart rate and blood pressure values on the same effort scale, the sooner values at rest come back to normal, and if the Dorgo values are negative [9, 13].

4. Conclusions

- After the halotherapy treatment, there was an increase in the respiratory volumes (VC, MEVS, V max., PEF) for all subjects investigated. There was also an increase in the percentage of subjects with “excellent” respiratory index
- As concerns the breathing system, there was an improvement in the breathing mechanics, as well as an increase in the oxygen saturation of arterial blood and in the resistance to apnea and hypoxia.
- Due to the recovery, which took place in mediums with saline aerosols, the breathing was more effective, both regarding the gaseous exchanges, and using tissue-level oxygen.
- The assessment of standard cardiovascular system during effort, the Martinet test, indicated better values during the final tests, and the cardiovascular assessment tests are indicators of body adaptation to effort and only indirectly of the effort capacity, allowing to assess the effectiveness of training methods used for a certain amount of time.
- We have also noticed a decrease in the heart rate and breathing rate during the training session effort, which was possible due to the cardiovascular adaptation and regulation of athletes’ organism.

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CARIES DETECTORS DYES IN EARLY DIAGNOSIS AND TREATMENT OF DENTAL CARIES

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Abstract: *Despite the progresses of the modern dentistry, the carious disease is still affecting a large number of peoples. The caries detectors would be helpful for diagnosis of early enamel caries as well as dentinal caries. The study focused on the role of caries detectors on objective criteria of assessment of the caries preparation, the early diagnosis of the incipient caries as well as monitorisation of the remineralising processes. The study used product Color-test of the Vladmiva (Rusia): solution and gel. The study was performed on 25 patients age 15-38 with medium and high level of cariogenic status. The statistical results show the practical importance of the caries detectors for the conservative treatment of the dental caries, with different degree of penetration in dental tissues. It also allow the monitorisation of the success of the non-invasive or minimal invasive treatment. The use of the caries detectors allow minimal preparation of the dental issues, accordingly to modern principles of the actual dentistry.*

Keywords: *incipient caries, caries detectors, remineralisation therapy.*

1. Introduction

Although many dentists know modern principles of dental caries therapy, the use of dental caries indicators is very limited in current practice (1,3). Today is more important that restorative dentistry to stand on minimal invasive approach, without idle sacrifices of healty dental tissues (2). The role of the research is to highlight dental caries in incipient stages, with caries detectors dyes and to monitor their evolution after remineralisation therapy.

2. Materials and methods.

The caries detector dyes Color-test (Vladmiva, Rusia) is used in study. The diagnostic and monitorisation of the incipient dental caries were made through Borovschii-Axamit method. This method allows us to assess depth and surface of demineralisation area. In study were included 36 patients and 65 demineralisation focuses (white-spot). These

demineralisation areas were divided in 4 lots: lot 1- 18 teeth (10 patients) with remineralisation therapy by fluor gel; lot 2- 15 teeth (8 patients) with remineralisation therapy by calcium, phosphat and fluor; lot 3- 17 teeth (12 patients) with remineralisation therapy by calcium-phosphat gel; lot 4 (6 patients)- 15 teeth without remineralisation therapy (witness lot). The patients were monitorised for 12 months, with assessment periodes at 6 and 12 months.

3. Results

The evolutions of the caries detector dyes intensity and of the demineralisation surfaces in the four lots are synthesised in tables I and II.

Table 1. The evolution of the caries detector dyes

	LOT 1 – F (Average values)	LOT 2 – CaFP (Average values)	LOT 3 – CaP (Average values)	LOT 4 – witness (Average values)
Initial	6,06	5,87	5,59	6,80
First application	4,94 <i>Decreasing 18,34%</i>	4,40 <i>Decreasing 24,99%</i>	2,71 <i>Decreasing 51,56%</i>	
After 2 weeks	4,72 <i>Decreasing 22,00%</i>	1,20 <i>Decreasing 79,50%</i>	3,06 <i>Decreasing 45,25%</i>	6,80 <i>Increasing 0,00%</i>
After 6 months	3,72 <i>Decreasing 38,50%</i>	3,07 <i>Decreasing 47,70%</i>	3,47 <i>Decreasing 37,88%</i>	7,07 <i>Increasing 3,92%</i>
After 12 months	1,78 <i>Decreasing 70,59%</i>	2,40 <i>Decreasing 59,06%</i>	1,47 <i>Decreasing 73,66%</i>	7,80 <i>Increasing 14,71%</i>

Table 2. Total surfaces of the demineralisation areas

	LOT 1 – F Total values	LOT 2 – CaFP Total values	LOT 3 – CaP Total values	LOT 4 witness Total values
Total surfaces (mm²)	54.50	48.20	51,80	46,90
Total surfaces- 6 months	46.90 <i>Decreasing 13.94%</i>	41,70 <i>Decreasing 13,49%</i>	48,90 <i>Decreasing 5,60%</i>	51,70 <i>Increasing 10,23%</i>
Total surfaces- after 12 months	42.30 <i>Decreasing 22.39%</i>	37,60 <i>Decreasing 21,99%</i>	43,40 <i>Decreasing 16,22%</i>	58,90 <i>Increasing 25,59%</i>

The results regarding **depth of the demineralisation focuses (colour intensity)** were different related to the four lots. For **lot 1 (F)** the results consisted in significant decreasing of colour intensity with 17,2% after first application, with 20,8% after 2 weeks, with 28,7% after 1 month and with 70,5% (after 6 months). For **lot 2 (CaPF)** the results consisted in colour intensity decreasing with 27% after first application, with 81% after 2 weeks, with 45,6% after 1 month and with 53,7% after 6 months. For **lot 3 (CaP)** the results consisted in colour intensity decreasing with 48,7% after first application, with 37,9% after 2 weeks, with 24,3% after 1 month and small increasing after 6 months. For **lot 4 (witness lot)** the results consisted in colour intensity increasing with 3,92% after 6 months and with 14,71% after 12 months.

The results regarding **surfaces of the demineralisation focuses (colour intensity)** were different related to the four lots. For **lot 1 (F)** the results consisted in significant decreasing from 54,50 mm to 42,30 mm (decreasing with 22,39%), for **lot 2 (CaPF)** the results consisted in decreasing from 48,20 mm to 37,60 mm (decreasing 21,99%), for **lot 3 (CaP)** the results consisted in decreasing from 51,80 mm to 43,40 mm (decreasing with 16,22%), and for **lot 4** there is a increasing with 25,59% of the total demineralisation surface.

4. Clinical cases



Fig. 1. Incipient caries detection to a patient with fixed orthodontic treatment



Fig. 2. Teeth 3.6, 3.7. Incipient occlusal caries detection



Fig. 3. Tooth 3.6. The aspect of the cavity after preparation

5. Discussions

Caries detector dyes are useful for early detection of the incipient dental caries in pits, fissures and smooth dental surfaces (4,5). The retention of the caries detector dyes allows precise assessment of the depth and surface for demineralisation areas, through assessment of the colour intensity and use of a graph paper (6). The caries detector dyes are an useful instrument for detection of secondary dental caries and fissures or microfractures (1,3). The scientific progress of the modern dentistry allows more effective caries detector dyes that can be visible in special spectrum. In fact, these caries detector dyes make possible a less invasive treatment (1,6).

6. Conclusions

The caries detector dyes are extremely useful in early detection of incipient dental caries located in pits, fissures and smooth dental surfaces.

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THE INFLUENCE OF WATER ADSORPTION ON CERVICAL LEAKAGE OF RESTORATIONS WITH NANOHYBRID COMPOSITE RESIN

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Abstract: The aim of this study was to evaluate the influence of water storage on the cervical leakage of composite restorations. 30 extracted human teeth were used in this study. Class II cavities were prepared and restored using nanohybrid composite and a total-etch adhesive system. The teeth were randomly divided in three groups, each of them being stored in deionized water for one hour, 24 hours and 7 days. After the storage period, the teeth were immersed in methylen blue 1%, for 24 hours. Specimens were axially cut and the dye penetration within the cervical interface was evaluated using optic microscope. Cervical leakages were statistically compared. The mean value of dye penetration decreased from 0,39 mm to 0,27 mm but this reduction was neither statistically significant nor clinically relevant. Hygroscopic expansion cannot significantly improve the sealing in cervical margins of composite restorations.

Keywords: hygroscopic adsorption, nanohybrid composite, cervical leakage.

1. Introduction

Polymerization shrinkage of resin-based materials causes significant tension within the walls of the dental restoration, which sometimes results in adhesive failure at the interface between the material and the tooth tissues. Though the sealing is relatively good in enamel margin immediately after restoration, at the cervical margin, seal is still inconstant due to the particularities of the dental support and inappropriate access and isolation during the restorative procedure. It has been shown that adsorption of water in resin materials can cause a phenomenon of expansion that can partially compensate for the polymerization shrinkage. Numerous studies have concluded that the hygroscopic expansion can reduce the marginal hiatus in restorations with resin-based materials [1, 2, 3, 4, 5]. This effect would be especially important in the cervical area, which is particularly susceptible to leakage.

This study aimed to evaluate the influence of water storage on the cervical leakage of a nanohybrid composite applied with a total etch adhesive system.

2. Materials and Methods

The study group consisted of 30 freshly sound teeth extracted for orthodontic or periodontal reasons. Class II cavities (3 mm width and 2 mm depth) were prepared with cervical margin placed 1mm below the cement-enamel junction. Cavities were restored with a nanohybrid composite - Ceramic Mono-X (Dentsply DeTrey) applied with the total etch technique using the adhesive system Prime & Bond NT (Dentsply DeTrey). The restored teeth were separated randomly into 3 groups of 10 teeth. Group I was stored in distilled water for one hour, group II for 24 hours and group III for 7 days. After the hydrating period, the apex of the teeth was sealed with a resin and the teeth were isolated with varnish covering all surfaces exposed up to approximately 1mm outside the contour restoration. Then the specimens were stored for 24 hours in solution of methylene blue 1%. After staining, the teeth were axial sectioned through the mass restorations. Samples were examined in optical microscope Neophot 21, in order to assess the marginal leakage at the cervical margins. The leakage scores were then compared using statistical analysis.

3. Results

The average values of marginal leakage were 0.39 mm for the group hydrated for one hour, 0.29 mm for the batch of samples stored for 48 hours, 0.27 mm for the samples hydrated for one week (table I).

Table 1. Leakage scores in cervical margins (mm)

Leakage (mm)	Group I	Group II	Group III
1	0,29	0,18	0
2	0,26	0,39	0,32
3	0,06	0,31	0
4	0,37	0,21	0,57
5	0,39	0,17	0,4
6	0,53	0	0,12
7	0,56	0,18	0,25
8	0,48	0,5	0,35
9	0,44	0,51	0,29
10	0,47	0,41	0,39
Mean value	0,39	0,29	0,27

None of the samples hydrated for an hour has presented a satisfactory marginal sealing, while at the end of the other two hydrating periods, only one respectively two samples scored 0 for marginal leakage at the cervical margin (Fig. 1, 2, 3).

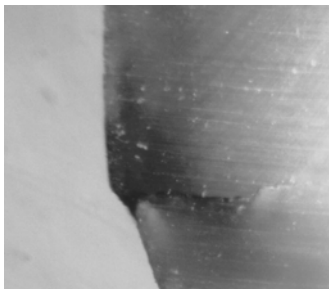


Fig. 1. Image of cervical area of one specimen hydrated for 1 hour. Notice the significant marginal leakage. Measurement indicated 0,56mm dye penetration, which is the highest value of leakage recorded in this study group.

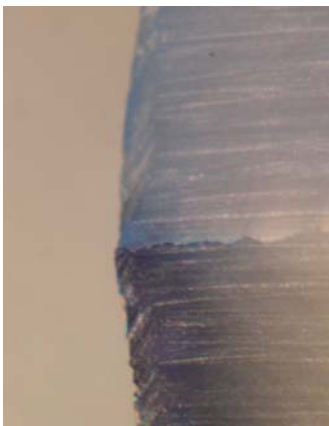


Fig. 2. Image of cervical area of one specimen hydrated for 24 hours. No penetration of methylene blue was observed at the cervical margin.

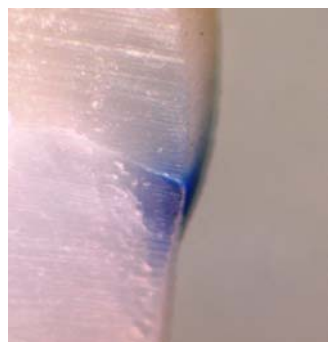


Fig. 3. Image of cervical area of one specimen hydrated for 7 days. Measurement indicated 0,25 mm dye penetration, score which is close to the mean value of leakage for this group.

The decrease of marginal leakage was approximately 0.10 mm after 24 hours, respectively 0.12 mm after one week of hydration.

Shapiro-Wilk test was used to verify the distribution normality, because of the reduced number of specimens included in the study. No deviations from normal distribution were found, allowing the application of parametric statistical tests. Leven test led to the conclusion that the dispersions within the three groups were homogeneous. Therefore, F test and post hoc Bonferroni test were used to test the differences between the 3 groups (Table II, III). Analysis shows no significant differences in the statistical values between the leakage scores, depending on the duration of the hydration period.

Table 2. Results for ANOVA analysis

	Sum of Squares	df	Mean Square	F	p
Between Groups	,078	2	,039	1,418	,260
Within Groups	,747	27	,028		
Total	,825	29			

Table 3. Bonferroni test results

(I) nrert	(J) nrert	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
I	II	,09900	,07439	,583	-,0909	,2889
	III	,11600	,07439	,392	-,0739	,3059
II	I	-,09900	,07439	,583	-,2889	,0909
	III	,01700	,07439	1,000	-,1729	,2069
III	I	-,11600	,07439	,392	-,3059	,0739
	II	-,01700	,07439	1,000	-,2069	,1729

4. Discussion

The results have demonstrated once again the difficulties of sealing in cervical margins even when the technique is optimum as it was in this in

vitro study that eliminated the clinical difficulties related to access and isolation. Immediately after the restoration, none of the specimens presented a perfect marginal seal, the values of the dye leakage ranging between 0.29 and 0.56 mm. After hydrating the restorations, the leakage had a downward trend that was most obvious after the first 24 hours. The results are consistent with the findings of numerous studies in literature and can be explained by hygroscopic expansion mechanisms. Interaction between composite resin and water results in both water adsorption and dissolution of some components of the material [7, 8, 9]. Decreased marginal leakage secondary to water storage supports the hypothesis that hygroscopic expansion could partly compensate the contraction of the material, improving the restoration sealing [1, 2, 3, 4, 5, 6].

However, the reduction of the marginal hiatus secondary to the adsorption of water does not appear to be statistically significant and clinically relevant - only 0.10 and 0.12 mm. In 8 cases of 10, the dye leakages persist and the average value is 0.27 mm even after 7 days of hydration without termocycling. The results can be explained by the significant difference between the polymerization shrinkage - more than 2% [10] and reduced hygroscopic expansion (0.5% according to the producer) due to the hydrophobic monomers and decrease permeability of the nanohybrid composite.

5. Conclusions

The results of this study support the hypothesis that sealing of the cervical margin in nanohybrid composite restorations is not constant, when polymerization shrinkage is not adequately controlled using appropriate techniques. Hygroscopic expansion appears to reduce cervical leakage but this reduction is neither statistically significant nor clinically relevant. Hygroscopic expansion is therefore not a guarantee of compensation of polymerization shrinkage and does not seal a marginal hiatus when occurred.

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SYNTHESIS OF METALLIC NANOTUBES ARRAYS IN POROUS ANODIC ALUMINUM OXIDE TEMPLATE

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Abstract: *Nanotubes have attracted intensive interest because of their fundamental significance and potential applications in nanoscale devices, sensors, delivery, catalysts and energy storage/conversion.*

In this paper, we report an easy method for the synthesis of metallic nanotubes (Pb, Co and Ni) by using a sol-gel method and anodic aluminum oxide (AAO) templates. Metallic nanotubes by ultrasonic vibrations were grown, the colloidal solution has penetrated into the pores of AAO substrate. The surface morphology and the structure of the AAO template and metallic nanotubes were investigated by using scanning electron microscopy.

The results showed that the length and outside diameter of nanotubes are determined by the thickness and pore size of AAO templates.

Keywords: *Keywords: metallic nanotubes, anodic aluminium oxide (AAO), sol-gel, metal*

1. Introduction

In the last decade, the field of preparation of materials with low dimensionality and the investigation of their properties attracted more and more scientists [1].

Since the discovery of carbon nanotubes [2], hollow nanotubes have attracted considerable attention due to their fundamental significance and potential application in nanoscale devices, sensors, delivery, catalysts and energy storage/conversion [3]. In particular, metallic nanotubes raise special interest because of their conductivity, catalysis, magnetism and the feasibility of chemically modifying their outer/inner surfaces and edges.

The template approach represents an interesting path towards preparation of nanoobjects with controlled morphological properties mainly due to the fact that by appropriate choosing of host templates, the shape and dimension of the prepared structures are precisely determined.

Martin and al [3],[4] were manufactured for the first time Au nanotubes by using Au electro deposition in the pores of an anode of AAO (anodized aluminum oxide) aluminum oxide. The Au nanotubes have had a length of about 2µm.

Using co-electro deposition and methods of electrochemical corrosion, Wang and colleagues [3] have synthesized nickel nanotubes on a

hard support of AAO aluminum oxide. Changing the electro deposition parameters can be controlled the length and thickness wall of the nanotube.

Mu and others [5] have developed a method in many steps of replication of the support using electro deposition to manufacture nanotubes. They have managed to increase the ratio between width and height to a very large value and also managed to control the uniformity of thickness and diameter.

Although nanotubes produced by Wang and Mu are much longer and with a degree of order and uniformity in terms of wall thickness and diameter than other nanotubes obtained through electro deposition, both methods are complicated.

Sol-gel method is simple and easy to use in preparation of one-dimensional nanomaterials and has successfully been used in the manufacture of nanotubes with oxides.[3]

2. Methods

In this paper, we report an easy method for the synthesis of metallic nanotubes (Pb, Co and Ni) by using a sol-gel method and anodic aluminum oxide (AAO) templates. Metallic nanotubes were grown by pulsed electrochemical deposition of metals in template (matrix) AAO pores.

2.1. Porous aluminum oxide template preparation (matrix)

High purity aluminum sheets (99.999%, 30 × 20 mm) were used as the starting material for preparation of anodic porous alumina template.

An aluminum foil (Al) (99,99% purity) was skimmed and then heat-treated at the temperature of 500°C about 5 hours in air. The foil obtained after the treatment has been used as anode in a aqueous solution of oxalic acid ($H_2C_2O_4$) of 3% concentration, being subjected to a constant potential of 45V DC voltage, at the temperature of 30°C for 10 hours. Then the sample was etched by $CuCl_2$ solution to remove the aluminum substrate.

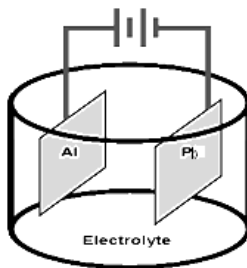


Fig. 1.Apparatus for anodize aluminum in electrolyte (e.g. Oxalic Acid)

Finally, in order to widen the pore diameter, the AAO template was immersed in a solution of 6 wt% H_3PO_4 for 40 min at 30°C. After this process, the thickness of the obtained template is about 100 μm , the diameter of the pores is adjusted to about 100 nm, and the aspect ratio of the pores is about 1000. Considering simplicity, the AAO template was made by a one-step, not a two-step, anodizing process [3].

2.2. Preparation of colloidal solution

The colloidal solutions were obtained using ethylene glycol as solvent, citric acid as corrosion agent and dissolved salts of the corresponding metals as solutions.

Metallic salts used to produce Pb, Ni and Co solutions are: lead acetate, nickel acetate and cobalt acetate.

To obtain the colloidal solution, the solution was heated at 50°C for 8 hours using a thermostat. After that it was obtained a solution of 0,8M with a certain viscosity, by adding several drops of distilled water (only if necessary).

Process 1.

At the beginning the substrate was submerged in the colloidal solution for 15 minutes. With ultrasonic vibrations, the colloidal solution has penetrated into the pores of AAO substrate. The fabrication process is sketched in figure 2.

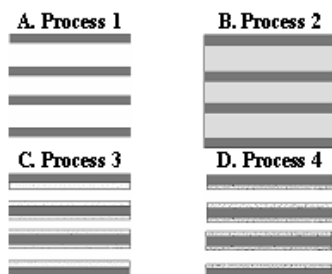


Fig. 2. The process of manufacturing metallic nanotubes: (A) AAO matrix empty; (B) AAO matrix filled with solution; (C) metal oxide nanotubes inside the AAO, obtained by preheating; (D) metallic nanotubes inside AAO obtained by the hydrogen reduction.

Process 2.

The AAO support are incorporated in the pores the colloidal solution, has been removed from the colloidal solution and then the support was heated from room temperature to 400°C.

In order to obtain nanotubes with the proper wall thickness, the

entire ‘dip–anneal–dip’ process was repeated three times for each sample.

After the second process was composed the nanotubes from the metallic oxides into the pores of the AAO substrate.

Process 3.

Finally, nanotubes have been obtained by additional burning at 560°C for one hour, except lead nanotubes that were burned at 340°C.

3. Results

The surface morphology and the structure of the AAO template and metallic nanotubes were investigated by using scanning electron microscopy.

Figure 3 shows SEM image of a typical porous alumina film formed by anodization used as a template for fabrication of aluminum nanotube. This figure shows that the surface of the resulting film is composed of pores with narrow or nearly closed entrance.

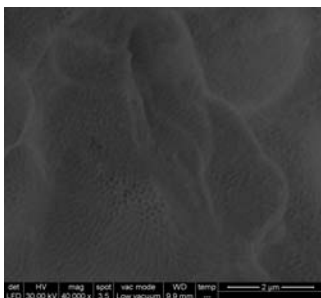


Fig. 3. SEM image of the top surface view of the typical porous alumina film after anodization in a 3% oxalic acid solution at 30°C at 40 V.

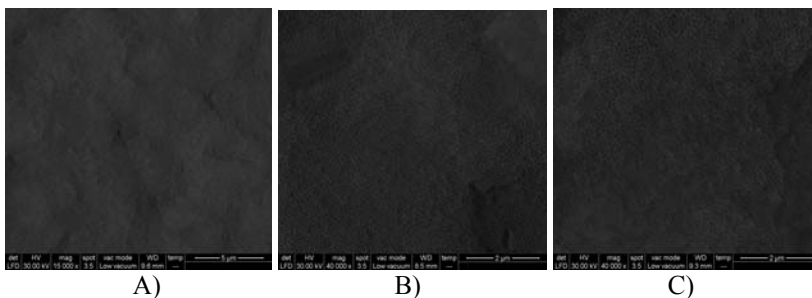


Fig.4. SEM images for anodizing the aluminum in oxalic acid, for 10h at 40V: A) with lead precipitation from the lead acetate precursor; B) with nickel precipitation from the nickel acetate precursor; C) with cobalt precipitation from cobalt acetate precursor.

The diameter of the pores is about 100 nm. With increasing of pore widening time, the diameter of the pores increases, but the interpore distance does not change. Thus the outer diameter of the obtained nanotubes can be adjusted through the pore diameter by controlling the AAO widening process. Though the pore array within the AAO template is not well ordered, due to the one-step anodizing process, the pore diameter is approximately uniform. Fortunately, the regularity of the nanotube array has little effect on its performance.

SEM images and EDX analysis belonging to samples obtained after electrochemical deposition of Pb, Co and Ni respectively (figures 3, 4, 5, 6) on AAO membranes evidenced that the deposition process took place. In order to analyze the sizes and structure of nanotubes HRTEM investigations are necessary.

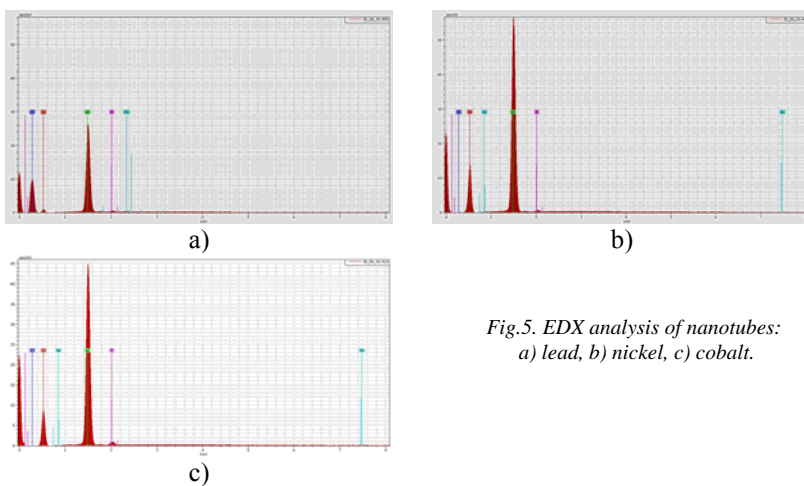


Fig.5. EDX analysis of nanotubes: a) lead, b) nickel, c) cobalt.

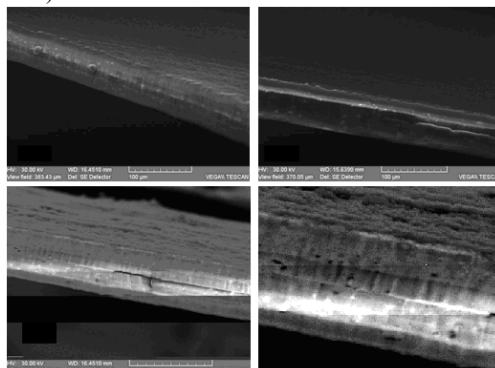


Fig.6. Cross-section SEM images of nickel nanotubes.

4. Conclusions

In summary, we have developed a universal sol-gel method for synthesizing metal nanotubes. The outer diameter of the nanotubes, equal to the pore diameter of the AAO template, can be adjusted by controlling the AAO widening process, meanwhile the wall thickness of the nanotubes can be adjusted by controlling the concentration of the metal ion(s) in the sol and the 'dip-anneal-dip' times. The nanotubes obtained are uniform in wall thickness. The aluminum anodizing method to obtain the matrix for nanotubes can be realized in laboratory.

This method can be used to manufacture a variety of metallic nanotubes with different chemical compositions.

The small amount of deposited material did not allow a structural analysis of nanotubes.

Applications of the metallic nanotubes with magnetic and conductor properties:

- sensors and microsensors for gases;
- catalysts of big surface in chemical, biochemical processes;
- nanodevices and nanostructures of data hold;
- The conduction and controlled discharge of the risk drugs (chemotherapeutics etc.).

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STUDY REGARDING THE EFFICIENCY OF DENTAL MATRIX USED IN PROXIMAL CARIES LESIONS RESTORATION

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Abstract: *The aim of the study was to compare the efficiency of 8 different types of dental matrix usually used in dental practice for proximal caries restoration. Material and method. The study took place in the UMF „Gr.T.Popa“ simulation lab. On 8 mandibular molars were prepared class II cavities. The cavities were then restored with a composite resin (Ceram X mono, Dentsply) using 8 different types of metal and translucent dental matrix. The fillings were analysed according to 8 different criterions. Results. The best results in the most criterions used in evaluation (marginal adaptation, proximal face morphological restoration, contact point restoration, cervical margin adaptation) were obtained when metal matrix were used. The poorest results were obtained using universal translucent strips. Conclusions. Metal matrix are more efficient in proximal cavities restoration with composite resins then translucent matrix and we recommend them in dental practice.*

Keywords: *dental matrix, composite resins, proximal cavities*

1. Introduction

The restoration with composite resins of the proximal cavities on the lateral teeth is a difficult treatment stage. An excellent adaptation of the restoration material to the dental structure is extremely hard to obtain because of the special architecture of the cavity and also because of the necessity to reconstruct particular elements of dental morphology (the contact point with the neighbour tooth correctly accomplished and placed, an adequate morphology of the absent face, contact points with the antagonist tooth correctly disposed).

The aim of the present study was to compare the efficiency of eight matrix and portmatrix systems usually used in dental practice in the restoration of the carious lesions situated on the proximal faces of the lateral teeth

2. Materials and methods

The study has been developed at the simulation laboratory of UMF Iași. 8 4.7 teeth have been used, on whose mesial faces there have been prepared cavities with the following features: the gingival margin has been placed at 1 mm up from the enamel-cement junction, the vestibular and oral

walls have been placed 1 mm towards the vestibular and 1 mm towards the oral in relation with the contact area with the neighbour tooth, a fact which can be clinically verified by the free passage of the dental probe, the depth of the cavities (measured at the cervical margin level) was 3 mm, the vestibular and oral margins have been beveled on their entire length with a long flat bevel, with a diamond thinning-out bur, and the occlusional margin has been beveled with an ellipsoidal concave bevel made of a flame-shape diamond bur, the gingival margin has not been beveled because it has been placed at 1 mm up from the enamel-cement junction.

For the restoration of the cavities there have been used the nanocomposite material with ceramics particles Ceram X mono (Dentsply) and the adhesive system XP Bond (Dentsply). To reconstruct the absent proximal face there have been used eight types of matrices and the corresponding portmatrices: the Tofflemire matrix and portmatrix (figure 1), the precontoured Kerr metallic matrix and the Tofflemire portmatrix, the circular metallic matrix with its own fixation system by screw (Kerr Hawe Composite Set), the Palodent metallic matrix with fixation ring (Dentsply) (figure 2), the circular translucent matrix with a fixation device (Kerr) (figure 3), the circular translucent matrix with its own adaptation system by screw (Kerr Hawe Composite Set), the autoadhesive translucent matrix (Dispens-O-Mat Posterior) and the celluloid translucent matrix without portmatrix device. The fixation and the correct adaptation of the matrices in the proximal area have been achieved by placing wood wedges. The work steps have been the classic ones for the restoration with composite resins.



Fig. 1. Tofflemire matrix and portmatrix used in this study



Fig. 2. Palodent metallic matrix with fixation ring



Fig. 3. Circular translucent matrix with a fixation device

Each restoration has been evaluated according to the following criterions: 1. *the adaptation to the vestibular and oral margins* – by visual inspection; 2. *the adaptation to the occlusal margins* –by visual inspection; 3. *the adaptation to the cervical margin* –by visual inspection, after the teeth have been removed from the simulator; 4. *the reconstruction of the morphology of the proximal face* –by visual inspection, after the teeth have been removed from the simulator; 5. *the correct reconstruction of the contact point* –using the floss and by visual inspection; 6. *the reconstruction of the morphology of the occlusal face* –by visual inspection; 7. *the reconstruction of the embrasures* –by visual inspection; 8. *the comfort of the doctor and the easy utilization* of the matrix system.

For each of the 8 criterions the restorations have been evaluated between 0 and 5, where 0 corresponds to a clinically unacceptable restoration for the respective criterion, and 5 corresponds to a clinically excellent restoration.

3. Results

The results obtained for the 8 matrix systems are presented in Table I.

Table 1. The results obtained for the 8 matrix systems

		Criterions							
		1	2	3	4	5	6	7	8
Matrices	1	4	3	5	5	5	5	3	4
	2	5	4	5	5	5	5	4	4
	3	4	4	5	4	4	4	4	4
	4	5	4	5	5	5	5	4	4
	5	4	5	5	5	4	5	5	4
	6	4	5	5	5	4	4	5	4
	7	4	5	5	5	5	5	4	5
	8	3	5	5	3	4	3	4	5

Regarding the adaptation to the vestibular and oral margins, the best results have been obtained with the metallic and preformed celluloid matrix systems (figure 4). The less convincing results have been obtained with the universal celluloid matrix system.



Fig. 4. Aspect of a restoration having good adaptation to the vestibular and oral margins when preformed celluloid matrix systems was used

Regarding the adaptation to the occlusal margins, good results have been obtained with all types of translucent matrix systems, with overcontours in the case of metallic matrices (figure 5).



Fig. 5. Aspect of a restoration having poor adaptation on occlusal margins when metal matrices were used

Regarding the adaptation to the cervical margin, excellent results have been obtained with all the matrix systems, the use of the wedges proving to be indispensable. Regarding the reconstruction of the morphology of the proximal face, the preformed metallic matrix have been the most efficient one. This type of matrices has also proven to be the most recommended one for the correct reconstruction of the contact point. However, the translucent matrices have been the most efficient in the reconstruction of the morphology of the occlusal face. Regarding the doctor's comfort and the easy utilization, despite the subjective nature of this consideration, we can affirm that the most convenient system has been represented by the universal celluloid matrix system, but this easy

utilization is annulled by the poor results which have been obtained for the other criteria (figure 6).



Fig. 6. Aspect of a restoration having low scores when universal celluloid matrix system was used

Moreover, we must specify that the easiness in employing a system also depends on the doctor's experience in using it, which is acquired in time.

4. Discussions

The matrices (in association with the corresponding portmatrix systems and with the wedges) are absolutely indispensable when it is necessary to restore one or more absent dental faces (Lowe A.H. et al., Qualtrough A.J.E. et al.). Considering the less and less time available for restoration maneuvers, most of the times doctors choose the matrix systems which can be rapidly fixed, without any effort, but which, unfortunately, prove to be incapable to lead to a restoration respecting the required quality standards. It is the case of the universal celluloid matrix, extremely used in practice, but which did not lead to good results in our survey. Nevertheless, the system has a plus regarding the possibility of reconstruction of the morphology of the occlusal face through the direct visibility and of a correct polymerization owing to transparency. The utilization of translucent circular matrix systems provided with their own fixation system offers clear benefits related to a good proximal face contour through the preexistent convexity, to the achievement of an acceptable occlusional embrasure and to the rather good adaptation (with slight overcontours) to the vestibular and oral margins (Demarco F.F. et al.). However, they do not succeed in reconstructing a tight enough point of contact, and this thing is ascribed to the elasticity of the matrix (Loomans B.A.C. et al.). These matrix systems should be preferred to the universal celluloid matrix, particularly since they do not require special fixation devices and since they can be applied extremely easy.

The precontoured metallic matrix systems (Toflemire, Kerr, Palodent), despite the perception that it is difficult to use them (impression which is due especially to the existence of several forms of these matrices and of their manipulation and fixation devices), have proven to be an excellent alternative to reconstruct the proximal cavities on the lateral teeth. Since they are preconformed and rigid, they fulfil all the qualities for the reconstruction of the proximal morphology, of the point of contact and of the embrasures. A minus would be related to the incorrect achievement of the occlusal morphology through the anatomic modelling, but this shortcoming can be corrected in the functional modelling step.

5. Conclusions

The preconformed metallic matrix systems have proven to be much more efficient than the celluloid ones in the restoration of the proximal cavities on lateral teeth with composite resins. This is the reason why we recommend them in the current dental practice.

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NEW PREMÉTALLISED DYE FOR WOOL INDUSTRY WITH LOW ENVIRONMENTAL IMPACT

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Abstract: *This study is mainly concerned with the interaction between a new acid dye and copper ion and its application for wool fibers along with implication over the ecological impact of the wastewaters, resulted after the dyeing process. The synthesized premetallised dye was applied to wool fibers under acidic dyeing conditions, to pH 2 and respectively 5. In order to carry out the dyeing performances in the experimental conditions, the wash, rubbing and light fastness, intensity of colour, expressed by K/S constant, dyebath exhaustions were evaluated. Also, using SEM, the possible changes of the wool fibers surface after the dyeing process with new synthesized premetallised dye were investigated. The metal distribution on/into the wool fibers registered by EDX, XPS, respectively TEM was carried out. The tensile strengths of dyed wool samples were recorded before and after dyeing process*

Keywords: *premetallised dye, EDX, TEM, XPS*

1. Introduction

The complexation process of organic compounds with metal atoms is widely exploited in many fields, and the complexes are useful in various textile applications [1-5].

As a result of this reaction dyes molecule can form strong links with the fiber and they tend to have low migration properties. They could be divided in a distinctly types of 1:1, 1:2 metal complex dye, unsulphonated, monosulphonated and disulphonated. The disulphonated types are the most soluble, have a greater pH dependence and in the end, they have a low neutral affinity and require a low pH, in order to obtain good exhaustion of the process bath. Also, they are a very important class of the metal complexes, highlighted by the highest fastness to light and wet treatments (wash and rubbing tests) [6-7].

The most successful metals used in wool dyeing is by far chrome which is followed by the cobalt ion but, in the last period it was proved that these metals can affect the environment in a negative way.

The main concern of scientists is to realise the compounds synthesis with a decreased environmentally impact, which to affect the environment as less it's possible. For dyes which contain metals in their structure it's important that they improve the dyeing performances, but in the same time their presence in the wastewaters in a high amount can cause many unexpected effects on the life from aquatic system and over the soil fertility.

In general, the heavy metals are hardly soluble or insoluble in waters systems, and their concentration depends on a series of parameters as: pH, redox potential, the organic matter content and the amount of metal present in the solution. Also, the presence of the heavy metals in the dyes structure plays an important role in their aquatic toxicity evaluation[8-9].

This concept, along with necessity of the replacement of chromium salts leads to consideration of other metallic ions as complexing reagent [10].

In this paper, was studied the dyeing behavior of the new synthesized premetallised dye derived from a azoic dyes, together with the dyeing performances investigation.

2. Experimental part

2.1. Materials

The dye ligand was synthesized and tested for protein substrates, exhibiting a good affinity for wool fibers (fig.1.a) [11-12]. The monoazo ligand could be framed in the azo-compounds category which have solubilising sulphonic groups which gives the solubility in the waters systems, and specific hidroxy groups which are localized in *orto* position to the azo groups, capable to give the hydrogen proton, leading in this way with metal ion to the metal complex formation.

The reaction of two moles of bidentate system with one equivalent of metal, leads to the symmetrical structure of the resulted complexed dye, which was synthesized and characterized in order to obtain the premetallised dyes, and further tested in technological processes from textile industry [13]. The chemical structure of the synthesized premetallised dyes is shown in the figure 2.

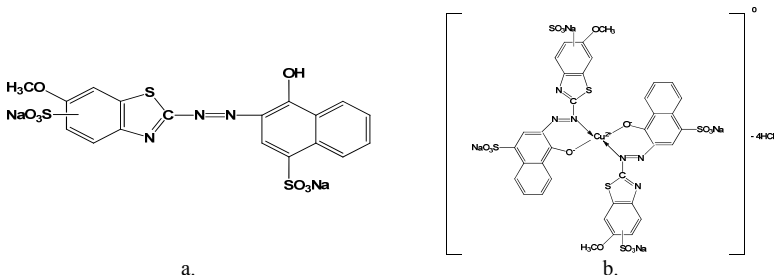


Fig.1. Chemical structure of studied compounds: a. – HL, b. - CuL₂

2.2. Dyeing procedure

Dyeing process was achieved on wool untreated fabric and was performed in a Mathis „Polycolor P4702” equipment, at acid medium – pH=2 and pH=5, using liquor ratio 100:1, in according with diagram shown in figure 2.

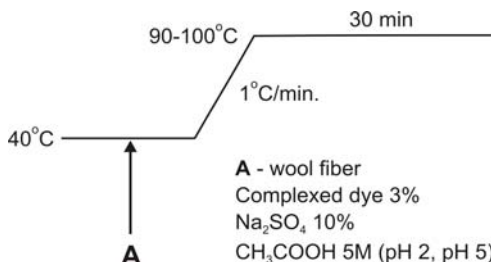


Fig. 2. The dyeing diagram used in dyeing process

2.3. Methods

The evaluation of the dyeing performances was realised according with the followed standards: SR EN ISO 105-C06 for washing strengths, SR EN ISO 105-X12 for friction (wet and dry) fastness and SR EN ISO 105-B01 for light fastness. K/S constant and the chromatic parameters were recorded automatically using Spectroflash 300[®] spectrophotometer Data color Company, based on Micromatch^R program. All of these tests were analysed compared with those results obtained for fibers dyed with acid dye.

X-ray photoelectron spectroscopic (XPS) characterization was carried out using a Kratos Ultra system with a monochromatized Al K_α X-ray source.

The possible morphological changes occurred by dyeing process with studied compounds salts were accomplish using a scanning electronic

microscope S-3000 N of HITACHI with 15 UV, under vacuum condition, equipped with - X-ray dispersion system.

3. Results and discussions

Table 1 contain the obtained results for dyeing performances expressed by tinctorial strengths for dyed samples at different pH in comparison with uncomplexed and premetallised dyes.

Analyzing the resulted values obtained for both pH values can be concluded that the complexation process has an important influence in the dyeing process, as certifying the fact that the improved values were obtained when premetallised dye was used.

Table 1. The tinctorial strenghts obtained from dyed samples

Compound	pH	Tintorial strenghts			
		Friction		Washing	Light
		Wet	Dry		
HL	2	3-4	3-4	3	4
	5	3	3-4	3	3-4
CuL ₂	2	4-5	4-5	4-5	5-6
	5	4	4	4-5	5

Also, as can be observed form table 2, the dyeing capacity is practically enhanced by using lower pH values, the highest intensity dyeing being achieved at pH=2, concluding that the both dyes can be considered having average capacity leveling.

The chromatic parameters showed that the complexation process and the pH values lead to a slightly change in the colour of the samples (Table 2).

Table 2. The chromatic parameters, K/S, and exhaustion obtained for each case taken into account

Sample	pH	Chomatic parameters			K/S	Exhaustion [%]
		L*	a*	b*		
HL	2	33.86	29.40	-9.11	9.14	56
		28.44	13.03	-9.94	7.04	78
CuL ₂	5	29.12	14.51	-2.70	7.46	93
		30.28	9.07	-9.75	6.05	84

In all cases, $L^* > 0$, but the obtained values showed that the samples dyed with premetallised dye are darker compared with samples dyed with uncomplexed dye. For both studied cases (uncomplexed and premetallised dye) and disregarding of the used pH in the dyeing process,

chromatic parameter $a^* > 0$ and $b^* < 0$, which carried out that the samples could be framed in the fourth trigonometric quadrant, the samples color being in average of blue-purple-red domain of colours.

Because of the small amount of the metal on the surface of dyed sample with premetallised dye, EDX was unable to detect the metal distribution on the fiber's surface. In addition, the metal distribution was achieved by XPS (Fig. 3.a), which is an argument that the metal exist inside of the dye structure. TEM investigation as could be seen from the above picture shows a uniform distribution of the metal into the cortex (Fig. 3.b).

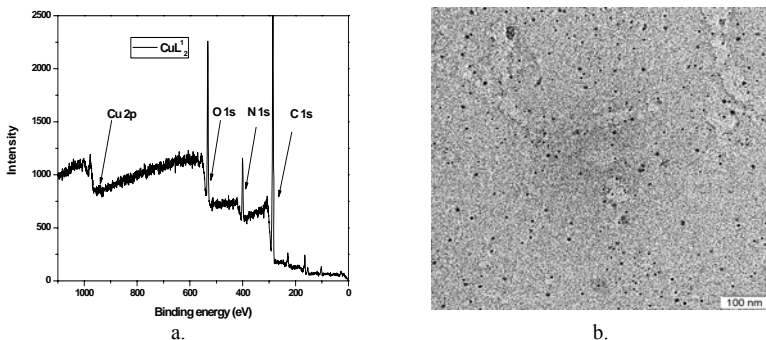


Fig. 3. The distribution of the metal: a.- on the surface of the dyed wool fibers achieved by XPS, b.- into the dyed wool fibers achieved by TEM

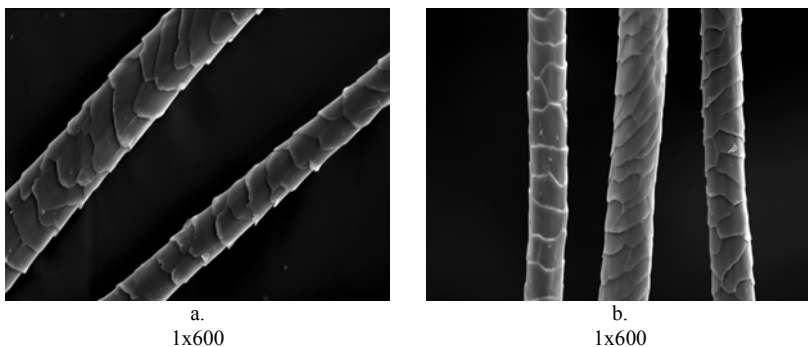


Fig. 4. SEM images obtained from dyed samples: a.- pH 2, b.- pH 5

As could be observed, the influence of the different pH values in the dyeing bath and also the treatment conditions over the wool surface is not detected (Fig. 4.a,b). In conclusion, the use of these premetallated dyes in mentioned dyeing procedure does not lead to dyed wool surface morphology modification.

4. Conclusions

For dyeing technological process was chosen wool fabric, which is a natural fiber, and, in addition, the dyeing process don't involved maximal changes for the implementation.

The results evaluation shows that the dyeing with synthesized premetallised dye could improve the features of the dyed wool fibers, the properties being slightly modified after the complexation process.

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NEW ASPECTS ON THE ANTIBACTERIAL ACTIVITY OF ZnO DISPERSED NANOPARTICLES INTO SBA-15

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Abstract: Objectives of this study was to estimate the ability of antimicrobial activity of ZnO/clinoptilolite and ZnO/SBA 15. We investigated their antibacterial activity in liquid media. The cells of *Escherichia coli* DH5 α in the samples treated with different concentration ZnO/clinoptilolite and ZnO/SBA 15 per ml.

Keywords: *Escherichia Coli*, ZnO, SBA-15, antimicrobial

1. Introduction

Inorganic materials such as metal and metal oxides have attracted lots of attention over the past decade due to their ability to withstand harsh process conditions[1,2]. Of the inorganic materials, metal oxides such as TiO₂, ZnO, MgO and CaO are of particular interest as they are not only stable under harsh process conditions but also generally regarded as safe materials to human beings and animals [1,3]. The use of nanoparticles of silver and zinc oxide has been seen as a viable solution to stop infectious diseases due to the antimicrobial properties of these nanoparticles. The intrinsic properties of a metal nanoparticle are mainly determined by size, shape, composition, crystallinity and morphology [4].

Outbreaks of foodborne pathogens such as *Escherichia coli* continue to draw public attention to food safety. There is a need to develop new antimicrobials to ensure food safety and extend shelf life. The use of antimicrobial agents directly added to foods or through antimicrobial packaging is one effective approach. In recent years, the use of inorganic antimicrobial agents in nonfood applications has attracted interest for the control of microbes. In contact with water contaminated with various bacteria, bacterial inhibition occurs at the surface of zeolite-bearing shown

by a three-dimensional mechanism of action, so that charge zeolite is available to control microbial growth. [5,6].

In this study ZnO nanoparticles have been incorporated into the structure of SBA-15. The antibacterial effect was studied of different ZnO/SBA-15 samples for *Escherichia coli*.

In contact with water contaminated with various bacteria, bacterial inhibition occurs at the surface of zeolite-bearing shown by a three-dimensional mechanism of action, so that charge zeolite is available to control microbial growth.

2. Experimental

Preparation of ZnO/SBA-15

ZnO nanoparticles were obtained by sol-gel method. Prepare a clear ethanolic solution (50 mL) containing zinc acetate Zn (Zn (ac)₂ · 2 H₂O, 1.0975g), magnetic stirring and refluxing at 70°C for ~ 2hours. Separately, 0.29g LiOH · H₂O were dissolved in ethanol (50 mL) at room temperature and were gradually added, under magnetic stirring over Zn²⁺ ethanolic solution previously cooled to 20°C. Finally, a clear, colorless solution was obtained containing Zn²⁺ and Li⁺. 0.5g supports (SBA-15) was impregnated with the solution obtained, and the mixture was kept in an autoclave at 80 ° C for 12h. Results Samples were left in an oven at 80°C overnight to remove solvent. Transformation of Zn in ZnO precursor was achieved by calcination in air at 550°C for 1 hour with a heating rate 1°C/min.

Resulting samples were analyzed by means of SEM and EDX analysis.

Thus synthesized samples were used to test the antibacterial effect from *E. coli*.

Procedure for determination antimicrobial activity

The ZnO samples were tested to see the effect of antibacterial activity from strain *Escherichia coli* DH5 α (Express T7 Sampler, New England, BioLabs)

In these tests has worked in LB liquid medium. To prepare the environment take 25 g powder (LB) to prepare 1L solution. Since pH affects bacterial growth it must be adjusted to 7.5. After preparing the solution is placed in autoclave at 121 ° C for 30 min for sterilization.

A single bacterial colony *Escherichia coli DH5α* (T7 Express Sampler, New England, BioLabs) strain was used to inoculate a 100 mL LB medium (Roth, Germania) for liquid medium, which was grown 17 hours at 37 °C in a rotary shaker (100 rpm). Preculture thus prepared was used for the following tests.

Solid samples tested at different amounts were incorporated into the 5 mL culture medium and sterilized with it at 121°C for 30 minute, after which it was seeding with 10 µL bacterial inoculum, represented by *Escherichia coli DHα*. Incubation was performed at 37° C for 9 hoursat 100 rpm.

The cell density was determined by reading optical density at 580 nm using a UV-VIS Libra spectrophotometer.

3. Results and discussion

Sample characterization

The SEM images reveal that crystal morphology is composed of flat (blade) and small particles. The particles are closely similar in size and appearance, which suggest that the loading of ZnO do not have effect on the size of the SBA-15 particles.

The EDX results shows that the Si and O are the principal components of the SBA-15 sample. When the SBA-15 was loaded with ZnO constituents are Si, O and Zn.

Nonetheless, the strong zinc signals can be clearly observed in the EDX spectrum of ZnO/SBA-15 as depicted in Fig. 1, confirming the presence of ZnO in SBA-15. Together with the absence of zinc oxide phase in the XRD patterns of ZnO/SBA-15, it is reasonable to believe that the majority of the zinc oxide guest has been well dispersed in the channel of SBA-15; otherwise, the aggregation of ZnO located on the external surface of the host should be detected by XRD technique.[7]

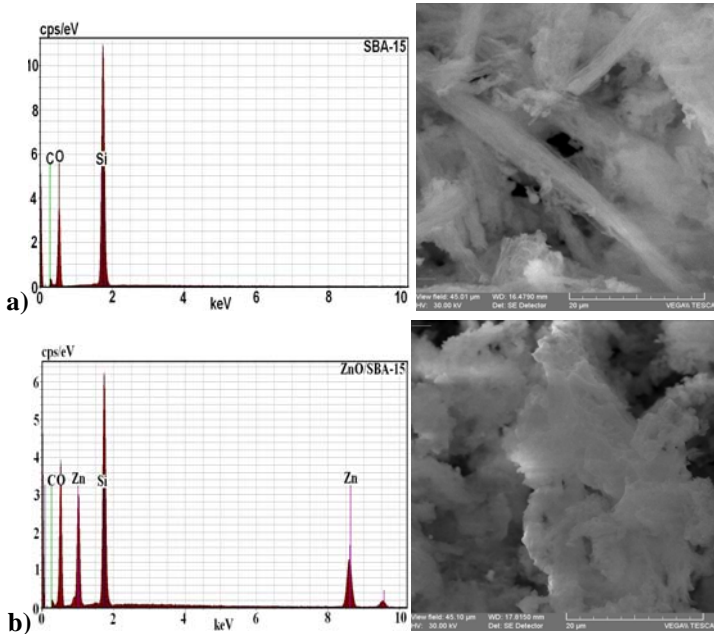


Fig.1. SEM micrographs and EDX spectra of SBA-15 (a) and ZnO/SBA-15 (b)

Study of antimicrobial activity

At lower concentration (less than 0.5 mg/ml) the antibacterial effect was lower, for higher concentration the ZnO/SBA-15 is more prolific. Thus ZnO/SBA-15 is a good candidate with potential antibacterial applications.

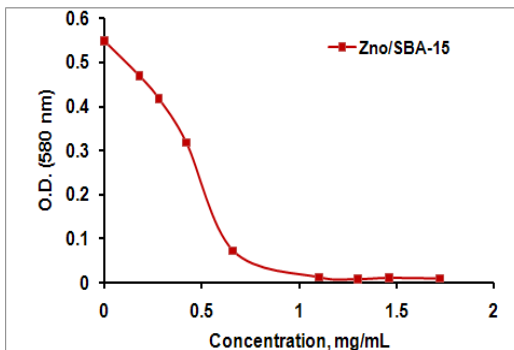


Fig. 2: The optical density of Escherichia coli samples at different concentrations of ZnO/clinoptilolite and ZnO/SBA-15

The antibacterial activity of the ZnO particles were studied by Zhang *et al.*, 2009 [8]. It seems that active oxygen species generated by ZnO particles could be a mechanism although there is no direct evidence from the results of this study. The presence of active oxygen species has been detected by Yamamoto *et al.*, [9]. It has already been proved that both nano-sized and micron-sized ZnO suspensions are active in inhibiting the bacteria growth; the nano-sized ZnO suspension clearly has a much higher activity than the micron-sized ZnO suspension [8]. These results corresponds with the results of our study as SBA-15 loaded with ZnO nanoparticles.

There are several methods for preparing nanosized ZnO powders such as spray pyrolysis [10], precipitation [11], thermal decomposition [12], hydrothermal synthesis [13] and electrochemical growth [14]. Different methods yield different particle sizes of ZnO, depending on the type of precursor, the solvent, the pH and the temperature of the reacting solution. The choice of method depends on the final application. From the above results we clearly came to know about the enhanced bioactivity of ZnO nanoparticles by studying the antimicrobial activity of ZnO nanoparticles treated fabrics. The enhanced bioactivity of smaller particles is attributed to the higher surface area to volume ratio. For smaller ZnO nanoparticles, more particles are needed to cover a bacterial colony (2 μ m) which results in the generation of a larger number of active oxygen species (released from ZnO on the surface of the colony), which kill bacteria more effectively. ZnO nanoparticles were found to be more abrasive than bulk ZnO, and thus contribute to the greater mechanical damage of the cell membrane and the enhanced bactericidal effect of ZnO nanoparticles [15,16] .

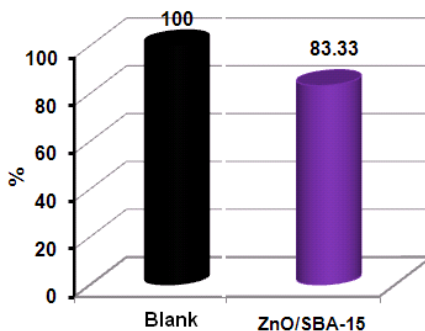


Fig.3. Degree of microbial growth (%) for 0.1mg ZnO/clinoptilolite, SBA-15 respectively per mL medium for *Escherichia coli*

Taking into account the different amounts were incorporated into the 5 mL culture medium, the degree of microbial growth (%) of *E. coli* (Fig.3 and Fig.4) was calculated.

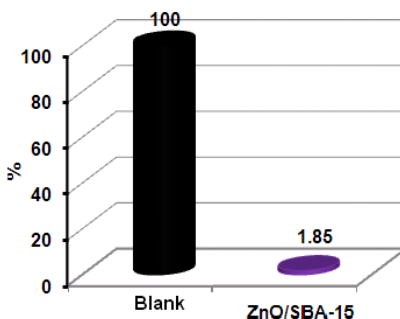


Fig.4. Degree of microbial growth (%) for 0.72mg ZnO/clinoptilolite, SBA-15 respectively per mL medium for *Escherichia coli*

The antibacterial effect is stronger for **the 0.72mg ZnO/clinoptilolite..**

Generally, the antibacterial mechanism of chemical agents depends on their specific binding with surface and the metabolism of agents into the microorganism.

4. Conclusions

Results showed that the ZnO from zeolite support exhibited a good inhibition effect on the growth of *Escherichia coli* and its ability was attributed to the ZnO nanoparticles. The inhibitory effects of ZnO were concentration-dependent and also related to storage temperature and the type of application.

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SBA-15 -- NEW ADSORBENT FOR BIOACTIVE COMPONENTS FROM WINE

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1. Introduction

The quality of a wine depends on its numerous constituents, the presence/absence and amount of a given compound playing a considerable role. Phenolic compounds contribute markedly to the color, flavor, bitterness and astringency of the final product. Browning of wines is a result of an auto-oxidation process due to presence of oxygen (the initiator of the process), polyphenols (the oxidable mater) and of certain metal ions, $\text{Fe}^{2+}/\text{Fe}^{3+}$, Cu^{2+} (as activators of the process). The retention of some phenolic compounds by means of an adsorbent is the method frequently used for eliminating this phenomenon.

Silica SBA-15 exhibit pore sizes from 5 to 30 nm, wall thicknesses of 3.1–6.4 nm and BET surface areas from 630 to 1040m²/g. The silanol groups (Si–OH), always present, are responsible for the adsorption of organic molecules. These OH groups are mainly placed on the SBA-15 internal surface that represents the main contribution to the total surface area of the porous material. Up to our knowledge, there are no scientific reports on the application of the mesoporous SBA-15 material in oenology.

The aim of this study is to investigate the potential use of a mesoporous material SBA-15 as adsorbent for the polyphenols from a Cabernet Sauvignon wine originated from Romania.

2. Experimental

Synthesis and characterization of the mesoporous silica SBA-15

The purely siliceous molecular sieve SBA-15 was synthesized hydrothermally in acidic media via a hydrogen bonding (S^0H^+) (XT^+) templating route according to a procedure reported earlier, with some modifications [1]. The typical gel molar composition was

1TEOS:0,017P123:5,95HCl:194H₂O. Fig.1 shows the SAXRD pattern of the calcined silica SBA-15 used as adsorbent. The diffractogram presents three clear peaks which are characteristic of 2-D hexagonally ordered structure (P6m symmetry) namely the (100), (110), (200) crystal planes and the corresponding d_{hkl} spacings of 9.007, 5.1905 and 4.5502nm.

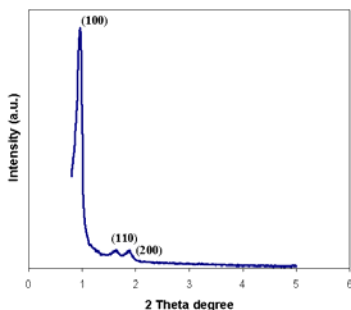


Fig.1. Small-angle XRPD pattern of Si-SBA-15

Fig.2 shows the nitrogen adsorption-desorption isotherm at -196⁰C and the pore size distribution curve calculated with BJH formula from the adsorption isotherm. The structural parameters of calcined mesoporous silica-SBA-15 are summarized in Table 1.

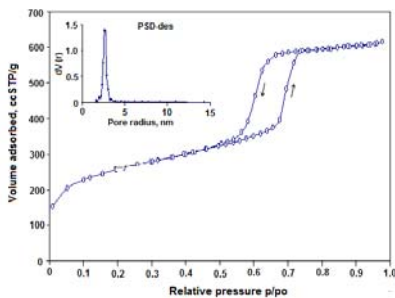


Fig.2. The N₂ adsorption – desorption isotherm at -196⁰C of silica-SBA-15. Inset: the pore size distribution (PSD)

Table 1. Structural parameters derived from XRPD data and nitrogen physisorption

Sample	d_{100} spacing (nm)	a_0 (nm)	S_{BET} (m ² /g)	D_{BJH} (nm)	Total pore volume (cm ³ /g)	Wall thickness (nm)
Si-SBA-15 (calcined)	9.007	10.40	774	6.62	0.942	3.78

Standard chemical analysis of wine

Total acidity, ethanol, pH, volatile acidity, total and free SO₂, sugars and total dry extract (TDE) of the used wine were analyzed according to the methods proposed by O.I.V. (2006) (Table 2).

Table 2. Traditional analysis of Cabernet Sauvignon wine.

Parameter	Value
pH	3.5
Total acidity	6.18 g/L (as tartaric acid)
Volatile acidity	0.52 g/L (as acetic acid)
Free SO ₂	33.62 mg/L
Total SO ₂	170.42 mg/L
Sugars	2.3 g/L
TDM	22.45 g/L

Identification and quantification of phenolic compounds

Identification of the phenolic compounds from wine adsorbed on SBA-15 was carried out using a HPLC method. In this case, 500 mL of red wine were mixed with 4.0273 g of SBA-15 for 30 minutes and kept for 24 hours at a temperature of 5°C. The solid adsorbent was filtered, dried at the room temperature and then was treated with 13 mL of methanol; the methanolic extract was used for the qualitative analysis of phenolic removed compounds.

The optimization of the separation of these compounds was achieved after experimenting with various gradient profiles and mobile phase flow rates [2].

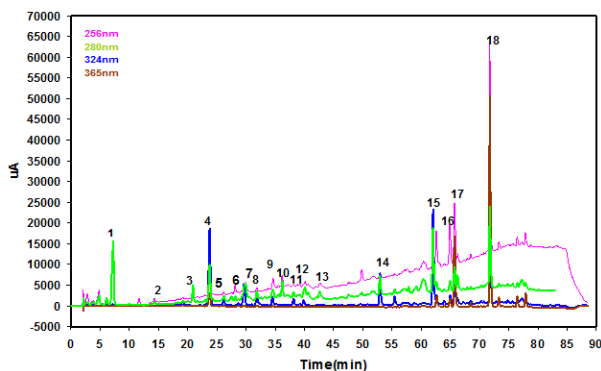


Fig. 3. The chromatogram of methanolic extract of polyphenols adsorbed onto SBA-15: 1-gallic acid; 2-protocatechuic acid; 3-para-hydroxybenzoic acid; 4-gentisic acid; 5-meta-hydroxybenzoic acid; 6-vanillic acid; 7-catechin; 8-caffeic acid; 9-clorogenic acid; 10-syringic acid; 11-para-coumaric acid; 12-epicatechin; 13-salicylic acid; 14- sinapic acid; 15-trans-resveratrol; 16-rutin trihydrate; 17-cis-resveratrol; 18-querucitin

The chromatograms of methanolic extract of phenols removed from SBA-15 are shown in Fig. 3.

The chromatographic analysis shows that SBA-15 selectively retains the phenolic compounds from wine, following the order: quercetin > trans-resveratrol ~ cis-resveratrol > gallic acid ~ gentisic acid. As above mentioned, the SBA-15 contains a large number of silanol groups (Si-OH) located on both inner and outer surface of the pores. Therefore, the adsorption on the SBA-15 may be attributed to the dipole moment of these molecules (due to the presence of the hydroxyl groups). Moreover, the availability of electrons on the phenyl rings may enhance the interactions with Si-OH group and thereby the adsorption (the case of *cis*- and *trans*-resveratrol and quercetin) [3].

3. Conclusions

Mesoporous SBA-15 silica was obtained using Pluronic 123 triblock polymer as structure directing agent. The structure and the textural properties were investigated using XRD and N₂ sorption techniques. The obtained SBA-15 sample was further used for the adsorption of polyphenols from a Cabernet Sauvignon wine. The identification of the phenolic compounds from wine adsorbed on SBA-15 was carried out using a HPLC method. The chromatographic analysis shows that SBA-15 selectively retains the phenolic compounds from wine. The obtained data showed that mesoporous silica SBA-15 is capable to concentrate quercetin from wine.

The present results demonstrated that the SBA-15 could be an excellent adsorbent for polyphenols from wines. The observations done through the present study open the opportunity for considering the mesoporous SBA-15 as an alternative material for extraction of quercetin or other valuable compounds from wines.

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USE SnO₂ – MONTMORILLONITE NANOCOMPOSITES IN WASTEWATER REMEDATION

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Abstrac: In this study we prepare SnO₂ – montmorillonite nanocomposites by the original method of impregnating the oxide between the layers of clay, followed by roasting. The clay (by Valea Chiuoarului from Romania) was exchange with Na⁺ form and after it was treated for obtain different concentration of tin oxide interlayer. This sample it was test for the photocatalytic activity. The SnO₂ – clay nanocomposites having photocatalytic activity in terms of mineralization of 2,4-phenol dichloride from wastewater were analysed. These studies have followed a performance evaluation of catalysts synthesized in the mineralization of 2,4-phenol dichloride, which is why the initial parameters: concentration of 2,4-dichloridephenol, and hydrogen peroxide, as well as the solution pH, temperature were kept constant.

Keywords: SnO₂-clay nanocomposite, heterogeneous photocatalysis, waterwaster, organic pollutants, adsorption.

1. Introduction

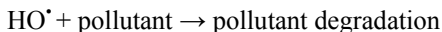
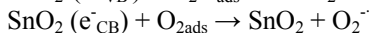
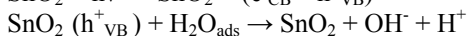
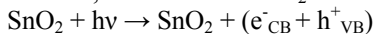
One of the biggest global challenges is the limited quantity of unpolluted water available in the future to be used for drinking. The presence of chlorinated phenolic compounds in surface waters is prohibited because they are toxic, carcinogenic, tended to be persistent and bioaccumulative. An alternative to conventional water treatment processes is the advanced oxidation processes and especially advanced oxidation processes (AOPs - Advanced Oxidation Process).

Recently, attention has been given to the use clays, microporous and mesoporous materials with special properties and features in environmental photocatalysis. [1-5]

The current research work is directed towards the development of treatment processes for mineralizations of phenols in waste water are based on photocatalysis.

It is known that tin dioxide is a versatile material, applicable in many physical-chemical processes, being one of the most intensively studied semiconductors. SnO₂ is an n-type semiconductor with a direct band gap of 3.6 eV between the full oxygen 2p valence band and the tin states at the bottom of the conduction band.

Description of the photocatalytic process occurs on the n-type semiconductor, as substrate SiO_2 based on the following reactions:



Optimize the response of the molecules adsorbed species and catalyst photogeneration (SnO_2) involves increasing the speed of transfer $e^-_{\text{b.c.}}$ (SnO_2) and holes $h^+_{\text{b.v.}}$ (SnO_2) by species in aqueous solution and the dissolved oxygen.

Therefore it is necessary to use very fine particles whose size should be in nanometers.

2. Experimental methods

The starting material

We are used as raw material montmorillonite clay type of Valea Chioarului from Romania. Given the compositional complexity of clay materials, we considered useful as a first step to perform an ion exchange process, for their cleansing, their respective transition cations sodium form.

The natural clay of Valea Chioarului exchange in Na^+ form by treating with 1M NaCl solution with a ration a solid/liquid 1:10 [6].

Chemical analysis indicates the following chemical composition (% by weight): SiO_2 -72.87; Al_2O_3 -14.5; MgO -2.15; Fe_2O_3 -1.13; Na_2O -0.60; K_2O -0.60; CaO -0.90; PC -5.70. Cation exchange capacity (CEC) was determined by ammonium acetate method (Sumner et al., 1996).

The CEC was established that the value entered in the form of sodium clay is 82 meq/100g. the specific surface (98 m^2g) was measured using a methylene blue adsorption (Kahr et al., 1995) [7, 8].

Preparation of SnO_2 – montmorillonite nanocomposites

SnO_2 - montmorillonite nanocomposite material has been prepared by a original method of impregnating the oxide between the layers of clay, followed by roasting. The clay exchanged in sodium form was treated with a different amount of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (as precursor) with constant stirring (magnetic stirrer); stirring was continued for 1 day for ion exchange processes to be completed. After, the 0.5 M NaOH solution was added with dropwise. The process was followed by washing with an alcoholic solution, filtration, and calcination.

The clay was treated with this solution-based impregnating tin in different concentrations. The contents of the tin oxide SnO₂ -montmorillonite nanocomposites was varied as 15, 30 and 40%.

Studies of heterogeneous photocatalysis

The study was conducted in an initial concentration of pollutant (2,4-dichlorfenol Merka) in water of 20 mg/L, using SnO₂-clay as photocatalyst. Other working conditions: report solid/liquid = 0.25 g/L, initial pH=7±0,2, temperature 25°C±2°C, initial sample volume is 500 ml, (for analysis of degree mineralization at time t the volume of sample is 25 mL). Photocatalytic test was done using a type UV lamp UVP, 254 nm surface. Photocatalist sample was shaken 30 min to reach equilibrium and then adding hydrogen peroxide, coupled to the UV lamp and start the timer. Residual H₂O₂ interference was eliminated by the use of analytical Na₂SO₃.

Characterization methods

X-ray diffraction (XRD) powder patterns of natural clays were recorded with a Philips PW 1830 diffractometer (45 KV, 25 mA) using Ni-filtered CuK_α radiation (0.154 nm).

Thermogravimetric analyses of the clays were carried out on a Mettler TG50 thermogravimetric analyzer. The mid-FTIR-PAS spectra were recorded on a Nicolet 20SX spectrometer equipped with a cell photoacoustics McClelland. The adsorption isotherms of N₂, specific surface areas and porosities were determined with a Nova 2200e (Quantachrome Instruments) automated sorptometer at 77 K. To obtain the UV-VIS diffuse reflectance using a JASCO 550 spectrometer.

To determine the values of total carbon, using a device type Shimadzu TOC-Vcpn. Adsorption isotherm for iron Fart clay samples was obtained using a Autosorb Schimadzu, Nova 2002.

3. Results and discussion

The XRD patterns reveals the presence of clays and clay minerals essential crystalline phase as tectosilicate (mainly quartz, feldspar) and also provides that the clay material with the remaining principal and small amounts of other minerals such as quartz, muscovite, feldspar. [9]

All peaks (Fig. 1) can be identified in cubic structure known to SnO₂. Measurement parameter $a = 6.068 \text{ \AA}$, resulting in a value in accordance with the reported value ($a = 6.077 \text{ \AA}$).

Diffraction of X-radiation measurements were made using Scherrer equation, tin oxide particle sizes lying between layers of montmorillonite in diameter in a range from 4-8nm.

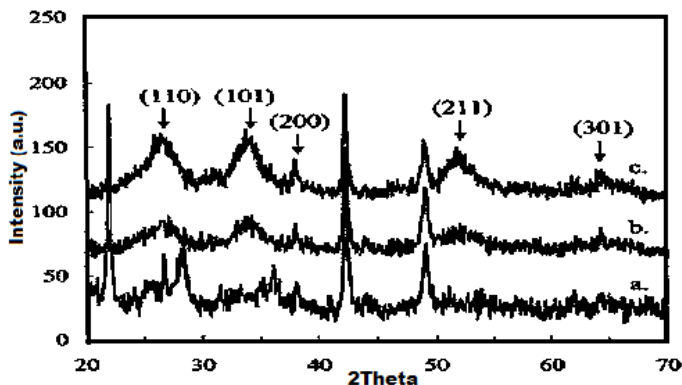


Fig. 1. XRD patterns of SnO₂-nanocomposite samples: a- sample 3; b-sample 2; c-sample 1.

The experimental data show that the preparation of SnO₂-clay nanocomposites centered on Sn leads to an increase for all values of the studied structural-adsorptive properties (Table 1) with respect to the Na-clay. From the stand point of the catalysis efficiency the surface area, pores volume, acidity, nature and accessibility of active sites has an important impact.

Table 1. The main data of some prepared samples

Sample	Conditions of preparation (%SnO ₂ /1g clay)	Surface area, m ² /g	Pores volume, 10 ³ cm ³ /g
Initial sample	-	98.0	1.24
3	15	140.2	3.61
2	30	139.7	3.59
1	40	140.3	3.79

Tin oxide nanoparticles can be present both on the surface of montmorillonite clay and the area of layer silicate interlamellar when you change the adsorbed amount of ions in excess of cation exchange capacity.

TEM images of the samples (Fig. 2) reflects the presence of the oxide cluster tin oxid, nanometer, which is a confirm to the process of obtaining a nanocomposite material with clays SnO₂.

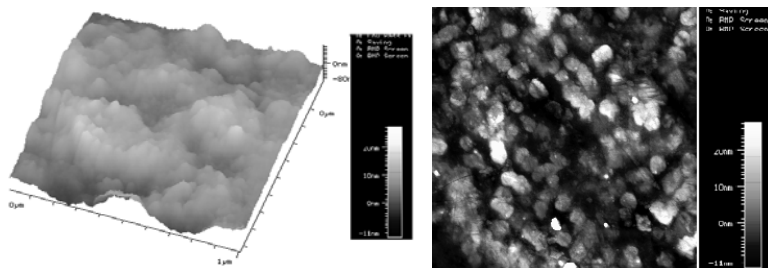


Fig. 2. TEM images of SnO₂ nanoparticles on clay surface

Then calcination was performed in the oven, the behavior is different spectra, they showed a decrease in absorption intensity for the same position. That two absorption intensity decreases more. Samples 1 and 2 shows the adsorption intensity: 233 nm and 305 nm, and the sample 3 at 233 nm and 317 nm (Fig. 3).

Investigations revealed that the nanoparticulate SnO₂ crystallization process reaches an optimum temperature of calcination at around (400°C).

Can be observed an increase in the intensity of the absorption spectra with increasing concentration of tin content, which correlated with x-ray diffraction data indicate the presence of SnO₂ crystalline phases at higher concentrations of its composite material. SnO₂ bulk shows absorption at 358 nm. The thermoanalytical investigations revealed the optimal calcination temperature of the nanocomposites (400 °C) and proved the presence of the SnO₂ nanoparticles by the heat effect of their crystallization process.

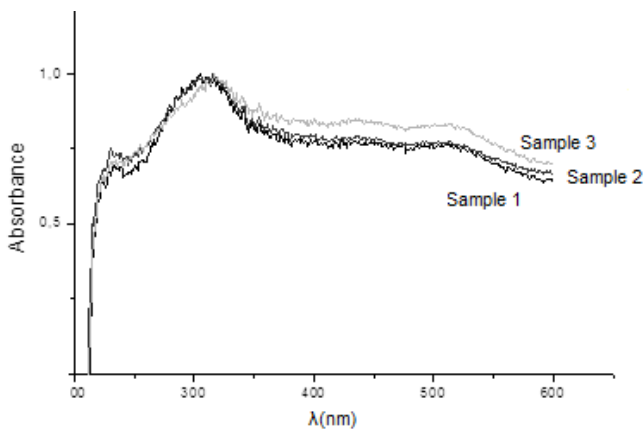


Fig. 3. UV-VIS spectrum of diffuse reflection of different surfactant samples containing calcined in the oven.

UV-Vis spectra show a reduction in particle size compared with the raw material.

Efficiency of oxidation was expressed by the time evolution of the degree of mineralization, X_{TOC} , as determined by the relationship:

$$X_{TOC} = \frac{TOC_0 - TOC_t}{TOC_0} \cdot 100$$

$$\ln(TOC_0 / TOC_t) = -\ln(1 - X_{TOC}) = k_{ap,TOC} \cdot t$$

unde: TOC_0 – total initial organic carbon, $mg L^{-1}$;

TOC_t – total organic carbon at time t , $mg L^{-1}$.

Although at certain moments/phases of the process, the degree of mineralization achieved in the presence of these catalysts has been higher at 90 min., it is noticed that its values were very close. In case of sample 1, whose concentration of SnO_2 is greater efficiency was significantly higher than other catalysts, the degree of mineralization being 40.63%, at 90 min.

In fig. 4 a comparative study of evolution of degree of mineralization in time on synthesized catalysts, is presented.

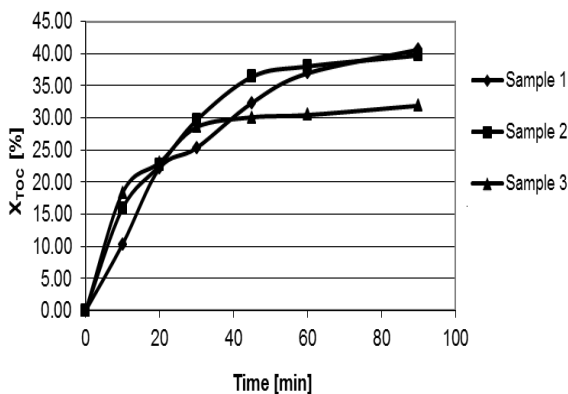


Fig. 4. Time dependence of the degree of mineralization of 2,4- phenol dichloride: duration of balance determining -30 min, 10 mM H_2O_2

Dependencies in Fig. 5 allowed calculation of apparent constants of mineralization. They are presented in Table 2.

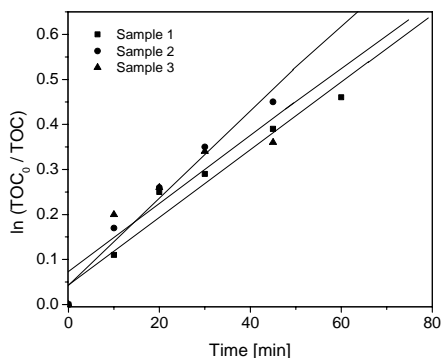


Fig. 5. Determination of apparent constants of mineralization

Table 2: Values of the apparent constants of mineralization.

Parameter	Photo-catalyst type		
	Sample 1	Sample 2	Sample 3
k, min^{-1}	$7.5 \cdot 10^{-3}$	$9.7 \cdot 10^{-3}$	$7.6 \cdot 10^{-3}$
R^2	0.9537	0.963	0.8363

The results presented in this paper highlights the contribution it can make use of SnO_2 - clay samples in the phase of laboratory processes to remove 2,4-diclorfenolului from synthetic wastewater by advanced oxidation processes.

4. Conclusions

SnO_2 intercalation is favored high concentrations of precursor (40%). Intercalation of tin dioxide nanoparticles was unambiguously proven by X-ray diffraction.

The natural montmorillonite from Romanian type clays exchange in sodium form is a good matrices for tin oxide nanoparticles.

It was established that the size of SnO_2 nanoparticles are strongly dependent on the method of preparation. The distinct blue-shift of absorption edges in DR-UV-Vis spectra point to a decrease of the particles size in comparison to the bulk material.

By appropriate selection experimental conditions, allows the realization of size-controlled synthesis that makes possible the preparation of nano-crystalline tin dioxide with much more advantageous photocatalytic properties.

Establish clay-based nanocomposite materials clays tin oxide contributes to the development of promising materials with good quality for wastewater remediation, and thus to reduce environmental pollution.

Using native clays as host, has managed the preparation of efficient systems in advanced oxidation processes, namely photo-oxidation of phenol polluted priority in the hazardous wastewater.

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Synthesis, structure and properties of potassium-doped $\text{La}_{0.54}\text{Ho}_{0.11}\text{Sr}_{0.35-y}\text{K}_y\text{MnO}_3$ manganites

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Abstract: A new type of manganites, with $\text{La}_{0.54}\text{Ho}_{0.11}\text{Sr}_{0.35-y}\text{K}_y\text{MnO}_3$ chemical composition, was obtained by sol-gel method. Chemical composition was obtained by means of EDX method. XRD analysis was performed with a Huber diffractometer at room temperature, data being handled with a Rietveld type program. The samples contain main one phases, which have an orthorhombic phase, identified as $Pnma$, GS 62. Lattice constants, unit cell volume and the atomic positions in the unit cell were determined. The FT-IR spectra put in evidence the increase of amount of the foreign phase at the increase of K cations. The Curie temperature was put in evidence. The molar magnetization decrease with substitution Sr with K. The samples have a metal insulator transition (T_M) in the range 210-245 K.

Keywords: sol-gel synthesis, manganites, X-ray diffraction, FT-IR, UV-Vis, magnetoresistance

1. Introduction

Lanthanum orthomanganites of general formula $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ (A= alkali earth elements) are a subject of recent interest due to their interesting properties such as insulator-to-metal transition, paramagnetic-to-ferromagnetic transition, charge ordering and colossal magnetoresistance (CMR) [1-3]. These compounds exhibit ferromagnetic and antiferromagnetic ordering depending on the relative concentrations of trivalent and tetravalent manganese ions. The magnetic structure observed in these compounds can be understood by considering the competing $\text{Mn}(e_g)\text{-O}(2p)\text{-Mn}(e_g)$ ferromagnetic and $\text{Mn}(t_{2g})\text{-O}(2p_\pi)\text{-Mn}(t_{2g})$ antiferromagnetic exchange interactions [4]. Highest CMR effect was observed near the ferromagnetic transition temperature T_C , and hence the search for new materials having T_C near 300 K. The nature of magnetic ordering in the entire compositional range depends on the relative concentrations Mn^{3+} and Mn^{4+} and on structural properties, via Mn–O–Mn angles and distances. In order to understand the mechanisms involved in the DE interactions and the influence of superexchange (SE) interaction on the magnetic structure, many works have been then done through doping on the

A perovskite-site [2, 3]. Monovalent ions (K, Na or Rb) doped lanthanum manganites show similar electrical and magnetic properties to that of the divalent ion doped lanthanum manganites [5- 8]. The DE/SE interactions ratio depends on the geometrical features of the perovskite structure and the observed decrease of T_{I-M} with the reduction of $\langle rA \rangle$ was explained by the narrowing of the bandwidth due to a bending of the Mn–O–Mn bond angle [9, 10].

We studied the influence of the potassium concentration on the structure and the physical properties for $\text{La}_{0.54}\text{Ho}_{0.11}\text{Sr}_{0.35-y}\text{K}_y\text{MnO}_3$ ($y = 0.0; 0.05; 0.1$) manganites.

2. Experimental

The samples with the chemical composition $\text{La}_{0.54}\text{Ho}_{0.11}\text{Sr}_{0.35-x}\text{K}_x\text{MnO}_3$ with ($0 \leq x \leq 0.1$), were obtained by sol-gel method, using as precursors rare earth oxides (La_2O_3 , Ho_2O_3), nitrates (KNO_3), carbonate (SrCO_3) and acetate $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, in stoichiometric ratio. The precursors were solved first in an aqueous solution of nitric acid (0.05 M) and an aqueous solution of acetic acid (0.05 M), respectively [11]. Then the precursors were mixed in corresponding stoichiometric ratios and the coprecipitation was carried out using a solution of citric acid. The gel was heated at 105°C to remove the excess of the solvent and calcinated at 300°C to decompose the organic constituents. The resulted powders were ground and pressed into pellets and presintered at 800°C for 17 hours in air. The presintered samples were again ground and finally sintered at 1200°C for 10 hours in air atmosphere.

Sintered manganites were monitored by X-ray analysis a diffractometer Huber Guinier CAMERA 670 with $\text{Cu K}\alpha_1$ radiation, electronic microscopy and EDS analysis using a JEOL JSM-5300 microscop and IR methods using a JASCO 660 Plus FT-IR spectrophotometers in KBr disk. The FT-IR spectrum was taken in the frequency range from 1000 to 300 cm^{-1} . The UV-VIS diffuse reflectance spectra (DRS) were performed with VSU-2P spectrophotometer using MgO pellets as a blank. Diffuse reflection spectra were measured to know variation of the band in compounds and the d-d transition energy of Mn^{3+} and Mn^{4+} . The number and energy of bands were resolved by deconvolution of electronic spectra with Excel –Office Word programs.

Lattice constants, space group, positions of cations/anions in the unit cell were determined and refined by means FullProf programs [12].

The presence of K in the perovskite were determined by EDS analysis (Fig. 1).

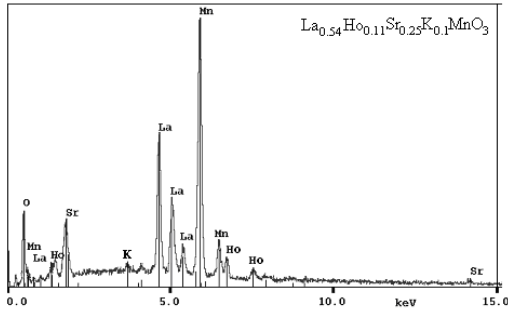


Fig. 1. EDS analysis for $\text{La}_{0.54}\text{Ho}_{0.11}\text{Sr}_{0.25}\text{K}_{0.1}\text{O}_3$ manganites

The magnetic and transport measurements were performed between 77 and 350 K by using a Foner-type magnetometer and, respectively, by means of four probe method. The average size of the A places radius was calculated with:

$$\langle r_A \rangle = C_{\text{La}}r_{\text{La}} + C_{\text{Ho}}r_{\text{Ho}} + C_{\text{Sr}}r_{\text{Sr}} + C_{\text{K}}r_{\text{K}} \quad (1)$$

where C_A and r_A are the concentration and, respectively, the radius of A cation. The tolerance and the chemical disorder factors were obtained with formula:

$$t_{\text{calc}} = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad \sigma^2 = \sum C_i r_i^2 - r_A^2 \quad (2)$$

where r_A , r_B and r_O represent average radius of A and B places, respectively, of oxygen.

3. Results and discussions

The samples contain an orthorhombic majority phases (S.G. Pnma) and a small amount of the rhombohedral phase (S. G. R -3c). The diffractograms indicated the presence of some supplemental maximums at relatively small angles, which can be attributed to superstructure or to a small amount of foreign phase (s. Fig. 2). The positions of the atoms in the unit cell of Pnma are given in table3 and were refined for each sample with a Rietveld program (s.Fig. 3). We have performed tests with I4/mcm, R-3c and Pnma unit cells, but the best fit between the observed and calculated XRD data was obtained for a Pnma structure.

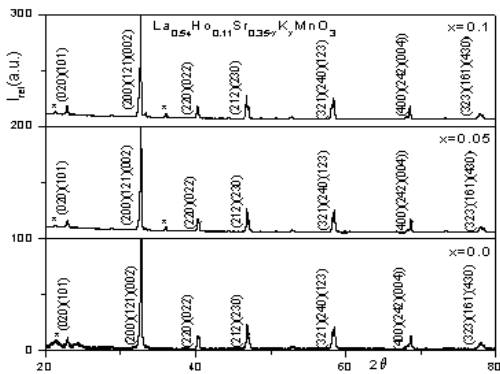


Fig. 2 Diffractograms of the LHSKMO manganites

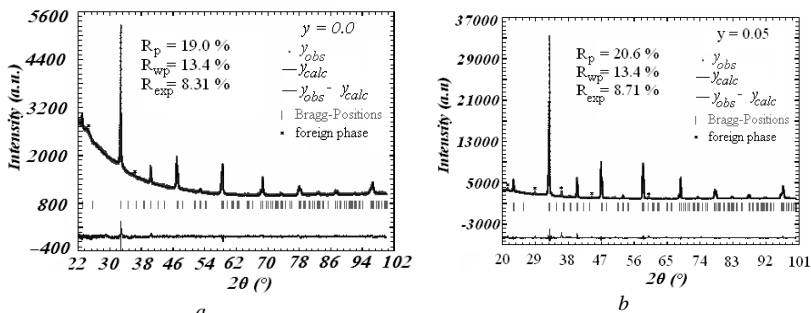


Fig. 3. The observed and calculated diffractograms of the LHSKMO manganites: a) $x=0.0$ and b) $x=0.05$

The substitution of Sr with K leads to an increase of the unit cell volume in agreement with the variation of the tolerance factor (Tab. 1).

Table 1. Parameters (a, b, c) and volume (V) of the Pnma unit cell for LHSKMO manganite

x	a(Å)	b(Å)	c(Å)	V(Å ³)
0.00	5.4899(1)	7.7001(1)	5.4584(1)	230.472(8)
0.05	5.4918(1)	7.7002(1)	5.4710(1)	230.770(8)
0.10	5.4972(0)	7.7088(0)	5.4621(0)	231.464(0)

Table 2. Tolerance factor (t^*), average size of A places ($\langle r_A \rangle$), distances ($\langle d_{Mn-O} \rangle$) and angles ($\langle \angle Mn-O-Mn \rangle$) for LHSKMO manganite.

x	t^*	$\langle r_A \rangle$ (Å)	$\langle d_{Mn-O} \rangle$ (Å)	$\langle \angle Mn-O-Mn \rangle$ (°)
0.00	0.961	1.519	1.975	156.224
0.05	0.964	1.529	1.977	156.225
0.10	0.968	1.539	1.974	156.224

*calculated with ionic Shannon's radii

The calculated values t^* and $\langle r_A \rangle$ increase with the increase of K concentration on A sites (s.Tab.2), while average values of Mn-O distances and Mn-O-Mn bond angles have a nonmonotonous variation, depending on the oxygen position in the unit cell. The manganite structure is formed by chains of MnO_6 octahedra. Between the MnO_6 octahedra are sitting A cations, twelve coordinated with oxygen (Fig.4).

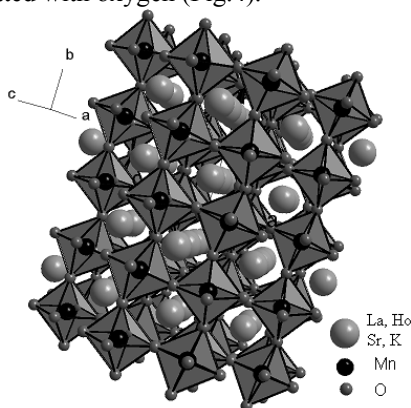


Fig. 4. MnO_6 octahedra chains and Mn-O-Mn chains in orthorhombic structure of LHSKMSO.

The atomic positions and isotropic temperature factors are reported in table 3. The final R value are presented in figure 3(a, b) and table 3, according to the pertinence of the proposed models.

Table 3. Atomic positions and equivalent isotropic displacement parameters (B_{eq}) for LHSKMSO.

Atom	Site	x	y	z	$B_{eq}(\text{\AA}^2)$	Occ.
La	4c	0.00556(66)	0.25000(0)	-0.00549(56)	0.699(17)	2.16
Ho	4c	0.00556(66)	0.25000(0)	-0.00549(56)	0.699(17)	0.44
Sr	4c	0.00556(66)	0.25000(0)	-0.00549(56)	0.699(17)	1.0
K	4c	0.00556(66)	0.25000(0)	-0.00549(56)	0.699(17)	0.4
Mn	4b	0.00000(0)	0.00000(0)	0.50000(0)	0.890(29)	4.0
O1	4c	0.48029 (444)	0.25000(0)	0.02571(557)	1.230(296)	4.0
O2	8d	0.28801(191)	-0.02648(163)	0.75796(242)	1.260(301)	8.0

$R_p = 19.56$; $R_{wp} = 12.95$ $R_{exp} = 8.47$ (%)

Note: Equivalent isotropic temperature factors are computed according to the relation $Beq = 4/3 \sum_{ij} \beta_{ij} a_i a_j$.

The vibrational spectra of perovskites have been described as the internal vibration of the octahedron containing highly charged and small Mn ion because of relatively weak A-O bonds. The group analysis predicts that

there are two infrared active vibrations modes for the MnO_6 octahedra, regarded as a molecular unity. The absorption peaks around 350 cm^{-1} correspond to the bending mode of O-Mn-O bond angle ($\delta_{\text{O-Mn-O}}$) and the other peak around 600 cm^{-1} corresponds to the stretching mode ($\nu_{\text{Mn-O}}$) which is sensitive to the Mn-O bond length (fig. 5)

In our detecting frequency range, the experimental FT-IR spectra show the expected main peaks in both region with an splitting of the $\nu_{\text{Mn-O}}$ band. We interpreted this splitting as a structural doublet allowed by the non-centrosymmetric MnO_6 octahedric groups or/and existence of two crystalline phases. The symmetry of MnO_6 groups is correlated with the existence of manganese ions into a mixture of two valence states, Mn^{3+} and Mn^{4+} , the Jahn-Teller effects partly related to the average ionic radius and electronegativity of ions on the A sites.

The substitution of Sr^{2+} cation with K^+ produce the shifting of $\nu_{\text{Mn-O}}$ to higher frequencies that is determined by a small increase of local symmetry of perovskites (Fig.5 and Tab.4). Also, this could be the effect of the increase covalent degree of Mn-O_{eq} bonds through the axial Jahn-Teller effect.

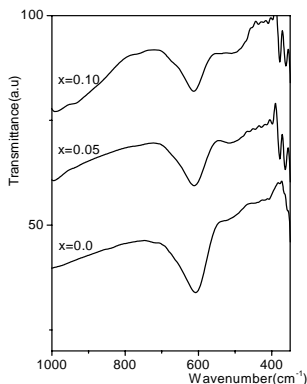


Fig. 5. FT-IR spectra for LHSKMO manganites

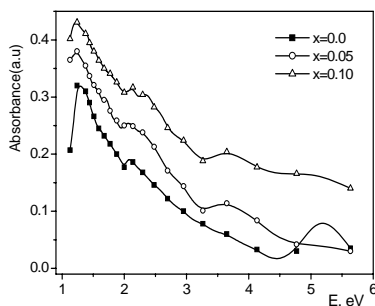


Fig. 6. The DRS of LHSKMO manganites.

Table 4. The FT-IR values of stretching frequency band $\nu_{\text{Mn-O}}$, and stretching bandwidth, $\Delta\nu_{\text{Mn-O}}$, for LHSKMO manganites.

x	ν_1 (cm^{-1})	$\Delta\nu_1$ (cm^{-1})	ν_2 (cm^{-1})	$\Delta\nu_2$ (cm^{-1})
0	607	171	495	83
0.05	608	163	515	77
0.10	612	145	506	101

The intensity of the ν_1 band decrease with the increase of K atoms concentration in the samples. The process is accompanied by the proportional increase of the second stretching band, ν_2 . The explanation is based on the presence of a harder Lewis acid (K^+) on the A sites, the decrease of antisymmetric stretching vibration and that the grain boundaries are associated with a supplementary polarization (dipole moment) of Mn-O bonds, due to the local distortion of the lattice near the grain boundary.

The range of broad frequencies ($\Delta\nu_1+\Delta\nu_2$) decrease from $x=0$ (254 cm^{-1}) to $x=0.1$ (246 cm^{-1}) increase with the increases of K ion concentration (Fig 5.). This process is due also to a small increase of the average grain size.

The fundamental term of Mn^{4+} (d^3 configuration) is ${}^4A_{2g}$, which is associated with minimum 3 d-d electronic transitions. The effect of spin-orbital coupling and the distortion of MnO_6 octahedra lead to the increase of the number of observed electronic transition (bands) into UV and near IR ranges. The Mn^{4+} cation is associated with a decrease of Jahn-Teller effect and its influences on the splitting of the spectral terms. The Mn(III) cation – high spin at room temperature (d^4), in octahedral symmetry, presents an E_g fundamental term and a strong Jahn-Teller effect. For $Mn^{III}O_6$ chromophors were observed minimum two electronic transitions attributed the splitting of ${}^5T_{2g}$ (${}^5B_{2g}$ and 5E_g) and 5E_g terms. For the strong distorted octahedra the transition energies of 5E_g terms are enough high to have values in near IR range. Mn^{3+} ions present maximum 4 d-d electronic transitions[13].

The DRS of LHSKMO manganites show between 4.13 and 6.3 eV a band attributed the Ln-O absorption charge transfer (CT) (fig. 6). The Mn-O CT transitions, due to more oxidative character of Mn(IV) than Ln ions, are observed in 2.48 -4.13 eV range where are superpose with d-d electronic transition. For this reason the intensities of VIS (3.1-1.55 eV) and near IR ($< 1.55\text{ eV}$) are much higher than the d-d pure transition.

The increase of K^+ concentration determines the hypsochromic shifts from 5.166 eV for $x=0$ to 5.124 for $x=0.05$ and 4.882 eV for $x=0.1$ and the decrease of the relative intensity of CT_{LnO} transition. The decrease of energy of CT_{LnO} transition could be explained by the increase of covalent contribution of the Ln-O bonds induced to the increase of amount of K^+ ions from the sample. In the same time, the presence of alkaline ions in the second coordination sphere of Mn cation determined the increase of the overlap between Mn t_{2g} orbitals and 2p orbitals of O atom and the splitting

energy between hybrid bonding orbitals of Ln and π anti-bonding orbitals, unoccupied, of MnO_6 chromophor groups. As a consequence, the energy and relative intensity of the d-d (${}^5\text{B}_{2g} - {}^5\text{E}_g; {}^5\text{E}_g - {}^5\text{E}_g$), of Mn(III) (1,263 eV and 1.754 eV for $x=0$; 1,163 eV, and 1.546 eV for $x=0.05$; 1,129 eV and 1.508 eV for $x=0.10$) and $\text{CT}_{\text{Mn(III)O}}$ decrease by the increase the concentration of Mn^{4+} ions (Fig 6). The diminish of Mn(III) concentration determined the decrease of distortion degree of MnO_6 groups.

The Curie temperature was determined in agreement with the magnetic methods used in the study of manganites (fig. 7).

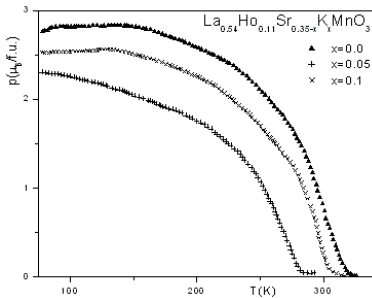


Fig. 7. Variation of molar magnetization with the temperature for LHSKMO samples

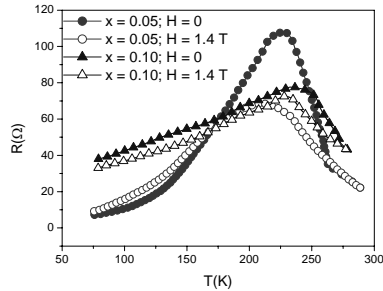


Fig. 8. Variation of resistance with the temperature for LHSKMO manganites

Table 5 The variation of the observed and calculated molar magnetization (p_{max} , p_{calc}), Curie (T_C) and transition temperatures (T_{MI}) for the LHSKMO manganites

x	p_{max} (μB)	p_{calc} (μB)	T_C (K)	T_{MI} (K)
0.0	2.84	2.45	303.6	226.5
0.05	2.31	2.80	268.7	211.7
0.1	2.57	3.15	295.6	241.4

We have observed a minimum of the molar magnetization and of the Curie temperature (Fig. 6 and Tab.2). That minimum is in agreement with the observed values of Mn-O distances and Mn-O-Mn bonds angles of Pnma phase (s. Tab. 2). The substitution of La with Ho in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ leads to an increase of disorder degree and to the appearance of the spin-glass state [14]. At low temperature for some actually investigated manganites it can be observed a decrease of the molar magnetization with the temperature (Fig.7).

We have observed the magnetoresistive effect for all LHSKMO manganites (Fig.7). The effect is important also close to room temperature (Fig. 8).

The observed values of the resistivity for the LHSKMO manganites are due to more mechanisms: a charge transport into the crystallites and a charge transport in the boundary layers of the crystallites (Fig.8).

The variation of the magnetoresistance with the temperature indicated as possible the presence of two components: an extrinsic component, due to the transport of the carriers through the boundary layers, and an intrinsic component due to the transport of the carriers through the crystallite “core”.

4. Conclusions

The samples were obtained by sol-gel method containing a main perovskite phase with Pnma structure and an amount of foreign phase attributed to a superstructure. The substitution of Mn with Sc leads to an increase of the unit cell volume.

The FT-IR spectra put in evidence the increase of amount of the foreign phase at the increase of K cations.

Presence of the large cations (K) in the manganite lattice promotes the appearance of spin-glass state and can induce a large magnetoresistance at room temperature.

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INTERDISCIPLINARY STUDY OF METAL ARTIFACTS TO DISCOVER THE SITE IBIDA, ROMANIA

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Abstract: *The paper presents results of tests carried out by SEM-EDX and micro-FTIR techniques on metal artifacts discovered during archaeological excavations in the site Ibida, village Slava Rusa, Tulcea, Romania. These studies help establish the characteristics of objects made of materials that are studied, namely identifying the type of alloy.*

Keywords: *metal, SEM-EDX, micro-FTIR, archaeology*

1. Introduction

SEM-EDX and micro-FTIR techniques are increasingly used in the analysis of artefacts discovered in archaeological excavations. The investigation of metal artifacts requires close cooperation between specialists in the fields of archeology, history, chemistry, physics, geology, etc. [1, 2, 3].

One of the largest Roman-Byzantine fortified complex in the lower of Danube region is settlement the village Slava Rusă, Tulcea county, with an outstanding archaeological interest, mentioned by Procopius of Ceasarea, as the Ibida [4].

The excavations at Ibida revealed an array of objects with different uses: jewelry, clothing items and other objects used in daily activities. Several of these have been selected and investigated using SEM-EDX and micro-FTIR techniques to determine the material components used in their manufacture [5, 6, 7, 8].

2. Materials and methods

The artifacts selected for investigation were discovered by specialists from Eco-Museum Research Institute Tulcea, Institute of Archaeology Iasi and Institute of Anthropology Bucharest from the archaeological excavations at the site Ibida of the village Slava Rusa. These are presented in Fig. 1. and consist of:

- Bracelet of metal found in 2006, sector Necropolis, S2, plaid 3, M 116, -2.90 m, inv. 48291, kept in very good condition (intact). Presents a

setting in the terminal parts consisting of four concentric circles. Sectional diameter of the brass band is the median of 3.15 mm thick and the piece ends, to about 4.25 mm. Maximum opening of 36.37 mm. It has 7.66 grams.

- Earring discovered in 2002, Necropolis, S3, M 18, a plaid, -1.23 m, inv 45 843, being in very good state of preservation. The piece has a diameter of 21.40 mm. Bronze wire at the bottom shows a polyhedral form factor with size of about 5.88 mm per side, with the corners cut in the center of the each party may have noticed a simple decoration, the circular (in photo). It has 1.97 grams. It is part of a fairly common type of earrings for the ladies of IV-V century AD. when is dated the present piece. The closing was very simply by turning the sharp side.

- Ring discovered in 2001, Fortress, Curtina G, S1, plaid 6, -3.00 m, inv 45637, being in very good state of preservation. The ring had a stone that has not been found. It has a diameter of 18.16 mm and weighs 1.45 grams. Chaton's form suggests that the stone had ovoid shape with approximate maximum diameter of 7.44 mm and 6.69 mm at low. It features a ring that is not very spectacular, and could be included chronological II-IV centuries AD.

- Metal fragment discovered in 2002, Curtin G, S1, -1.20 m, no inventory, are in reasonable state of preservation, is in the form of tape, with a rivet fastening the missing head . The fragment is curved part, probably a curved object. It has a length of about 31.30 mm and a width of 10.37 mm in the right rivet, with a weight of 1.74 grams.

- Buckle discovered in 2001, Necropolis, Tomb Tudorca, inv. 45909. A buckle loop, rectangular with rounded corners, kept together with the needle that spill over the rim. It has dimensions of 29.87 and 19.77 mm on the long side on the small side and is a measure 22.72 mm needle. Weighs 8.61 grams. The play is common in male clothing IV-V century AD in the Danube region.

- Apply discovered in 2001, Curtin G, S1, plaid 5, - 2, 30 m (in the Early Roman), inv. 45904, kept in poor conditions. It has the shape of a disc with a hole in the center to lock. The piece diameter is about 38 mm diameter circular hole 5 mm and weighing 0.97 grams. On the left side to present a simple decoration consists of concentric circles, of which only two are visible, located near the center. From the chronological point of view within seconds. II-III AD.

- Handle discovered in 2002, Fortress, Curtin G, S1, plaid 15, -0.95 m, inv 45 641, good conservation. It seems to be the handle of a mirror that has a rectangular mounting hole with a rivet. It was quite possibly the most complex decoration on one side of which is preserved only a simple decoration on the upper part, consisting of interlocking lines. Its dimensions are 52.95 mm in length, thickness mounting hole is 3.07 mm and depth of the hole is about 9 mm. The weight piece is 7.62 grams. Chronology: III-IV centuries AD.

- Stylus fragment, passim, inv. 42413, good conservation status, has one end provided with a trapezoid with the long side parallel array of 10.78 mm, the small 6.30 mm and sides of unparallel of 31.44 mm. Weighs 2.44 grams. The shank diameter is 3.27 mm. The other end was sharpened, used to burn. Chronological: sec. IV-VI AD



Fig. 1. Artifacts found in archaeological excavations at Ibida (Tulcea county): a. Bracelet, inv. 48290; b. Earring, inv. 45843; c. Ring, inv. 45637; d. Metal fragment, no inventory; e. Buckle, inv. 45909; f. Apply, inv 45904; g. Handle, inv. 45641; h. Stylus fragment, passim, inv. 42413.

For the investigate to these were used SEM-EDX and micro-FTIR techniques, in order to determine the material components used in their manufacture.

a. The SEM-EDX Electron-scan Microscopy

The researches have been carried out with a SEM VEGA II LSH scanning electronic microscope manufactured by the TESCAN Co., the Czech Republic, coupled with an EDX QUANTAX QX2 detector manufactured by the BRUKER /ROENTEC Co., Germany.

This technique, together with the microphotogram visualization, allows the rendering of the image with the mapping (arrangement) of the atoms on the studied surface, and, on the basis of the X-rays spectrum, the determination of the elementary composition (in gravimetric or molar rates) of a microstructure or of a chosen area as well as the estimation of the composition variation along a vector set in the analysed area or section.

b. Micro-FT-IR analyses

The spectra were recorded with a FT-IR spectrometer coupled to a HYPERION 1000 microscope, both equipment from Bruker Optic, Germany.

The FT-IR spectrophotometer is a TENSOR 27, which is designed for measurements mainly in the mid-infrared region. DLATGS standard detector covering the spectral range 4000 - 600 cm^{-1} and working at room temperature. The resolution is typically 4.0 cm^{-1} , but may reach 1.0 cm^{-1} .

The techniques used for analysis found in the Laboratory of Scientific Investigation and Conservation of the Cultural Heritage of the Platform for Interdisciplinary Training and Research from "A.I. Cuza" University Iasi.

3. Results and discussion

From the elemental composition by mass (Table 1) artifacts were analyzed with following results:

- in the bracelet and earring were identified as basic elements, which are copper, zinc and iron and small amounts of Si, Al, Ca and Cl, which are present due to contamination of the storage environment.
- in the ring, apply and handle are present the basic elements: copper, zinc and small amounts of tin, apply has and iron, other components are from contamination;
- in the metal fragment has in the compositional basic elements: copper and tin;
- in the buckle has been identified iron and contaminated elements;
- in the stylus fragment was identified copper as the basic element, the remaining elements from contamination.
- all artifacts containing C and O from contamination.

Table 1. Chemical composition of investigated artifacts.

Artifact/No. inv.	Elemental composition – mass percent (%)										
	Cu	Sn	Zn	Fe	O	C	S	Cl	Ca	Al	Si
Bracelet/48291	32,780	-	14,993	0,781	22,607	20,889	-	4,932	0,387	2,203	-
Earring/45844	31,712	-	9,860	1,122	39,793	16,432	-	0,399	0,331	-	0,444
Ring/45637	44,873	1,595	9,339	-	26,614	15,173	0,161	0,279	0,364	1,108	-
Metal fragment/ no inv.	26,446	2,992	-	-	47,933	21,866	0,203	0,142	-	0,418	-
Buckle/45909	-	-	-	68,634	23,993	0,814	-	6,182	-	0,374	-
Apply/45904	62,332	1,996	10,857	0,592	14,529	9,691	-	-	-	-	-
Handle/45641	73,284	2,674	5,682	-	11,926	6,068	0,229	0,134	-	-	-
Stylus fragment/ 42413	69,341	-	-	0,641	19,879	3,931	0,751	2,374	0,554	0,740	1,2 3

The spectra resulting from micro-FTIR analysis have revealed the functional groups in Table 2.

Table 2. Group frequencies for common inorganic ions

Group frequency (cm⁻¹)	Functional group/assignment
670-745; 800-890; 1040-1100; 1320-1530	carbonate ion
940-1120	orto-phosphate ion
830-920; 1600-1900; 2150-2500; 2750-2900;	orto- phosphate dibasic ion
570-680; 960-1030	Sulfate ion
610-630; 900-1050	Chlorate ion
600-660; 1050-1150	Perchlorate ion
600-700	Stanate ion
860 – 1175	Silicate ion
800 - 920	Aluminat

Comparing the spectra resulting from micro-FTIR analysis of the artifacts with those investigated in specialized studies [9, 10] to identify the presence of ions carbonate, sulfate, phosphate silicate etc.

4. Conclusions

Following tests carried out have identified the basic elements: Cu, Sn, Zn and Fe and the elements resulting from contamination: Si, Al, Ca, Cl, C and O.

Thus, bracelet, earring, ring, apply, metal fragment and handle are ancient bronzes because are brass were made using the process technology with copper, zinc and tin alloy. Tin was added in small quantities to facilitate casting and to increase the workpiece hardness.

The buckle is made of iron, its conservation status is precarious.

The stylus fragment is made of copper.

Corroborating the results obtained from SEM-EDX analysis with those obtained from micro-FTIR analysis can reveal the presence of chemical compounds, such as oxides (CuO, Cu₂O, Fe₂O₃, Fe₃O₄, SiO₂, etc.), hydroxy carbonates and sulphates (CuCO₃·Cu(OH)₂, CuSO₄·3Cu(OH)₆ etc.), hydroxy chlorine compounds (Cu₂(OH)Cl₃, CuCl₂·3Cu(OH)₂ etc. These compounds were formed from the alteration processes of alloying components and the segregation/monolitization chemical components coming from the site during the laying period [11, 12].

Acknowledgements

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METHODOLOGICAL ASPECTS OF ALCOHOL DETERMINATION IN THE INVESTIGATION OF DINITROPHENOL TOXICITY

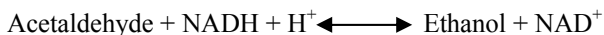
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Abstract: Dinitrophenols and related dinitrophenyl ethers are very poisonous compounds used as pesticides, drugs or weight loss agents. In order to determine the level of toxicity of these chemical compounds we investigated their relationship with bread yeast. First, we have introduced and characterized a method for determining the ethanol produced by yeast in the presence of dinitrophenyl derivatives. This paper demonstrates the feasibility of a method based on the absorption of dichromate ions at 350 nm and of Cr³⁺ ions at around 600 nm.

1. Introduction

In the 1850s, Louis Pasteur concluded that fermentation of sugar into alcohol by yeast is catalyzed by "ferments." He postulated that these ferments were inseparable from the structure of living yeast cells; this view, called vitalism, prevailed for decades. Then in 1897 Eduard Buchner discovered that yeast extracts could ferment sugar to alcohol, proving that fermentation was promoted by molecules that continued to function when removed from cells. Fermentation is defined as an energy-yielding metabolic pathway that involves no net change in oxidation state. Anaerobic glycolysis is a type of fermentation. The lactic acid fermentation (conversion of glucose to lactate) is important in the manufacture of cheese. Another involves cleavage of pyruvate to acetaldehyde and CO₂, with the acetaldehyde important fermentation then reduced to ethanol by alcohol dehydrogenase in the reaction that follows:



As carried out by yeasts, this fermentation generates the alcohol in alcoholic beverages. Yeasts used in baking also carry out the alcoholic fermentation; the CO₂ produced by pyruvate decarboxylation causes bread to rise, and the ethanol produced evaporates during baking. Among the dozens of other useful fermentations are those leading to acetic acid (manufacture of vinegar) and propionic acid (manufacture of Swiss cheese). Fermentation of sugars by yeast is the oldest and largest application of this technology. Many types of yeasts are used for making many foods: baker's yeast in bread production; brewer's yeast in beer fermentation; yeast

in wine fermentation and for xylitol production. So-called red rice yeast is actually a mold, *Monascus purpureus*. Yeasts include some of the most widely used model organisms for genetics and cell biology. Their size can vary greatly depending on the species, typically measuring 3–4 μm in diameter, although some yeasts can reach over 40 μm . Researchers have used it to gather information about the biology of the eukaryotic cell and ultimately human biology. Other species of yeast, such as *Candida albicans*, are opportunistic pathogens and can cause infections in humans. Yeasts have recently been used to generate electricity in microbial fuel cells, and produce ethanol for the biofuel industry. Yeasts do not form a single taxonomic or phylogenetic grouping. The term "yeast" is often taken as a synonym for *Saccharomyces cerevisiae*, but the phylogenetic diversity of yeasts is shown by their placement in two separate phyla, the Ascomycota and the Basidiomycota. The budding yeasts ("true yeasts") are classified in the order Saccharomycetales. The useful physiological properties of yeast have led to their use in the field of biotechnology.

2,4-Dinitrophenol (DNP), $\text{C}_6\text{H}_4\text{N}_2\text{O}_4$, is a cellular metabolic poison. It uncouples oxidative phosphorylation by carrying protons across the mitochondrial membrane, leading to a rapid consumption of energy without generation of ATP. Dinitrophenols as a class of compounds, of which there are six members, do not occur naturally but are all manufactured compounds. Commercial DNP is primarily used for making dyes, other organic chemicals, and wood preservatives. It is also used to make photographic developer, explosives, and insect control substances. DNP is sold under many trade names, some are Caswell No. 392®, Sulfo Black B®, and Nitro Kleenup®. DNP is considered an important environmental contaminant by the United States Environmental Protection Agency. This agency recommended drinking water limit for DNP is 10 $\mu\text{g}/\text{L}$. 2,4-dinitrophenol (DNP) is considered to be the most toxic substance of this group with an LD_{50} of 30 mg/kg body weight in rats. It is regulated as a priority pollutant by the Clean Water Act. It has been found in 61 of 1400 priority sites that need clean-up of industrial waste. It can enter the air from automobile exhaust, burning of certain industrial substances, and from reaction of nitrogen in air with other atmospheric chemicals. The major site of degradation is the soil, where microorganisms metabolize it. DNP was used in the 1930s in diet pills, since it promotes the metabolizing of carbohydrates and fats, the patient losing the energy as heat and causing dramatic weight loss over a relatively short time. However, there were concerns about carcinogenic mutations, as well as the risk of overdose leading to severe health risk and death, and this use was discontinued.

Today, DNP is used by bodybuilders, often illegally, to rapidly lose body fat before contests.

2. Materials & Methods

Materials: ordinary yeast, glucose (Merck) , $K_2Cr_2O_7$ (10^{-2} M, 10^{-1} M), NaOH 0,1 N, H_2SO_4 96% (Lach-Ner) , distilled water, DNP aqueous solution (5×10^{-4} M)

Equipment: Single beam UV-VIS spectrophotometer type Libra S35 PC (Biochrom, UK), Conway dish, 1cm quartz cuvettes (Helma, Germany)

Alcohol monitoring assay: 5 g yeast and 5 g D-glucose were dissolved in 100 ml distilled. In the pot hole center of Conway dish 1 ml yeast suspension was mixed with 1 ml NaOH(0,1N). In the outlet 3 ml $K_2Cr_2O_7$ 10^{-2} M and 3 ml H_2SO_4 96% were added. Conway dish was incubated on a hotplate at a temperature of 55° C at different time intervals



Fig 1. Dish Conway

After reaction, the outlet content was diluted to 10 ml final volume. The absorption spectra of resulted solution were recorded within UV-VIS spectrophotometer type Libra S35 PC in quartz cuvettes of 1 cm in the range $\lambda = 250- 650$ nm. Measurements were made with different amounts of suspended yeast.



Fig 2. UV-VIS spectrophotometer type Libra S35 PC

A comparative study was in aerobic and anaerobic conditions using a 1% yeast suspension containing 1%. We found out that the alcohol amount (quantified after 1 hour) was 25% higher in anaerobic than standard conditions (Figure 5)

3. Results & Discussions

The spectra of Cr^{6+} and Cr^{3+} (as control spectra) were used as reference spectra. Molar absorption coefficients in acidic media are $160.6 \text{ M}^{-1}\text{cm}^{-1}$ (350 nm), $31.6 \text{ M}^{-1}\text{cm}^{-1}$ (444 nm) Cr^{6+} and $68 \text{ M}^{-1}\text{cm}^{-1}$ (300 nm), $47.9 \text{ M}^{-1}\text{cm}^{-1}$ (410 nm) and $39.6 \text{ M}^{-1}\text{cm}^{-1}$ (577 nm) for Cr^{3+} .

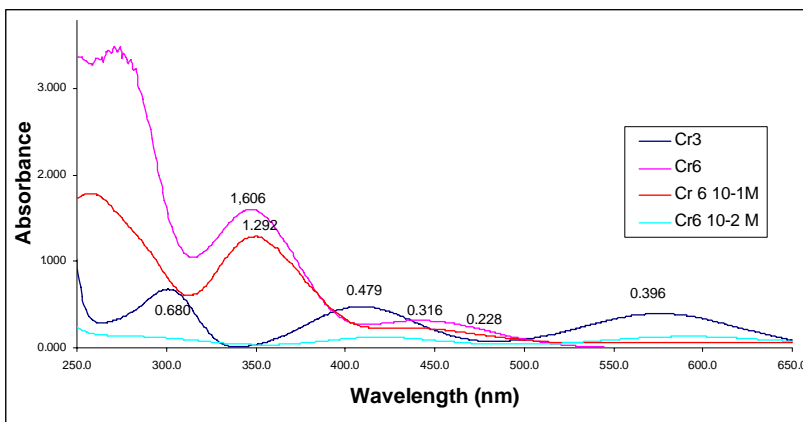


Fig 3. UV-VIS spectrum in the absence of yeast suspension (Cr^{6+} - Cr^{3+}) and . UV-VIS spectrum Cr^{6+} (10^{-2}M & 10^{-1}M) in the presence of yeast suspension

We found out that for different yeast suspension solutions an optimal concentration (10^{-2}M Cr^{6+}) for Cr^{6+} - Cr^{3+} conversion. If the Cr^{6+} concentration is one order of magnitude higher this phenomenon is absent. Molar absorption coefficients an concentration of 10^{-2}M Cr^{6+} are lower than molar absorption coefficients of control $1.4 \text{ M}^{-1}\text{cm}^{-1}$ to $160.6 \text{ M}^{-1}\text{cm}^{-1}$ (350 nm), $18.8 \text{ M}^{-1}\text{cm}^{-1}$ to $31.6 \text{ M}^{-1}\text{cm}^{-1}$ (444 nm) Cr^{6+} and $19.5 \text{ M}^{-1}\text{cm}^{-1}$ to $39.6 \text{ M}^{-1}\text{cm}^{-1}$ (577 nm) for Cr^{3+} .

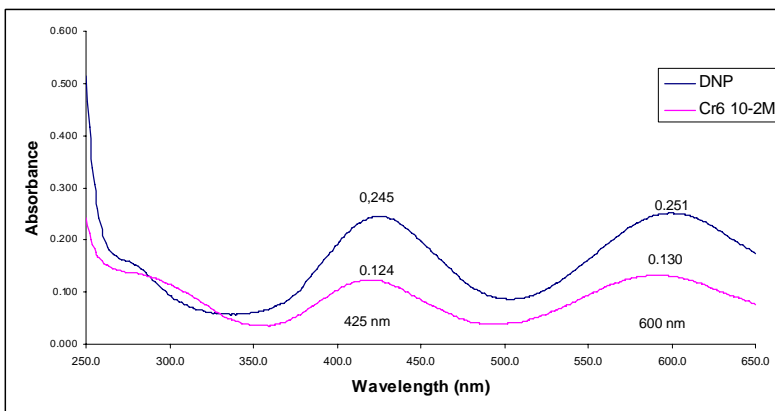


Fig 4. UV-VIS spectrum Cr^{6+} in the absence ($\text{Cr}^{6+} 10^{-2}\text{M}$) and presence of DNP($5 \times 10^{-4}\text{M}$)

Following the experimental determinations we noted that DNP inhibits the alcohol production. Samples containing DNP possess a larger molar absorption coefficient than the untreated sample, $24,5 \text{ M}^{-1}\text{cm}^{-1}$ vs. $12.4 \text{ M}^{-1}\text{cm}^{-1}$ (425 nm) and $25.1 \text{ M}^{-1}\text{cm}^{-1}$ vs. $13 \text{ M}^{-1}\text{cm}^{-1}$ at 600 nm therefore we attribute this to the existence of a small amount of alcohol.

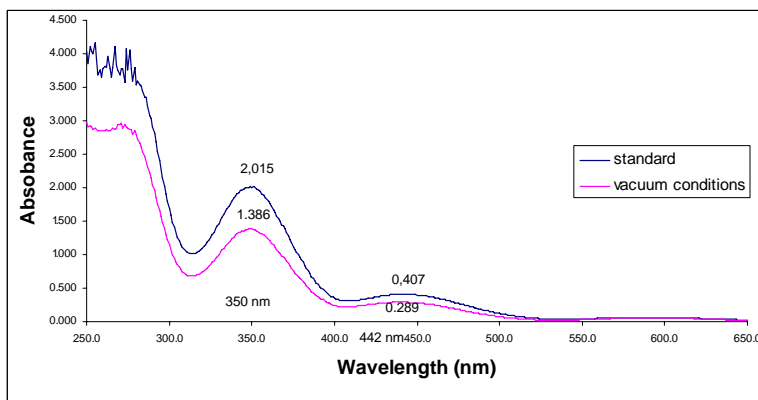


Fig 5. UV-VIS spectrum of the solution: $\text{Cr}^{6+} (10^{-2}\text{M})$ standard & vacuum conditions

Conformity data from a range greater amount of alcohol is released into the suspension under vacuum case, the proof being the molar absorption coefficient lower than in

the standard conditions $138.6 \text{ M}^{-1}\text{cm}^{-1}$ to $201.5 \text{ M}^{-1}\text{cm}^{-1}$ (350 nm) and $40.7 \text{ M}^{-1}\text{cm}^{-1}$ to $28.9 \text{ M}^{-1}\text{cm}^{-1}$ (442 nm).

4. Conclusions

A simple spectrophotometric method for alcohol detection in suspension was improved. We found out that the optimal Cr^{6+} concentration was 10^{-2}M . Although preliminary, these results are suitable for designing a methods to follow the effect of dinitrophenols on alcohol production in yeast. For example, DNP has an effect on diminishing the production of alcohol within the fermentative process. This aspect needs further research.

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CONSEQUENCES OF TREATMENT ON THE DIMENSIONAL STABILITY OF WOOD PANEL

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Abstract: *Dimensional stability is a characteristic of wood tightly connected to the other qualities that are conferred by the wood treatment: hygroscopicity, fire and insectofungic character. Evaluation of dimensional stability is achieved through trapped indicators and standardized tests in ASTM D-1037 v. There are effective treatments in this study developed by researchers in the wood dimensional stabilization effort: acylation, treatment with resins, fire retardant treatments.*

Keywords: *dimensional stability, acylation, resins, fluid balance, ASTM D-1037v*

1. The importance of dimensional stabilization of wood

Physical and structural changes in certain environmental conditions are indicators of the impact on the treatment of preservation wood. In the laboratory characteristics were pursued density, porosity, expansion, compression, volume.

Dimensional stability properties are closely related to the hygroscopic nature of wood, in general, slightly different between wood species, the application of various treatments and variable parameters of the environment - temperature, humidity, pressure, light. Changing these properties in particular lead to changes in shape, thickness, length, divided into three specific length of a timber element - the tangential, longitudinal and radial [1].

Changes in the three dimensions of wood can be as different in size and dynamics. Tangential growth is two times higher and 4-5 times faster than radial growth. Change is a specific dimensional wood, which takes place within certain limits with impunity. Overcoming their causes damage wood by precolaps.

It is well known that untreated wood varies greatly as a result of dimensional changes in atmospheric humidity. Influence properties repeatedly dimensional effects lead to deterioration of support, such as cracking, but also the layer where polychrome painting wood, referring to the separation of its evolutionary nature, by painting layer losses [2].

2. Evaluation of dimensional stability of wood product

Wood put the work in natural products or in other forms of industrial wood-based panel, fiber-based panels of wood, hardboard, laminated rigid plates, particleboard, medium density fibreboard, particle board.

Dimensional properties of wood are listed and measured by ASTM D-1037 v. Stabilizing basic dimensional wood fiber and wood panel is tested in default under a variety of properties: size of sections, curved static appearance of pores, parallel tensions surface perpendicular to the surface tension, compressive strength parallel to the surface, narrow side faces resistance, hardness.

3. Modern methods of dimensional stabilization of wood in the laboratory

Regarding keeping the temperature constant laboratory environment for the implementation phase, wooden works of art, but also to preserve their isolation offered an effective model with fire retardant foam, organized by sets of drawers and rooms for specific purposes. Will appear by placing camphor wood in the drawer, cabinets are fitted with wheel brakes [3].

In pursuing that aim to stabilize dimensional steps: a study on the control sample, untreated, treatment solution characterization, setting the property which will be followed during the investigation, determination and interpretation of the main features of the wood after treatment: the coefficient of dimensional stability wood during exposure to certain heat-humidity conditions and keeping of consolidates well established after treatment. These two measures describing the efficacy of a treatment, that means the percentage ability to stabilize the product. This indicator helps to determine the minimum quantity needed to stabilize dimensional [4].

It was found that the fire retardant treatment has an effect on dimensional stability by influencing the properties of linear expansion and thickness swelling [5]. The smaller effects of treatment are given monoammonium phosphate (MAP), significant effects are present after treatment with the mixture of borax and boric acid 1:1 [6].

In our laboratory found that the treatment with propolis, the hydrophobic effect, dimensional changes are small and do not affect the polychrome layer. It was thus found that propolis solution does not allow adsorption of wood, as for untreated wood. Treating wood with an aqueous

solution of boron increases the compressive strength of wood parallel to the fibers, the various ways of fracturing and degradation by fungal attack [7].

Dimensional stabilization of wood products can be obtained by treating with thermosetting resins. An estimated 75% effective is obtained by treating with phenol formaldehyde (PF) by 69% melamine formaldehyde (MF) and 45% with urea formaldehyde (UF). Treatment of the resin in 30%, and is applied at 90-100 ° C under a pressure of 75 atmospheres. Consequences of applying the treatment are weight gain 33-35% of the treated product (indicator WPG), a reduced thermal load Polymer 9-15% (BC) and the humidity efficiency (MEE) 31 - 47%. Repeated hydration and dehydration does not change the load coefficient (BC) and shield efficiency (ASE) in the treated wood. Module of rupture (MOR) modulus of elasticity (MOE) increases by 12-20% and 5-12% respectively. This treatment is a repellent character, preventing termite attack (*Odontotermis*) [8].

Acylation, and hexanoilarea butirilizarea purpose procedures used are hygroscopic and dimensional stability (*indicator Meese*). Through three rounds of acylation to obtain a good conservation of the wooden properties, particularly excellent resistance to swelling. Water balance of acyl wood three times is considerably reduced to a wide range of atmospheric relative humidity (30-90%). Meese and better results are obtained by the group of hydroxyl substituents, and especially by the butirilization and hexanoilation. Higrofobic molecular volume and nature of the acyl group substituents directly influence dimensional stability indicator of fluid balance and treated wood in combination with the degree of substitution of hydroxyl group [9].

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PROMOTING THE ROMANIAN RESEARCH ON THE CUCUTENI CULTURE VIA MAJOR INTERNATIONAL EXHIBITIONS

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Abstract. To enhance the visibility of the Romanian archaeological and interdisciplinary research concerning the most notable Romanian and European prehistoric civilization – Cucuteni, an intense programme of exhibiting the most outstanding discoveries of this culture has been undertaken. The paper addresses several issues concerning the presentation methods and exhibition catalogues, as well as the impact that these “visiting cards” of the Romanian archaeology, on display between 2007 and 2010, have had on the academic world and the wider public from Italy, Switzerland, the United States, England, Poland, Greece and the Republic of Moldova.

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