



R&R, 2018



# 4<sup>th</sup> International Conference on Recycling and Reuse

## Book of Abstracts

October 24-26, 2018  
İstanbul - Türkiye



**RECYCLING AND REUSE, 2018**

**4th INTERNATIONAL CONFERENCE  
ON  
RECYCLING AND REUSE**

**BOOK OF ABSTRACTS**

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## **Preface**

International Conference on Recycling and Reuse (R&R, 2018) organized by on of the leading universities of Turkiye; Istanbul University-Cerrahpasa, was held in Istanbul, 24-26 October, 2018. The conference brought together engineers, scientists, practitioners and other environmental professionals from many countries all over the world to exchange emerging ideas and to investigate key issues such as: integrated waste management; novel applications for reuse and recycling; renewable energy sources and green technologies. Over 100 oral and poster presentations as well as eight plenary lectures and six invited talks from eminent researchers have been scheduled in an intensive three-day program. Most importantly, over 40 young master and doctoral students participated in the conference. The participation of about 20 young researchers was subsidized by R&R, 2018 organization through fee remission.

The organizers would like to express their thanks to the keynote speakers for their excellent presentations. Special thanks should also be addressed to the members of the Scientific Committee. Moreover, we are very grateful to the members of the Organizing Committee as well as to our Sponsors who made the R&R, 2018 Conference a great success. It is also worth to mention that presented contributions, both oral and posters, could be submitted as full research papers to the journals; *Desalination and Water Treatment*, *Water Science and Technology*, *Water Science and Technology: Water Supply*, *Water Practice and Technology*, *International Journal of Global Warming* which provided special efforts to publish the selected conference papers. Finally, we thank all participants without whom the R&R, 2018 Conference would not have been possible.

We would like to welcome you at the forthcoming 5<sup>th</sup> International Conference on Recycling and Reuse (R&R, 2020).

*Hoşçakalın,*

October 2018, Istanbul

Prof. Dr. Hüseyin Selçuk

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## Table of Contents

Preface	iii
Committees	iv
Table of Contents	vii
ORAL PRESENTATIONS	1
ID 7 Utilization of Lime, Gypsum and Cement as an Additive Material in Liner System <i>K. Dincer, S. Y. Guvenc, G. Varank</i>	2
ID 11 Release of Metals and Nutrients during Sewage Sludge Hydrolysis by Rhamnolipid and Saponin <i>A. Uysal, E. Celik</i>	5
ID 19 Enhanced Solar-Driven Water Splitting of 1D Core-Shell Silicon-Metal Oxide Nanopillars <i>I. Iatsunskiy, K. Siuzdak, M. Pavlenko</i>	7
ID 21 Elimination of Antibiotic Resistance at Urban Wastewater Treatment Plants by Iron-based Heterogeneous Advanced Oxidation Processes <i>I. Arslan Alaton, A. Karatas, Ö. Pehlivan, T. Ölmez Hanci</i>	9
ID 28 The Potential of Water Saving in Buildings: Greywater Reuse <i>N. Büyükkamacı, E. Bağcılar</i>	11
ID 31 Effect of Phosphate on Anammox Process <i>İ.Ç.Erdem, B. Çalli</i>	13
ID 33 Evaluation of Municipal and Petrochemical Industry Sludges as a Feedstock for Biodiesel Production: Effect of the Acid and Combined Acid/Microwave Pre-treatments <i>D. Alper, E. Babayiğit, A. Erdinçler</i>	15
ID 38 Industrial and Agricultural Wastes as a Potential Biofilter Media for Groundwater Nitrate Remediation <i>E. B. Özkaraoava, R. M. Kalin, S. Gkiouzepas, Charles W. Knapp</i>	17
ID 42 Hexavalent Chromium Removal Using Ion Exchange (IX) Enhanced Capacitive Deionisation (IX CDI) <i>H. Senoussi, K.E. Bouhidel *</i>	19
ID 44 Preliminary Assessment of Durian Peel Liquid Smoke Utilization as a Natural Preservatives for Mackerel <i>M. Faisala*, A. Gania, F. Mulanaa</i>	21
ID 49 Ammonia Recovery From Chicken Manure Digestate via Gas Diffusion Tubular Polypropylene Membrane <i>A. Bayrakdar</i>	23
ID 50 Sepiolite Supported Co-Ce-B Catalyst for Hydrogen Generation from NaBH <sub>4</sub> <i>S. Hoşgün, M. Özdemir</i>	24
ID 55 State-of-the-art Technology for the Stabilization of Pb in the Incineration Fly Ash Using Waste Fishbone Hydroxyapatite <i>A. Saffarzadeh, M. Nag, T. Nomichi, T. Shimaoka</i>	26
ID 58 Classification and Determination of Drinkability of Thermal Waters in Erciş and Çaldıran (Van, Turkey) <i>H. Düzen</i>	28
ID 60 Recycling of gallium from gallium nitride waste of LED industry by hydrometallurgical method <i>Li-Lin Hsu, Wei-Sheng Chen</i>	30
ID 66 The Effect of ZrMOF Types on Gas Permeability Properties of PEBA Mixed Matrix Membranes <i>Y.B. Ilgaz, S.Deniz</i>	32
ID 67 ZrO <sub>2</sub> supported on Bamboo Leaves Ash as Heterogeneous Catalyst in Microwave-Assisted Biodiesel Conversion <i>I. Fatimah, D. Rubiyanto, A. Taushiyah, F.B. Najah, U. Azmi, Y. Sim</i>	34
	vii

ID 68	Enhancing the effectiveness of methylene blue (MB) photodegradation by ion Cu <sup>+</sup> doped to magnetic-photocatalyst (Fe <sub>3</sub> O <sub>4</sub> /TiO <sub>2</sub> ) <i>M. M. Musawwa, E. S. Kunarti, Sutarno</i>	36
ID 73	Removal of Cu(II) ion from aqueous solution by activated carbons produced from banana fruit bunch ( <i>Musa paradisiaca</i> ) <i>Allwar Allwar, Ade Setiawan, Hendra Agitya Ermawan, Tomy Alviansah</i>	39
ID 77	Optimization of Dilute Acid Hydrolysis of Kitchen Wastes for Bioethanol Production <i>M. N. Kerimak Öner, S. Fersiz</i>	41
ID 82	Environmental Sensitivity of Printed Circuit Board (PCB) Manufacturing to Transportation, Cu Recycling Rate and Energy Source Variations <i>E. Ozkan, B. Bas, N. Elginöz, F. Germirli Babuna</i>	42
ID 84	Production of Levulinic Acid From Biomass With Using Recyclable Magnetite Solid Acid Catalysts <i>B. Kaya Özsel, B. Niş, D. Öztürk</i>	43
ID 90	Shale gas extraction by hydraulic fracturing and flowback treatment technologies from shale gas extraction: A review <i>H. Sari-Erkan, N. Bakaraki-Turan, G. Onkal-Engin</i>	44
ID 92	Synthesis of the Iron Nanoparticles by Using <i>Pinus brutia</i> Extract and Hydrogen Gas Production During the Synthesis <i>D. Uzunoglu, A. Özer</i>	45
ID 95	Effect of Seed Biomass on Wastewater Treatment Performance <i>E. Demirkaya, H. Unver, B. Ciftcioglu, G. Ozyildiz, G.E. Zengin, I. Pala-Ozkok, E. Cokgor, D. Okutman Tas</i>	47
ID 96	Synthesis and Characterisation of Silica gel 60 Supported Iron-Zinc Bimetallic Nanoparticles for the Adsorption of Malachite Green <i>F. Toprak, F. Karanfil, D. Uzunoglu, M. Ergüt, A. Özer</i>	49
ID 101	Treatment of Pharmaceutical Wastewater by Combination of Electro-Fenton, Electrocoagulation and Photocatalytic Oxidation Processes <i>G.B.Dindaş, Y. Çalışkan, E.E. Çelebi, M. Tekbaş, N. Bektaş, H.C. Yatmaz</i>	51
ID 102	Study Total Synthesis Of Natural Anti-Marine Fouling Agent (Synthesis of 7 <sup>th</sup> Intermediate Compound From Omeazallene Derivative) <i>N.I. Prakoso, T. Umezawa, F. Matsuda</i>	53
ID 105	A Novel Potential Way for Polyethylene Reuse: Reduction of NiO via Polyethylene Pyrolysis <i>M. Cumbul Altay, S. Eroğlu</i>	56
ID 106	Comparison of Ozonation, Adsorption and Air Stripping Process for Ammonia Nitrogen Removal From Real Textile Wastewater <i>Y. Gunes, F. Barut, G. Kaykioglu</i>	58
ID 107	Madder Root as an Adsorbent for Chemical Oxygen Demand, Color and Aromaticity Removal of Natural and Synthetic Dyeing Effluents <i>E. Güneş, D.İ. Çifçi, R. Atav, Y. Güneş</i>	60
ID 109	Green Synthesis of Pd/Fe Bimetallic Nanoparticles: Catalytic in situ Generation of H <sub>2</sub> O <sub>2</sub> for Heterogeneous Fenton-like Decolourisation of Basic Red 46 and Direct Red 23 <i>M. Ergüt, A. Özer</i>	62
ID 114	Enhancement of Phytoremediation on the Removal of Lead (Pb) Using Electro-Assisted and Aeration System and Uptake by Water Lettuce ( <i>Pistia stratiotes</i> L.) <i>R.S. Putra, A.R.M. Hidayah, R.M.I. Wardani, A.P. Maulana, S. Fariduddin, and D. D. Darma</i>	64
ID 115	Phosphorus removal from sludge centrant liquor by a packed-bed electrocoagulation reactor using iron scrap anodes <i>S.M. Sarabi, P.I. Omwene, M. Kobya</i>	66
ID 121	Phosphorus Release and Nutrient Recovery from Waste Activated Sludge Through Mesophilic Alkaline Fermentation <i>S. Coşgun, B. Kunt, N. Semerci</i>	68

## Green Synthesis of Pd/Fe Bimetallic Nanoparticles: Catalytic in situ Generation of H<sub>2</sub>O<sub>2</sub> for Heterogeneous Fenton-like Decolourisation of Basic Red 46 and Direct Red 23

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**Keywords:** Palladium-iron bimetallic nanoparticles, Citrus limon, in situ H<sub>2</sub>O<sub>2</sub>, Heterogeneous Fenton-like reaction, catalyst, Basic Red 46, Direct Red 23

### **Abstract**

In this study, Pd/Fe bimetallic nanoparticles (Pd/FeNPs) were biosynthesized by aqueous lemon (*Citrus limon* (L.) *Burm. f.*) leaves extract as a reducing agent and were characterized by XRD, SEM, EDX and FTIR analysis methods. And then, Pd/FeNPs were utilized as a common heterogeneous catalyst for both in situ H<sub>2</sub>O<sub>2</sub> synthesis by formic acid decomposition in the presence of oxygen and heterogeneous Fenton like decolourisation of Basic Red 46 (BR 46) and Direct Red 23 (DR 23) azo dyes.

### **1. Introduction**

In recent years; the wastewater treatment methods are called as Advanced Oxidation Processes (AOPs), including homogeneous Fenton reaction (Fe(II)/H<sub>2</sub>O<sub>2</sub>), photo-Fenton reaction (Fe(II)/H<sub>2</sub>O<sub>2</sub>/UV), ozonation (O<sub>3</sub>), wet peroxide ozonation (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>), H<sub>2</sub>O<sub>2</sub>/UV, heterogeneous Fenton-like processes and photocatalytic (TiO<sub>2</sub>/UV and ZnO/UV) processes have attracted considerable attention for the removal of toxic and carcinogenic organic/inorganic pollutants from water sources. Heterogeneous Fenton-like reaction is one of the popular advanced oxidation processes. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is the most preferred oxidizing agent because of its environmental friendliness, rapid and easy formation of hydroxyl radicals for degradation of contaminants in heterogeneous Fenton-like reactions. However, the problems such as, the use of hydrogen peroxide is much higher than which is converted into hydroxyl radicals during the reaction due to the hydrogen peroxide is fed to the system in bulk, the cost of commercial hydrogen peroxide is expensive, difficulties in synthesis method, danger of transport and storage, affect the process negatively. Therefore, the indirect synthesis of H<sub>2</sub>O<sub>2</sub> catalytically in the reaction medium without adding H<sub>2</sub>O<sub>2</sub> from the outside (in situ hydrogen peroxide synthesis) offers an advantage in avoiding problems caused by unnecessary use of H<sub>2</sub>O<sub>2</sub>, in the heterogeneous Fenton-like reactions. In this method which is called as in situ H<sub>2</sub>O<sub>2</sub> synthesis; the catalytic decomposition of the organic compounds such as formic acid, hydrazine hydrate and hydroxyl amine etc., which have substituted hydrogen in their structure and mostly used for hydrogen production, leads to hydrogen gas generation and H<sub>2</sub>O<sub>2</sub> can be synthesized by the reaction of hydrogen and oxygen added in reaction media [1, 2].

In this study, Pd/Fe bimetallic nanoparticles will be biosynthesized as a catalyst by aqueous lemon leaves extract as a reducing agent for both in situ H<sub>2</sub>O<sub>2</sub> synthesis and the decolourisation of Basic Red 46 (BR 46) and Direct Red 23 (DR 23) azo dyes with heterogeneous Fenton-like reactions.

### **2. Materials and Methods**

#### **Green Synthesis of Pd/Fe Bimetallic Nanoparticles**

The lemon leaves were firstly washed with distilled water and then air-dried at ambient temperature. For the preparation of extract, 10 g of dried leaves were boiled in 500

mL of distilled water in a beaker under continuously stirring for 60 min. For green synthesis of Pd/Fe NPs, 0.5 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and 0.1 g of  $\text{PdCl}_2$  were dissolved in 60 mL aqueous extract of the lemon leaves at 60 °C under vigorous stirring. Then, a solution of 1.0 M  $\text{Na}_2\text{CO}_3$  was added dropwise to the mixture to obtain alkaline pH while changing the color to dark brown. After being stirred again for 3 hours at the same temperature, a suspension was formed which gave precipitate of Pd/FeNPs on centrifugation at 4000 rpm and the obtained nanoparticles were washed with distilled water, respectively, and then dried at 105°C in an oven.

### **Heterogeneous Fenton like decolourisation experiments with in-situ-generated $\text{H}_2\text{O}_2$**

In-situ generation of hydrogen peroxide was performed by formic acid decomposition and  $\text{O}_2$ . Heterogeneous Fenton like decolourisation experiments with in situ  $\text{H}_2\text{O}_2$  generation were carried out in a 250 mL magnetically stirred three-necked glass balloon. 50 mL of 20 mg/L BR 46 (or DR 23) and 50 mL of 500 mM formic acid were contacted with 1 g/L of catalyst. Initial pH of dye solutions was adjusted to 3.0 by 0.1 N HCl or 0.1 N NaOH solutions. Oxygen/air was passed into the reaction medium with a compressor. Dye concentrations were monitored by sampling at regular time intervals and analyzed by using the UV-vis spectrophotometer at the wavelength of 530 and 507 nm for BR 46 and DR 23, respectively. To further verify the in-situ generated  $\text{H}_2\text{O}_2$ , the solution (deionized water instead of dye) during the reaction was filtrated and monitored by spectrophotometric determination using titanium sulfate at 400 nm.

### **3. Results**

The crystalline structure of Pd/FeNPs was confirmed with XRD measurements. According to XRD analysis results, the presence of palladium and iron was confirmed in the structure of Pd/FeNPs. In order to identify the structure of catalyst in detail; SEM, EDX and FT-IR analysis will be also carried out. In this study, in situ  $\text{H}_2\text{O}_2$  generation was carried out by formic acid decomposition and the formation of  $\text{H}_2\text{O}_2$  was proved by the UV-vis absorbance spectrum of the resulting yellow complex between  $\text{H}_2\text{O}_2$  and titanium sulfate at 400 nm. In the heterogeneous Fenton like decolourisation studies with in situ  $\text{H}_2\text{O}_2$  generation, the decolourisation percentages  $\approx 95\%$  for BR 46 and  $\approx 93\%$  for DR 23 were obtained at the conditions of 20 mg/L of initial dye concentration, pH 3.0, 1 g/L of catalyst concentration, 25°C ambient temperature and 500 mM- 50 mL of HCOOH concentration. It was determined that Fe and Pd played important roles in the synergistic effect, that is, Pd nanoparticles worked in in-situ  $\text{H}_2\text{O}_2$  generation by formic acid decomposition and Fe nanoparticles worked in decompose  $\text{H}_2\text{O}_2$  for generating  $\cdot\text{OH}$  radicals to decolourisation of BR 46 and DR 23. Moreover, the adsorbent property of Pd/FeNPs was investigated in the same experimental conditions but the absence of formic acid and  $\text{H}_2\text{O}_2$ . These control experiments showed that, almost no colour removal percentages were found both two dyes. In order to determine the decolourisation efficiency of heterogeneous Fenton-like reaction which was carried out by in situ  $\text{H}_2\text{O}_2$  synthesis, the effects of reaction parameters such as, the concentration of formic acid, initial pH of dye solutions, initial dye concentrations and catalyst concentration will be also investigated experimentally in detail. Consequently, the synthesized catalyst displayed excellent performances for BR 46 and DR 23 removal by in-situ generation of hydrogen peroxide and heterogeneous Fenton-like catalytic reaction.

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