NiO-CeO$_2$ Nano-Catalyst for the Removal of Priority Organic Pollutants from Wastewater through Catalytic Wet Air Oxidation at Mild Conditions

Anushree, Chhaya Sharma, Satish Kumar

Abstract—Catalytic wet air oxidation (CWAO) is normally carried out at elevated temperature and pressure. This work investigates the potential of NiO-CeO$_2$ nano-catalyst in CWAO of paper industry wastewater under milder operating conditions of 90 °C and 1 atm. The NiO-CeO$_2$ nano-catalysts were synthesized by a simple co-precipitation method and characterized by X-ray diffraction (XRD), before and after use, in order to study any crystallographic change during experiment. The extent of metal-leaching from the catalyst was determined using the inductively coupled plasma optical emission spectrometry (ICP-OES). The catalytic activity of nano-catalysts was studied in terms of total organic carbon (TOC), adsorbable organic halides (AOX) and chlorophenolics (CHPs) removal. Interestingly, mixed oxide catalysts exhibited higher activity than the corresponding single-metal oxides. The maximum removal efficiency was achieved with Ce$_{40}$Ni$_{60}$ catalyst. The results indicate that the CWAO process is efficient in removing the priority organic pollutants from wastewater, as it exhibited up to 59% TOC, 55% AOX, and 54 % CHPs removal.

Keywords—Nano-materials, NiO-CeO$_2$, wastewater, wet air oxidation.

I. INTRODUCTION

WATER is the most abundant resource in nature and is essential to sustaining life, but its decreased availability is a well acknowledged problem facing people in different regions of the world [1], [2]. Large amounts of untreated industrial wastewaters, containing pollutants, able to present toxic, carcinogenic and endocrine disrupting effects to humans, animals and aquatic life, are disposed into fresh water sources. Many pollutants are found to be toxic and detrimental, even when they are present at very low concentrations [3], [4]. Wastewaters from industries also contain the organic bio-refractory compounds which inhibit biodegradation, as microorganisms are sensitive to these pollutants [5].

The paper industry is a water-intensive industry, which consumes a huge amounts of water (10-100 m^3/ton of produced paper). After various manufacturing stages i.e., pulping, pulp washing, screening, bleaching and coating operations, it produces a large amounts of heavily loaded wastewater. This wastewater is very complex in composition due to a large number of organic pollutants [6].

Anushree and Chhaya Sharma are with the Indian Institute of Technology Roorkee, Saharanpur Campus, Saharanpur- 247001, India.

Satish Kumar is with the Indian Institute of Technology Roorkee, Saharanpur Campus, Saharanpur- 247001, India (corresponding author, e-mail: kumarfpt@iitr.ac.in).

Approximately 700 organic and inorganic compounds identified in paper industry wastewater, includes; chlorinated compounds, fatty acids, tannins, stilbenes, resin acids, suspended solids, lignin and its derivatives, sulfur and its compounds, etc. [7]-[9]. Out of these, some compounds exhibit acute toxicity (chlorinated compounds, resin acids, chlorohydrocarbons, CHPs, furans, dioxins, chloroform, chlorate, etc.) and are collectively estimated as AOX [10], [11]. CHPs are formed primarily due to reaction between chlorine compounds and residual lignin during the bleaching stage [10]. CHPs constitute a particular group of priority toxic pollutants listed by the European Decision [12]. Toxic effects (on fish) of CHPs present in paper industry wastewater have been reported in various studies [13]. The conventional methods present some drawbacks like, transformation of pollutants from one form to another [14], and the presence of non-biodegradable compounds after treatment [15].

In order to overcome the above mentioned inconveniences of conventional treatment methods, various advanced oxidation processes have emerged in the last decades. With regard to its fast removal rate, CWAO technology is considered to be a promising technology for water remediation. In CWAO, high temperature (190-250 °C) and pressure (0.6-5 MPa) is required, which presents high capital cost of treatment [16]. Also the leaching of metal ions from catalysts limits its application [17].

It is well documented that these extreme conditions are required for easy carry out of reaction, as high temperature enhances the reaction rate; while, high pressure improves the oxygen buffering and makes it more available for the reaction [18], [19]. In the context of above discussed, the catalyst with high oxygen buffering capacity can be a better alternative for CWAO under milder operating conditions.

Ceria has been widely studied in CWAO, due to its oxygen storage and mobility capacities [20], [21]. Despite its widespread applications, pure cerium dioxide has several drawbacks, i.e. poor thermal stability, sintering, loss of surface area [22]. The introduction of transition metal into ceria lattice was observed to improve its oxygen storage and release properties, redox properties, surface area and thermal stability [23].

Nanoscience and nanotechnology hold out the promise of immense improvements in the field of catalysis. The nano-structured materials have great potential in the environmental applications due to their high stability, high efficiency, good reusability and operation at mild reaction conditions [24].

In the present study, we have reported the application of NiO-CeO$_2$ nano-catalysts in CWAO at mild operating conditions. The catalyst efficiency for CWAO of paper industry wastewater was evaluated in terms of TOC, AOX, and CHPs removal.

II. EXPERIMENTAL

A. Reagents and Effluent Samples

The wastewater samples were collected from the primary outlet of an integrated paper mill located in India. The *pH* of wastewater was adjusted with 1M H$_2$SO$_4$ solution. Analytical grade Ce(NO$_3$)$_3$.6H$_2$O, Ni(NO$_3$)$_2$.6H$_2$O and NaOH were used as starting material for catalyst preparation. Chlorophenols were obtained from Aldrich, Milwaukee, USA and Helix Biotech, Richmond B.C. Canada. The solvents (*n*-hexane, acetone and methanol) were of HPLC grade. Diethyl ether and ethanol were of LR grade. Analytical grade acetic anhydride was used after double distillation. Standard stock solutions of CHPs (20-30 mg/L) were prepared in acetone/water (10:90).

B. Experimental Procedures

The NiO-CeO$_2$ nano-catalysts with different molar ratios were prepared by co-precipitation method, as discussed elsewhere [25]. The treatment experiments were carried out at atmospheric pressure, 90 °C, *pH* 4 and catalyst dose of 1 g L^{-1} [26]. Aliquots were taken out at the end of process for analysis of various environmental parameters i.e. TOC, AOX and CHPs, while the catalyst was recovered by centrifugal separation before analysis. TOC values of all filtered samples were determined by a Shimadzu TOC-LCPH TOC analyzer based on combustion method. AOX analysis was carried out using a Dextar AOX analyzer by adsorption on activated charcoal. The qualitative and quantitative analysis of CHPs was done on Trace GC Ultra DSQ gas chromatography-mass spectrometer (GC-MS) equipped with TR-5 fused silica capillary column. CHPs were extracted from wastewater by the procedure outlined by Sharma et al. [27]. The wastewater (1L) was adjusted to pH 2 and extracted with 400 mL of diethylether:acetone mixture (90:10) for 48 h with intermittent shaking. Extracted samples were derivatized by acetic anhydride. Initially CHPs were identified by NIST library (National Institute of Standards and Technology) and further their retention times were confirmed by injecting the pure standard stock solution into GC-MS as outlined by [28].

The percent removal efficiency was quantified by:

$$RE = \frac{[C_o] - [C]}{[C_o]} \times 100 \qquad (1)$$

where, RE is removal efficiency (%); C$_o$ and C, are initial and final concentration of pollutants.

III. RESULTS AND DISCUSSION

A. Catalytic Activity Analysis

The wastewater obtained from the paper industry was characterized for various environmental parameters and the results are presented in Table I. The NiO-CeO$_2$ nano-catalysts with different Ni contents were evaluated in order to investigate the effect of Ni/Ce mole ration on CWAO efficiency, and the results are presented in Fig. 1.

TABLE I
ENVIRONMENTAL PARAMETERS FOR PAPER INDUSTRY WASTEWATER

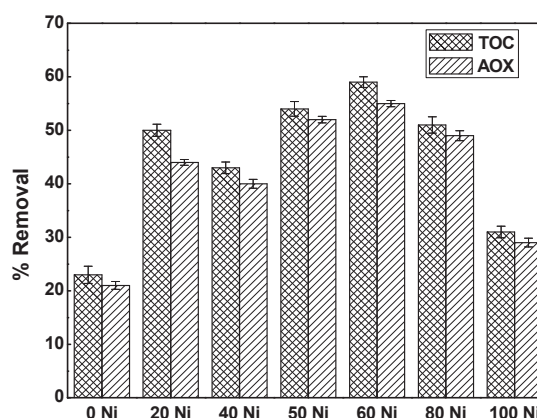| S. No.	Parameter	Average Value
1.	COD (mg L^{-1})	865 ± 32.14
2.	BOD$_5$ (mg L^{-1})	234 ± 12.84
3.	Color (mg Pt-Co L^{-1})	2768 ± 114.46
4.	TOC (mg L^{-1})	172.3 ± 4.8
5.	AOX (mg L^{-1})	16.2 ± 0.35
6.	CHPs (μg L^{-1})	485 ± 4.45

Fig. 1 Effect of mole ratio on TOC and AOX removal

CeO$_2$ was found to be less active catalyst with 23% TOC and 21% AOX abatement. NiO catalyst also exhibited the low abatement profile with 31% TOC and 29% AOX abatement. All the mixed catalysts exhibited high removal efficiency than the single oxides, which progressively increased with the increasing Ni content. The catalyst with Ni/Ce molar ratios of 60/40 presented a noticeable removal of TOC (59%) and AOX (55%). Highest activity of Ce$_{40}$Ni$_{60}$ nano-catalyst was in accordance with its small crystallite size (8 nm), high surface area (90m^2/g) and high pore volume (0.275 cc/g) [25].

B. CHPs Removal

To further explore the treatment efficiency of Ce$_{40}$Ni$_{60}$ nano-catalyst towards CWAO process, CHPs removal was studied. The GC-MS chromatograms for CHPs in paper industry wastewater, before and after treatment are given in Fig. 2. Quantitative analysis revealed the presence of total 25 CHPs (Table II).

On the basis of chemical family there were six categories i.e. chlorophenols (CP), chloroguaiacols (CG), chlorocatechols (CC), chlorovanilin (CV), chlorosyringols (CS) and chlorosyringaldehydes (CSA). Examination of CHPs data exhibits highest contribution of CP (56.6%), followed by CG (39.7%), CC (2.3%), CS (1.2%), CV (0.06%) and CSA (0.02%) (Fig. 3 (a)). On the basis of chlorine atom substitution, di-chlorophenolics (DCHPs) exhibited the highest share of 47.5%, followed by tri-chlorophenolics

(TCHPs, 30.5%), mono-chlorophenolics (MCHPs, 21.6%), tetra-chlorophenolics (TeCHPs, 0.37%) and penta-chlorophenolics (PCHPs, 0.08%) (Fig. 3 (b)). The data indicate that about 99.5% of identified CHPs include MCHPs, DCHPs and TCHPs. Among various CHPs, 2,4,5-TCP contributed maximum 27.4% followed by 4,5-DCG (21.2%), 4-CG (17.2%), 2,5-DCP (12.8%), 2,4-DCP (5.5%) and 2,6-DCP (4.7%), while the remaining CHPs were present in relatively low quantities.

After CWAO treatment, total 20 CHPs (out of 25) were detected with overall removal of 54%. The removal of most of CHPs was from 30-100%. Compounds like 2,3-DCP, 3,4-DCP, 2,4,6-TCP, 2,6-DCSA and PCP were completely removed or concentration fell below the detection limit of the instrument. 2,3,5,6-TCG was removed up to 83.2 % followed by 4,5-DCG (79.9%), 2,3,4-TCP (77%) and 4,5,6-TCG (75.7%). According to chemical family, complete removal was achieved for CSA, followed by CG (77%), CS (61.9%), CC (55.9%), CP (36.9%) and CV (32.5%) (Fig. 4 (a)). According to attached Cl atom, highest degradation was achieved for PCHPs and TeCHPs with 100% and 83.2% removal, respectively. MCHPs, DCHPs and TCHPs were reduced by 64.8%, 63.6% and 29.9%, respectively (Fig. 4 (b)).

C. XRD analysis

XRD of $Ce_{40}Ni_{60}$ nano-catalyst was carried out before and after use, in order to study any crystallographic change during treatment experiment. The XRD patterns were recorded on a Bruker D8 powder diffractometer equipped with CuKα radiation, operating at a scanning speed of $2°$ min^{-1}. The obtained diffraction data was compared against the known diffraction peaks using JCPDS files (Joint Committee on Powder Diffraction Standards). The diffraction pattern of fresh $Ce_{40}Ni_{60}$ nano-catalyst (Fig. 5) exhibited the reflections corresponding to both CeO_2 ($2θ = 28.5°$, $33°$, $47.4°$, $56.3°$, JCPDS 81-0792) and NiO ($2θ = 37.3°$, $43.3°$ and $62.9°$,

JCPDS 75-0197) phases. The XRD pattern of used catalyst was similar to the fresh catalyst, indicating that there was no crystallographic change in the catalyst after use. A slight shift of peaks towards lower angle indicates a small increase in crystallite size after use [25].

TABLE II
CHPs IN PAPER INDUSTRY WASTEWATER BEFORE AND AFTER CWAO

| S. No.	Compound	Initial (µg/L)	Final (µg/L)	% Removal
1.	3-CP	14.9 ±10.98	10.3 ± 0.08	31.2
2.	4-CP	6.2 ± 4.55	5.6 ± 0.25	9.4
3.	2,3-DCP	0.8 ± 0.01	ND	100
4.	2,4-DCP	26.5 ± 0.47	14.5 ± 0.60	45.3
5.	2,5-DCP	62.4 ± 0.78	34.5 ±1.23	44.7
6.	2,6-DCP	22.9 ± 4.45	7.8 ±1.87	65.9
7.	3,4- DCP	0.6 ± 0.08	ND	100
8.	2,3,4-TCP	3.3 ± 0.10	0.8 ±0.02	77.0
9.	2,3,5-TCP	2.5 ± 0.03	1.4 ±0.32	43.5
10.	2,3,6- TCP	1.2 ± 0.01	0.7 ±0.07	42.9
11.	2,4,5-TCP	132.9 ± 19.69	97.9 ±5.99	26.3
12.	2,4,6-TCP	0.4 ± 0.03	ND	100
13.	4-CG	83.6 ± 19.45	21.4 ±1.02	74.5
14.	4,5-DCG	102.9 ±1.92	20.7 ±2.03	79.9
15.	4,6-DCG	2.6 ± 0.52	1.4 ± 0.06	48.0
16.	3,4,5-TCG	0.6 ± 0.11	0.3 ± 0.10	55.5
17.	3,4,6-TCG	0.5 ± 0.19	0.2 ± 0.03	60.6
18.	4,5,6-TCG	0.7 ± 0.10	0.2 ± 0.04	75.7
19.	2,3,5,6-TCG	1.8 ± 0.22	0.3 ± 0.05	83.2
20.	3,5- DCC	2.9 ± 0.21	2.7 ± 0.13	8.9
21.	3,6- DCC	8.5 ± 0.05	2.4 ± 0.45	72.2
22.	5,6-DCV	0.3 ± 0.19	0.2 ± 0.06	32.5
23.	TCS	5.9 ± 0.89	2.2 ± 0.43	61.9
24.	2,6-DCSA	0.09 ± 0.02	ND	100
25.	PCP	0.4 ± 0.02	ND	100
	Total	485	225	54%

ND- Not detected
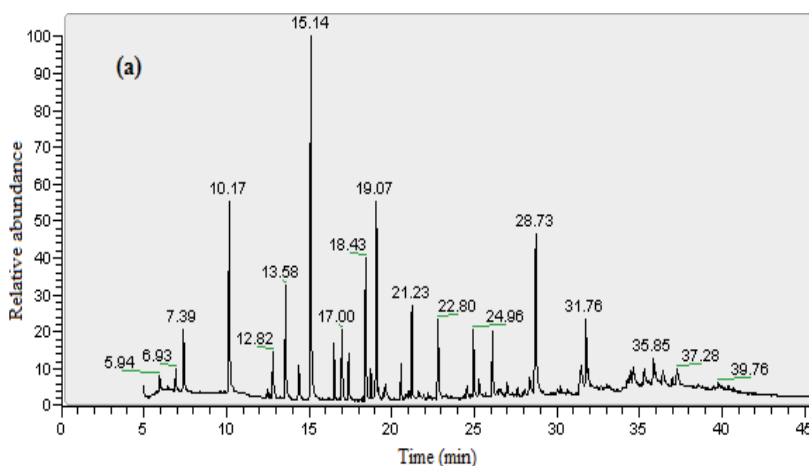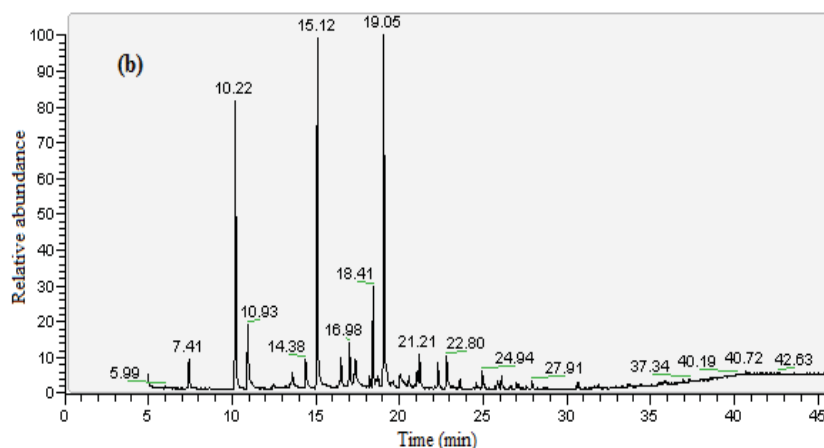
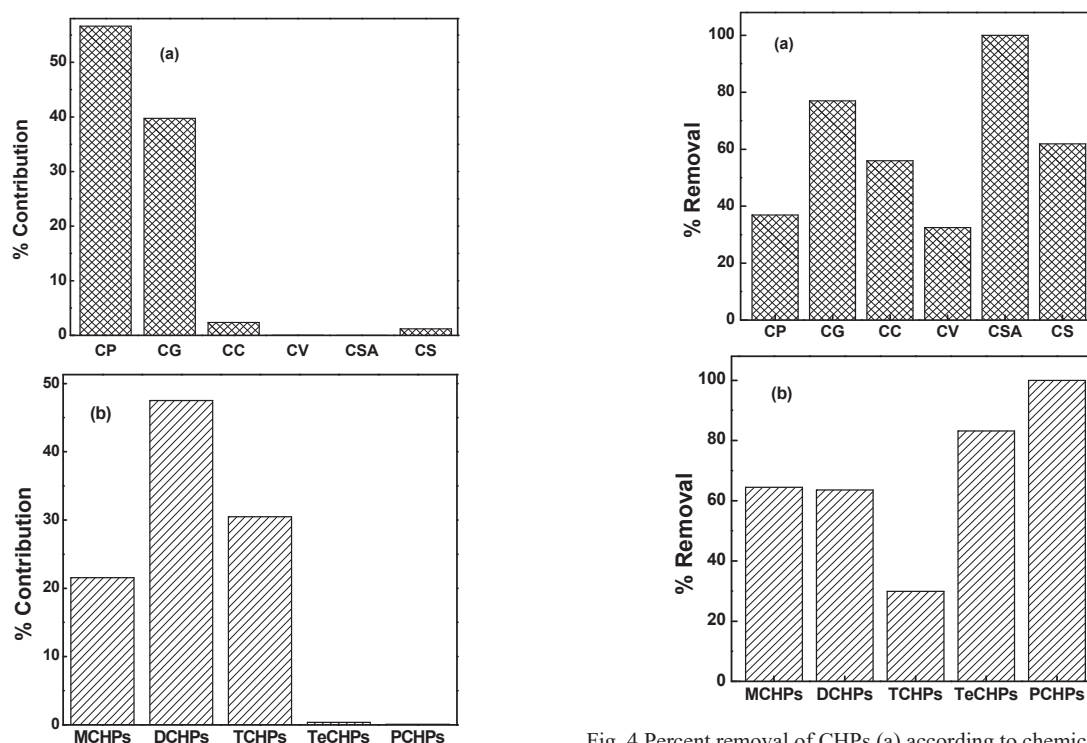Fig. 2 GC-MS chromatogram of CHPs in paper industry wastewater (a) before (b) after treatment

Fig. 3 Percent contribution of CHPs before CWAO (a) according to chemical family (b) according to attached chlorine atom

Fig. 4 Percent removal of CHPs (a) according to chemical family (b) according to attached chlorine atom

D. Reusability Studies

Reusability of catalyst is a serious issue which affects the practical utility of process. Catalytic run over the used $Ce_{40}Ni_{60}$ catalyst exhibited very low degradation of TOC. This deactivation of catalyst is mainly due to the: (i) leaching of Ce and Ni from the catalyst and (ii) poisoning of catalytic sites by adsorbed organic compounds [29]. Further, the reusability experiments of $Ce_{40}Ni_{60}$ nano-catalyst were carried out up to 4 treatment cycles, after calcination at 400 °C for 3 h, before each cycle (Fig. 6). It was found that the activity of re-calcined catalyst was almost restored up to 2 cycles.

E. Leaching Studies

The leaching of metallic ions from catalyst has a great impact on their activity and stability. To study the extent of metal leaching, the supernatant was analyzed at the end of experiment. The dissolved Ce and Ni concentration were determined using ICP-OES (Teledyne Leeman Labs, Prodigy Spec, 3043). The results showed that Ce concentrations in samples ranged from 0.12 mg/L to 0.16 mg/L and Ni concentration ranged from 0.218-0.643 mg/L for $NiO-CeO_2$ nano-catalysts. The values of metal leaching were comparably low [30], [31], indicating good stability of the catalyst during the treatment.
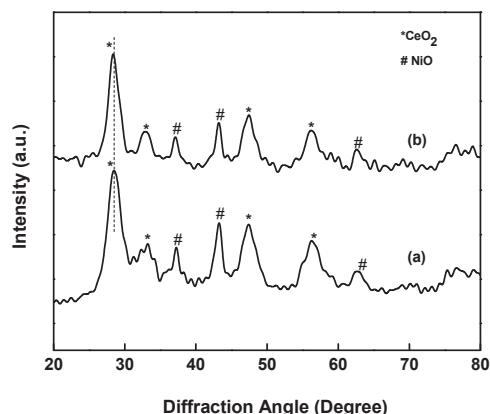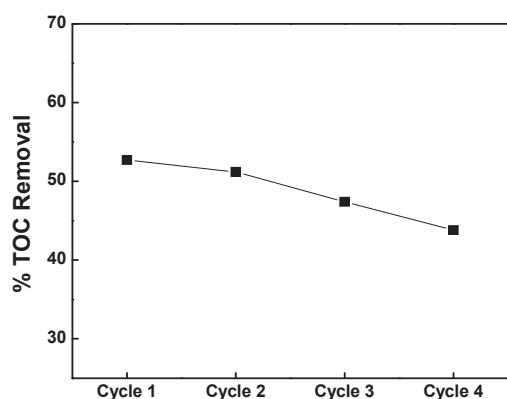
Fig. 5 XRD pattern of (a) fresh (b) used $Ce_{40}Ni_{60}$ nano-catalyst

Fig. 6 Effect of catalyst recycling on TOC removal

IV. Conclusion

The prepared $NiO\text{-}CeO_2$ nano-catalyst exhibited promising catalytic activity in CWAO of paper industry wastewater, under the milder operating conditions. A significant improvement in treatment efficiency was observed by addition of Ni into ceria lattice. Highest removal of TOC (59%) and AOX (55%) was achieved with $Ce_{40}Ni_{60}$ nano-catalyst. The $Ce_{40}Ni_{60}$ nano-catalyst also exhibited the CHPs removal of 54%, with complete degradation of 2,3-DCP, 3,4- DCP, 2,4,6-TCP, 2,6-DCSA and PCP. XRD indicated that there was no crystallographic change in catalyst after use and recycling studies indicated its suitability for reuse up to two treatment cycles. Additionally, the catalysts exhibited low leaching values.

References

[1] M. Hartmann, S. Kullmann, and H. Keller, "Wastewater treatment with heterogeneous Fenton-type catalysts based on porous materials," *J. Mater. Chem.,* vol. 20, pp. 9002-9017, 2010.

[2] P. Saranya, K. Ramani, and G. Sekaran, "Biocatalytic approach on the treatment of edible oil refinery wastewater," *RSC Adv.,* vol. 4, pp. 10680-10692, 2014.

[3] C. S. D. Rodrigues, L. M. Madeira, and Rui A. R. Boaventura, "Decontamination of an industrial cotton dyeing wastewater by chemical and biological processes," *Ind. Eng. Chem. Res.,* vol. 53, pp. 2412-2421, 2014.

[4] C. Wang, A. Yediler, D. Lienert, Z. Wang, and A. Kenttrup, "Toxicity evaluation of reactive dyestuffs auxiliaries and selected effluents in textile finishing industry to luminiscent bacteria Vibrio fischeri," *Chemosphere*, vol. 46, pp. 339, 2002.

[5] C. Barrera-Díaz, I. Linares-Hernández, G. Roa-Morales, B. Bilyeu, and P. Balderas-Hernández, "Removal of Biorefractory Compounds in Industrial Wastewater by Chemical and Electrochemical Pretreatments," *Ind. Eng. Chem. Res.,* vol. 48, pp. 1253-1258, 2009.

[6] A. Kohler, S. Hellweg, B. I. Escher, and K. Hungerbuhler, "Organic Pollutant Removal versus Toxicity Reduction in Industrial Wastewater Treatment: The Example of Wastewater from Fluorescent Whitening Agent Production," *Environ. Sci. Technol.,* vol. 40, pp. 3395-3401, 2006.

[7] M. Ali, and T. R. Sreekrishnan, "Aquatic toxicity from pulp and paper mill effluents: a review," *Adv. Environ. Res.,* vol. 5, pp. 175-196, 2001.

[8] B. Karrasch, O. Parra, H. Cid, M. Mehrens, P. Pacheco, R. Urrutia, C. Valdovinos, and C. Zaror, "Effects of pulp and paper mill effluents on the microplankton and microbial self-purification capabilities of the Biobío River," *Chile. Sci. Total Enviro.,* vol. 359, pp. 194-208, 2006.

[9] M. Vepsäläinen, H. Kivisaari, M. Pulliainen, A. Oikari, and M. Sillanpää, "Removal of toxic pollutants from pulp mill effluents by electrocoagulation", *Sep. Purif. Technol.,* vol. 81, pp. 141-150, 2011.

[10] E. C. Catalkaya, and F. Kargi, "Advanced oxidation treatment of pulp mill effluent for TOC and toxicity removals," *J. Environ. Manag.,* vol. 87, pp. 396-404, 2008.

[11] D. V. Savant, R. A. Rahman, and D. R. Ranadi, "Anaerobic digestion of absorbable organic halides (AOX) from pulp and paper industry wastewater," *Bio. Technol.,* vol. 30, pp. 30-40, 2005.

[12] EC Decision 2455/2001/EC of the European Parliament and of the Council of November 20, 2001, "Establishing the list of priority substances in the field of water policy and amending Directive" 2000/60/EC, *Official Journal of the European Communities, L331/1-5 of 15-12-2001*.

[13] G. Erisction, and A. Larsson, "DNA-A dots in perch (Perca fluviatillis) in coastal water pollution with bleaching pulp mill effluents," *Ecotoxicol. Environ. Saf.,* vol. 46, pp. 167-173, 2000.

[14] S. Ciputra, A. Antony, R. Phillips, D. Richardson, and G. Leslie, "Comparison of treatment options for removal of recalcitrant dissolved organic matter from paper mill effluent," *Chemosphere*, vol. 81, pp. 86-91, 2010.

[15] R. S. Rana, P. Singh, V. Kandari, R. Singh, R. Dobhal, and S. Gupta, "A review on characterization and bioremediation of pharmaceutical industries wastewater: An Indian perspective," *Appl. Water Sci.,* DOI: 10.1007/s13201-014-0225-3, 2014.

[16] J. A. Melero, F. Martínez, J. A. Botas, R. Molina, and M. I. Pariente, "Heterogeneous catalytic wet peroxide oxidation systems for the treatment of an industrial pharmaceutical wastewater," *Water Res.,* vol. 43, pp. 4010-4018, 2009.

[17] J. F. Zhao, L. Chen, Y. C. Lu, and W. W. Tang, "Catalytic wet air oxidation for the treatment of emulsifying wastewater," *J. Environ. Sci.,* vol. 17, pp. 576-579, 2005.

[18] A. M. Hosseini, A. Tungler, Z. Schay, S. Szabó, J. Kristóf, É. Széles, and L. Szentmiklósi, "Comparison of precious metal oxide/titanium monolith catalysts in wet oxidation of wastewaters," *Appl. Catal. B Environ.,* vol. 127, pp. 99-104, 2012.

[19] S. Azabou, W. Najjar, M. Bouaziz, A. Ghorbel, and S. Sayadi, "A compact process for the treatment of olive mill wastewater by combining wet hydrogen peroxide catalytic oxidation and biological techniques," *J. Hazard. Mater.,* vol. 183, pp. 62-69, 2010.

[20] A. Trovatelli, "Catalytic properties of ceria and CeO_2-containing materials," *Catal Rev - Sci Eng,* vol. 38, pp. 439-520, 1996.

[21] N. M. Dobrynkin, M. V. Batygina, A. S. Noskov , P. G. Tsyrulnikov , D. A. Shlyapin, V.V. Schegolev , D.A. Astrova , and B.M. Laskin, Catalysts Ru-CeO₂/Sibunit for catalytic wet air oxidation of aniline and phenol, Top. Catal., Vol. 33, pp 69-76, 2005.

[22] M. B. Reddy, and A. Khan, "Nanosized CeO_2-SiO_2, CeO_2-TiO_2, and CeO_2-ZrO_2 mixed oxides: influence of supporting oxide on thermal

stability and oxygen storage properties of ceria," Catal. Surv. Asia, vol. 9, pp. 155-171, 2005.

[23] G. Lafaye, J. Jr. Barbie, and D. Duprez, "Impact of cerium-based support oxides in catalytic wet air oxidation: Conflicting role of redox and acid-base properties," *Catal. Today*, vol. 253, pp. 89-98, 2015.

[24] M. Kurian, and D.S. Nair, "Manganese zinc ferrite nanoparticles as efficient catalysts for wet peroxide oxidation of organic aqueous wastes," *J. Water Process Eng.*, DOI: 10.1016/j.jwpe.2014.10.011, 2014.

[25] Anushree, S. Kumar, and C. Sharma, "NiO-CeO$_2$ nano-catalysts: Synthesis, characterization and application in catalytic wet air oxidation of wastewater," *Mater. Express,* vol. 5, pp. 419-428, 2015.

[26] Anushree, S. Kumar, and C. Sharma, "Synthesis, characterization and catalytic wet air oxidation property of mesoporous Ce$_{1-x}$Fe$_x$O$_2$ mixed oxides," *Mater. Chem. Phys.*, Vol. 155, pp. 223-231, 2015.

[27] C. Sharma, S. Mohanty, S. Kumar, and N.J. Rao, "Gas chromatographic determination of pollutants in the chlorination and caustic extraction stage effluents from bleaching processes of agricultural residues," *Inter. J of environ and analyt. chem.,* vol. 64, pp. 289-300, 1996.

[28] A. K. Choudhary, S. Kumar, C. Sharma, "Removal of chloro-organics and color from pulp and paper mill wastewater by polyaluminium chloride as coagulant," *Desalin. Water Treat.*, vol. 53, pp. 697-708, 2015.

[29] H. Sun, H. Liang, G. Zhou, and S. Wang, "Supported cobalt catalysts by one-pot aqueous combustion synthesis for catalytic phenol degradation," *J. Colloid Interface Sci.*, vol. 394, pp. 394-400, 2013.

[30] S. Yanga, M. Besson, and C. Descorme, "Catalytic wet air oxidation of succinic acid over Ru and Pt catalysts supported on Ce$_x$Zr$_{1-x}$O$_2$ mixed oxides," *Appl. Catal. B: Environ.*, vol. 165, pp. 1-9, 2015.

[31] Y. Liu, and D. Sun, "Development of Fe$_2$O$_3$-CeO$_2$-TiO$_2$/ϒ-Al$_2$O$_3$ as catalyst for catalytic wet air oxidation of methyl orange azo dye under room condition," *Appl. Catal. B: Environ.*, vol. 72, pp. 205-211, 2007.