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35 YEARS IN ASSESING THE IMPACT OF HEALTHCARE RESEARCH

3rd International Conference on Green Chemistry and Technology

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Scientific Tracks & Abstracts

35 YEARS OF EXCELLENCE IN MEDICAL PUBLISHING

Green Technology | Atom Economy | Natural Polymers

Session Introduction

Title: **Reductive amination of alcohols and ketones from biomass feedstock. A catalytic green route for synthesis of primary amines and amino acids**

Doris Ruiz, University of Concepcion, Chile

Reductive amination of alcohols and ketones from biomass feedstock. A catalytic green route for synthesis of primary amines and amino acids

Doris Ruiz
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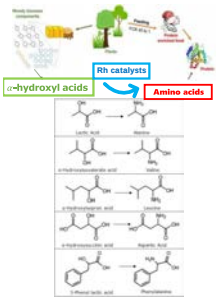
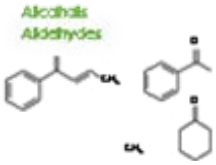
Amino acids (AA) are the basic building blocks of protein synthesis and for this reason are widely used in the field of biological, pharmaceutical, food and industrial medical intermediates. Currently the production of AA is mainly obtained via bio cultivation process and by the way of chemical methods. In both cases, the severe operation conditions and complicated separation procedures show some restrictions on industrial application. Therefore, developing new process for efficient amino acid production via a green and clean way is of significance but still an open challenge.

The purpose of this study is to describe the synthesis of amino-compounds from Biomass-derived chemicals, specifically compounds containing oxygen groups which can be used as a renewable feedstock. The reductive animation of compounds from biomass-derivative substrates with NH3 is a process that meets with the demand of economical and greener processes in AA production through reductive animation. For this purpose, Rh/SiO2 and bimetallic Rh-Ni/SiO2 catalysts were synthesized. Catalysts were characterized by N2 sorption, Chemisorption, XPS, SEM, TEM, NH3-TPD and TPR-H2. The catalytic reactions were carried out at 373 K, 4 bar of NH3, 2 bar of H2, using a substrate/Rh mol ratio=100 at 800 rpm in 50 mL of cyclohexane. Products of reaction were analyzed by GC-MS. The catalysts were active and selective in hydrogenation and amination reactions. The conversion to amines can be affected by factors such as metallic diameter, nature and amount of metal sites, metal dispersion, metal reduction ratio, among others. Specifically, in this study, better results are obtained for reductive amination of ketones in catalysts that present high hydrogenating capacity and high acidity. Conversion of ketones involves amination and hydrogenation steps to produce high conversion and maximum selectivity (100%) to primary amines. One of the AA studied, lactic acid, showed conversion to alanine by successive dehydrogenation-amination-hydrogenation pathways of reaction.





Biography

Doris Ruiz is currently Associate Professor in Physical Chemistry at the University of Concepcion, in Concepción, Chile (http://www2.udec.cl/cienciasquimicas/). She has her expertise in Heterogeneous Catalysis, specifically focused on: Enantioselective Catalysis, Hydrogenation and Amination reactions, valorization of compounds from Biomass feedstocks, Green Chemistry, Fine Chemistry and Nanomaterials. She leads the “Laboratory of Heterogeneous Catalysis for Valorization and Selective Chemical Processes”. She currently focuses her research on the catalytic synthesis of amino acids from α-hydroxy acids obtained from biomass feedstocks over supported bimetallic catalysts.

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Accepted Abstracts

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Quantitative investigation of the catalytic activities of analogues nickel complexes in ethylene oligo-/polymerization

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Catalytic activity is the most important property among the catalytic performance of transition metal complexes. Many achievements have been obtained previously on increasing the catalytic activity of complex, by the modification of ligands, the change of substitutions on ligands as well as the design of new structure of ligand [1-2]. However, the potential principle of transition metal complex with high catalytic activity is still necessary to be clarified at the molecular level. The catalytic activity is fundamentally determined by the structure of catalyst, including the electronic and steric effects. To expose the relationship between catalyst structure and reaction activity, two carbocyclic fused pyridineimine nickel analogue systems (Ni1 and Ni2) with different fused member ring are investigated [3-4]. Multiple linear regression analysis is performed by means of five electronic and two steric descriptors, including Hammett constant (F), effective net charge (Qeff), energy difference (ΔE), HOMO–LUMO energy gap (Δε1, Δε2), open cone angle (θ), and bite angle (β) [5]. The value of correlation coefficient values (R2) is over 0.938 obtained by using the combinations of effective net charge (Qeff) and open cone angle (θ) for both individual and comparison analogues systems. The contribution analysis indicates that the dominant descriptor is effective net charge (Qeff) in Ni1 system and open cone angle (θ) in Ni2 systems, respectively.

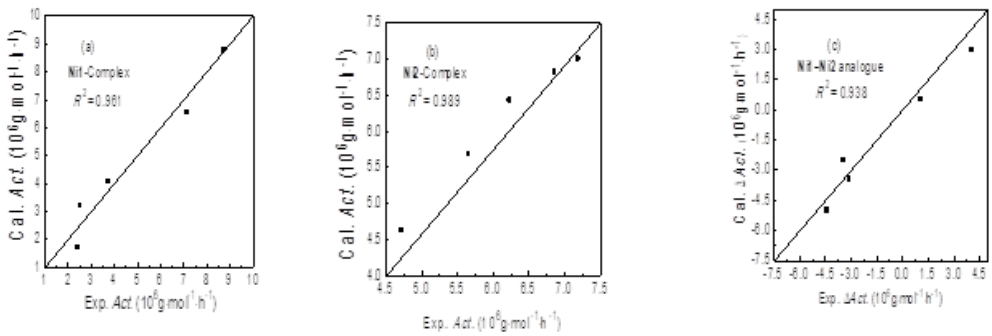

Fig 1. Comparisons between calculated and experimental activities of (a) Ni1 system, (b) Ni2 system, and (c) Ni1–Ni2 analogue system, using the descriptors of effective net charge (Qeff) and open cone angle (θ).

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Solvent and temperature dependent oxidative dehydrogenation reaction of ruthenium ions

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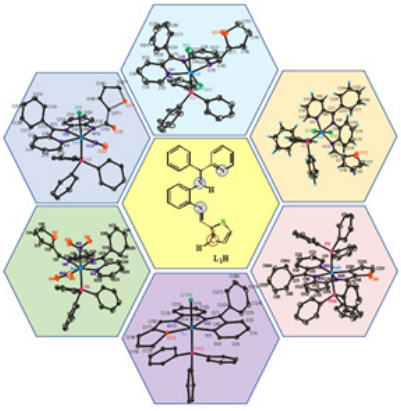
The versatile redox activities of (R1)CH=N-C6H4-NH-C(H)(Ph)(R2) (L1H), an o-phenylenediamine derivative where R1 = thiophene and R2 = pyridine functions, that exhibits flexidenticity and ambidenticity towards ruthenium(II) ion and undergoes oxidative dehydrogenation (OD) of the amine function, thiophene metalation via C-H activation, imine → imidic acid conversion and affords dinitro and [RuNO]7 complexes are reported. Reaction of L1H with [RuII(PPh3)3Cl2] (RuP) in boiling toluene in air promotes OD reaction affording cis-[RuII(L2NNN 0)(PPh3)Cl2] (cis-1), where L1H has been modified to (R1)CH=N-C6H4-N=C(Ph)(R2), a neutral [NNN] donor o-phenylenediimine derivative (L2NNN 0). The same reaction at room temparature furnishes the trans analogue, trans-[RuII(L2NNN 0)(PPh3)Cl2] (trans-1). Conversion of trans-1 → cis-1 has been achieved in boiling xylene. Reaction of cis-1 with I2 and PPh3 in toluene produces [RuII(L2NNNS 0)(PPh3)Cl]I3 (3+I3-), where L1H has been modified to (R1)CH=N-C6H4-N=C(Ph)(R2), a neutral tetradentate [NNNS] donor ligand (L2NNNS 0), where the coordination of thiophene to ruthenium(II) ion has been achieved. Reaction of L1H and RuP in boiling ethanol promotes a C-H activation reaction generating a thiophene metallated complex, trans-[RuII(L2NNNC-)(PPh3)2]+ (trans-2+), where, L1H has been modified to a tetradentate [NNNC] donor ligand (L2NNNC-). The same reaction in presence of excess NaNO2 promotes OD and chloride substitution reactions affording a cis-dinitro complex, cis-[RuII(L2NNN 0)(PPh3)(NO2)2] (cis-4), while the same reaction in presence of HClO4 promotes OD and the oxidation of the imine to imidic acid reactions producing a [RuNO]7 complex of the type [RuII(LOHNNN 0)(PPh3)(NO)Cl]+ (5+), where L1H has been modified to (R1)(OH)C=N-C6H4-N=C(Ph)(R2), o-phenylene-imine-imidic acid derivative (LOHNNN 0). The molecular structures of all the complexes were confirmed by single crystal X-ray crystallography and the electronic structure of 5+ ion was investigated by EPR spectroscopy and DFT calculations.



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Development of Eco-friendly Ethylene Scavenger Filters for Horticulture Application

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The preservation of climacteric fruits such as apples, plum, peach, pear, bananas, mangoes, kiwi, cucumbers, tomatoes and avocados, and vegetables such as carrots, potatoes and asparagus for a longer time is a biggest challenge for the horticulture industries. Most of fruits and vegetables produce a gaseous compound called "Ethylene" which increases the chlorophyll degradation process and accelerate ripening, senesce and softening of the same. Most of commercially available ethylene absorber sachets are composed of potassium permanganate (KMnO4) which is toxic in nature. In present study non- toxic, aqueous natural plant extract based ethylene scavenger filter was developed by green approach which increases the shelf life of fruits and vegetables in warehouses or in transportation and in household refrigerators. The eco-friendly ethylene scavenger filter was developed by the treating cotton woven or non-woven or viscose knit fabric with a highly stable water based emulsion which is composed of herbal oil extract, emulsifier and anti-oxidant agent. This filter showed much more higher ethylene absorption capacity (tested by NIOSH 1619) i. e. 95.47% and 99.89% antibacterial activity (AATCC 100-2019) as compare to potassium permanganate based ethylene absorber sachets.

Deprotection in simultaneous peptide synthesis

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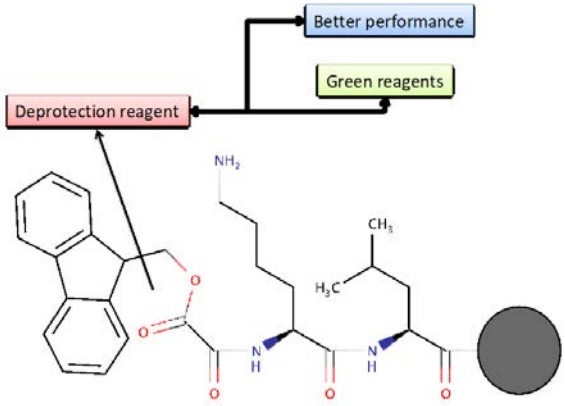
Statement of the Problem: deprotection in Fmoc solid phase peptide synthesis is a crucial step that influences the yield and purity of the product. One of the reagent commonly used is piperidine, a secondary amine that, in addition to being a toxic reagent and having a pungent odor, has a DEA-controlled substance status, therefore, it needs to be replaced. Our group explores the use of other reagents, as a replacement for piperidine, not only by their restriction but also looking for a greener chemistry in peptide synthesis. Methodology: four peptides with different sequences and characteristics were selected to be synthesized with two different methodologies, first by microwave-automated synthesis and second by tea-bag manual synthesis. Three deprotection reagents were used: Piperidine, piperazine, and 4-methyl piperidine. Findings: Although the three deprotection reagents showed similar performance in the microwave assisted synthesis, we found that 4-Methylpiperidine has better performance in the tea-bag simultaneous synthesis. Additionally, it has a lower toxicity than piperidine and it is not a controlled substance, which is why it is a good alternative as a removal reagent in the synthesis of peptides..



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Hydrothermal Pretreatment on Rice Straw to produce Reducing Sugars

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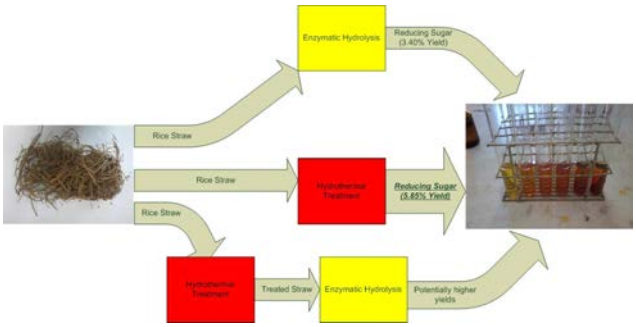
Statement of the Problem: Biomass is a type of material very common in the fields and as an agricultural by-product which is rich in sugars and phenolic compounds. Lignocellulosic biomass is a material that is usually resistant to influences from the environment and therefore difficult to process in order to obtain cellulose, hemicellulose and lignin. To enhance the separation of such materials from rice straw, for example, it can be applied heat and pressure, to a certain extent, in order to separate lignocellulosic biomass into its building blocks. Such substances can be obtained through hydrothermal treatment, using ionic liquids, enzymatic or acid hydrolysis, or a combination thereof. Methodology & Theoretical Orientation: Hydrothermal treatment is such a method that when applied pressure (15 atm) for one hour and temperature of 200 °C result in a aqueous solution with reducing sugars detected using 3,5-DNS standard method. When comparing two methods of obtaining reducing sugars, that is enzymatic hydrolysis and hydrothermal treatment, the latter yields more sugar than the prior. Such results are obtained mainly because when heat and pressure are applied to rice straw, the sheathing of hemicellulose and the lignin layers are broken, leaving the cellulose and the reducing sugars free to be extracted. The sugars mainly from cellulose are extracted only after breaking with the crystallinity of cellulose from rice straw. The results are sugars obtained in larger amounts when compared with enzymatic hydrolysis alone, because the lignocellulosic matrix is still recalcitrant to enzymes when reacted at biological reactors at mild conditions (around 50 °C for several hours). Conclusion & Significance: Extraction of reducing sugars by hydrothermal treatment render better results when compared with biological reactions using commercial enzymes only. Combinations of pretreatment methods can yield better results.



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1. Miranda Neto, Miral. Desenvolvimento de processo hidrotérmico e enzimático para a obtenção de açúcares redutores a partir da palha de arroz-BRS AG. MS thesis. 2018. Online at https://sistemas.furg.br/sistemas/sab/arquivos/bdtd/e3fee962546734f1d95a8d4fea98efe3.pdf

2. Miranda Neto, Miral, Lopes, T. J., Rodrigues, R. F., Beck, P. H., Augusto-Ruiz, W. Sacarificação enzimática da palha de arroz varietal 'BRS AG'. VI Reunião Técnica de Agroenergia. IX Simpósio de Energia e Meio Ambiente (2017).

3. Miranda Neto, Miral, Lopes, T. J., Rodrigues, R. F., Beck, P. H., Augusto-Ruiz, W. Análise da influência de tratamento hidrotérmico sobre a eficiência da sacarificação enzimática sobre palha de arroz varietal 'BRS AG'. VI Reunião Técnica de Agroenergia. IX Simpósio de Energia e Meio Ambiente (2017).

Technology of separation and recycling of waste the polymer-containing paper for obtaining heat insulation materials

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In modern conditions of intensive industrial development, one of the most important problems is the processing and utilization of household and industrial waste and protection of the environment from polymer contamination with waste paper and the rational use of forest resources of wood and paper. In this regard, it is important to develop and widely implement environmentally closed technological cycles of enterprises, design of equipment and technology for processing waste paper containing polymers, including Tetrapack packaging, with reuse of recycled cellulose and polymers.

A separate type of waste generated in the home and in industry is the waste of paper wallpaper, which contains various polymer coatings, of which 5 -10% of this product falls into the waste generated in production and everyday life. Waste wallpaper with a polymer coating, including polyvinyl chloride (PVC), is formed in accordance with the technological regulations of these industries. The amount of such wallpaper waste in Ukraine exceeds 5 - 8 million rolls or 250 thousand tons per year. Disposable household packaging for juices, water and other beverages made of multilayer cardboard and polyethylene, such as Tetrapack, also ends up in waste. For processing and separation of this waste polymer-containing paper is not yet environmentally friendly, dry separation technology, it falls into the waste, the amount of which exceeds 50 million / ton per year. According to the production technology, these paper-based wastes are made of natural cellulose and synthetic polymers. The high mass content of 5% to 60% of polymers in such waste paper makes it difficult to dispose of such waste by incineration, due to the fact that as a result a large number of harmful chemical compounds of pyrolysis of polymers: chlorine, hydrogen chloride, organic substances, including dioxins. The existing technology of water separation of paper from polymer films is a highly expensive and non-environmentally friendly method, because it requires a lot of water and creates secondary liquid waste, which also needs to be disposed of.

Thus, the development of anhydrous technology and equipment for the processing of such waste paper waste with the separation of polymers from the paper base-cellulose is of practical interest. Our proposed technology of dry separation of waste paper (polymer-containing wallpaper) and polymers, incl. packaging type "Tetrapack", allows with an efficiency of 85-95% to separate and recycle cellulose and polymers. In addition, it makes this recycling process environmentally friendly without the generation of secondary waste, simple and cost-effective for small businesses with high added value, and will additionally save forests from destruction when processing them into new paper - pulp-containing products.

In the course of the research, ecological, resource-saving technology and equipment for processing and reuse of industrial and household waste were developed, namely, waste paper, including polymer-containing wallpaper and Tetrapack packaging with a polymer coating, and obtaining separated cellulose fibers as a result of separated fibers. ecowool) and crushed polymers. To do this, we, together with the Ivano-Frankivsk company MPP "Imex", created industrial equipment - a universal 5-stage crusher and separator (DS-150 "IMEX"). Used for the technology of dry mechanical separation, separation of the paper base of waste paper from polymer PVC or PE coating (including "Tetrapack"), which is shown in Fig.1. It made it possible to completely separate 85-95% of the polymer from waste paper, and to obtain, at the same time, 90-95% pure cellulose and polymers. Additionally, we have developed a universal method for recycling-reuse of 90-95% of the obtained separated waste of pure expanded cellulose-ecowool, which provides their comprehensive utilization within one modern industrial complex of small enterprises and environmental safety of production as a whole, free of harmful gaseous and dusty emissions into the atmosphere and wastewater into rivers and lakes.

The validity and reliability of scientific results will be ensured by the use of modern physico-chemical research methods and physico-mechanical methods - grinding and separation, determination of strength, hardness, elasticity and resistance to rupture of insulating building materials containing waste. Physical and chemical methods of waste analysis, methods of gravimetric and spectral analysis, microscopy, infrared spectroscopy, methods of differential thermal analysis will be used to study the degree of purification of the obtained products.

Fig.1.Photo of universal crusher separation type DS-150 "IMEX", for separation of polymer-containing waste paper (wallpaper, packaging) to obtain two fractions: 1- loose cellulose-ecowool, as a heat-insulating material for insulation of residential premises in construction, and 2 - fractions of crushed polymers of PE, PVC ..

The study explored the possibility of creating and using new innovative composite materials from separated-treated waste to increase the cost of production through their practical use of new thermal insulation materials derived from waste paper waste. This would support creative small and medium enterprises and startups in context of application of highly innovative technological achievements in materials science for commercial and applied applications. The fraction of crushed and purified separated cellulose was reused to obtain thermal insulation material such as "Ecowool". as well as a filler for building materials. For example, instead of asbestos or natural pulp-paper in the production of construction asbestos-cement slate slabs at PJSC "Ivano-Frankivskcement" Ukraine, you can partially or completely replace natural materials - pulp and asbestos with shredded and separated pulp from wallpaper. The polymer fraction was additionally used as a component in the creation of new polymer composite materials from polyvinyl chloride and polyethylene.

Promising areas of use of technology of grinding, separation and recycling of polymer-containing

waste paper are the leading countries and Ukraine, which have a highly developed technological paper industry and creative small and medium enterprises for processing and utilization of waste paper and waste paper with high polymer content. to connect the following problems:

1. Provide Ukraine and other countries with new, environmentally friendly technologies and equipment for complex grinding, separation, processing and use of solid paper waste - polymer-containing waste paper (wallpaper, including packaging such as "Tetrapack") with recycling of separated waste - cellulose and polymers.
2. Will significantly reduce several times the needs of the paper industry in raw materials, namely in harvested wood and significantly reduce the number of forests cut down and preserve the ecology of the planet Earth;
3. Reduce by 90% the amount of unused paper waste of waste paper containing polymers and reduce environmental pollution by this waste.
4. Reduce several times the amount of waste paper containing polymers in Ukraine and other countries that can be disposed of by incineration, as a result will not pollute the atmosphere with harmful chemical gases;
5. Solve some social problems of Ukrainian and other small and medium business countries by creating new enterprises, reducing unemployment and creating new jobs, by increasing the innovative potential and competitiveness of European enterprises by selectively combining and transferring new and existing knowledge .

Vermifiltration Technology: Earthworm assisted green technology for wastewater treatment

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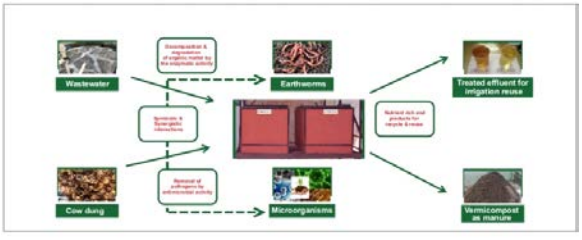
Statement of the Problem: In a developing country like India, the uncontrolled growth in urban areas has left many cities deficient in water supply, sewerage, and storm water drainage services and it is due to these deficient services that wastewater and its management has become a tenacious problem, even though a large part of the municipal expenditure is allotted to it. This, in turn, results in an increase in morbidity especially due to pathogens and parasitic infections and infestations in all segments of the population, particularly the urban slum dwellers. The potential of using earthworms (EWs) to treat municipal sewage sludge, domestic wastewater, and human faeces is increasing, and many previous research studies have already shown that earthworm assisted remediation technology - vermifiltration could constitute alternatives to existing municipal and domestic wastewater treatment as well as faecal waste treatment technology. Earthworms change the properties of biofilm present in the active layer by their burrowing activity and ingestion. They also help in the degradation of organic matter by symbiotic and synergistic interactions with the indigenous microbes. Vermifiltration is a bio-oxidative process in which earthworms interact intensively with microorganisms within the decomposer community, accelerating the stabilization of organic matter and greatly modifying its physical and biochemical properties. This technology is a stand-alone technology providing tremendous benefits such as decentralized solution and high value end products like vermicompost and can be considered as a new paradigm for wastewater treatment processes. Vermifiltration coupled with other technologies have been thoroughly researched upon, especially in the past two decades as the need for water reuse and wastewater treatment is increasing in line with climate change. If applied on a full scale, vermifiltration technology would help society reach the triple bottom line of sustainability: good for the environment, good for the economy, and good for the people..



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1. Sudipti Arora, Sakshi Saraswat, Rinki Mishra, Jayana Rajvanshi, Jasmine Sethi, Anamika Verma, Aditi Nag, and Sonika Saxena. Design, Performance Evaluation and Investigation of the Dynamic Mechanisms of Earthworm-Microorganisms interactions for wastewater treatment through Vermifiltration technology, Bioresource Technology Reports 12 (2020): 100603.

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