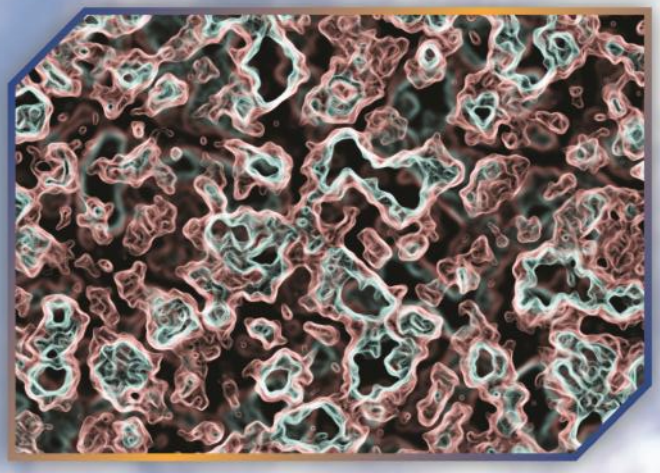
Environmental Research & Technology

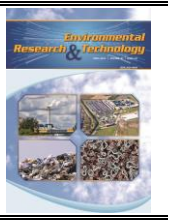
YEAR : 2018 | VOLUME : 01 | ISSUE : 03

ISSN: 2636-8498



Environmental Research & Technology

http://dergipark.gov.tr/ert



ACADEMIC ADVISORY BOARD

Prof. Dr. Adem Basturk

Prof. Dr. Mustafa Ozturk

Prof. Dr. Lutfi Akca

Prof. Dr. Oktay Tabasaran

Prof. Dr. Ahmet Demir

SCIENTIFIC DIRECTOR

Prof. Dr. Ahmet Demir (Yildiz Technical University)

EDITOR IN CHIEF

Prof. Dr. Mehmet Sinan Bilgili (Yildiz Technical University)

ASSISTANT EDITOR

Dr. Hanife Sari Erkan (Yildiz Technical University)

CONTACT

Yildiz Technical University
Environmental Engineering Department, 34220 Esenler
Istanbul – Turkiye
Web: http://dergipark.gov.tr/ert/
E-mail: ert@yildiz.edu.tr

Environmental Research & Technology

http://dergipark.gov.tr/ert

Environmental Research & Technology

http://dergipark.gov.tr/ert

Editorial Board

Environmental Research & Technology

http://dergipark.gov.tr/ert

TABLE OF CONTENTS

Environmental Research & Technology, Vol. 1(3), pp. 1-10, 2018

Environmental Research & Technology

http://dergipark.gov.tr/ert

RESEARCH ARTICLE

Turbidity and COD removal from leather processing effluents using TiO_2–assisted photocatalytic-ozonation by response surface methodology

Musa Buyukada*[1]

[1] Abant Izzet Baysal University, Environ. Eng. Dept., Golkoy Campus, 14200, Bolu, TURKEY

ABSTRACT

In the present study, concurrently removal of COD and turbidity from leather processing effluents (LPE) using TiO_2–assisted photocatalytic-ozonation were investigated by utilization of Box-Behnken design (BBD) in planning experiments. Effects of ozone dose (OD, mg L^{-1}), catalyst dose (CD, g L^{-1}), and aeration (A, mL min^{-1}) were performed as explanatory variables. An increase both in doses of ozone and catalyst and a decrease in aeration leaded increases both in removals of COD and turbidity. Values of 96.77% and 95.37% were obtained as the highest COD and turbidity removal efficiencies, respectively. This showed that TiO_2-assisted photocatalytic-ozonation process was significantly effective for the treatment of LPE. By using BBD, 2.95 g L^{-1} of CD, 19.99 mg L^{-1} of OD, and 1.63 mL min^{-1} of A were determined as BBD-optimized operating conditions. BBD suggested removals of 96.77% and 94.93% for COD and turbidity, respectively at these optimized conditions. Validation experiments at BBD-optimized conditions were resulted as 95.52%±1.28 and 94.36%±2.52 for COD removal and turbidity removal, respectively. Good agreement between predicted values and experimental results demonstrated the accuracy of BBD in optimization of explanatory variables of TiO_2-assisted photocatalytic-ozonation process. Finally, multiple non-linear regression (MNLR) studies were performed to state the variation in responses and also to predict the responses. The proposed models predicted COD and turbidity removals with regression coefficients of 99.99% and 99.97%, respectively. These findings also showed that MNLR was an efficient way to model and to predict the response variables of photocatalytic-ozonation process.

Keywords: Leather processing effluents, Photocatalytic-ozonation, COD, Turbidity, Empirical modeling

1. INTRODUCTION

Increase in human population in recent years has triggered the technological developments in all fields in industries. Leather as a developing industry, uses a lot of chemical compounds to process leather before their product is presented to customers' satisfaction. While leather is being processed, tons of effluents including toxic and hazardous chemicals are being occurred. Discharging these effluents before a complete treatment will cause a serious environmental problem. Thus, treatment of leather effluent before discharging has gained an importance to be addressed [1-5].

A lot of various methods for treatment of industrial effluents have been extensively investigated by researcher such as adsorption, coagulation, activated carbon, and etc. Although some good results have been obtained by these traditional methods, some negative situations are generally come together with them like desorption and long time to reach equilibrium. Unlike, advanced oxidation processes (AOPs) such as photocatalytic degradation, ultrasound, Fenton, and etc. can remove effluents in a short time period. Ozone can be also added into AOPs due to its advantages of highly effective and easy operating conditions. So, treatment of leather processing effluents (LPE) by incorporating photocatalytic degradation and ozone may contribute to related literature significantly in terms of novelty. By this way, a hybrid process is created and its effects on removal efficiency may be compared [6-10]. For example, ultrasonic degradation was incorporated with mineralization and detoxification for removal of diclofenac from wastewater [6]. Similarly, dielectric

Corresponding Author: musabuyukada@ibu.edu.tr (Musa Buyukada)
Received 19 March 2018; Received in revised form 18 April 2018; Accepted 19 April 2018
Available Online 1 July 2018
Doi: ISSN: 2636-8498

barrier discharge plasma process was utilized in some kind of advanced oxidation processes [7]. Additionally, sonolysis was used in both homogeneous and heterogeneous medium with various catalysts [10].

Designing experiments, determination of levels of operating conditions, and decreasing cost can be stated as ones of the most important steps in data-driven studies. To meet this criteria, design of experiments (DOEs) can be utilized. Response surface methodology (RSM) as a kind of DOEs provides a cost-effective way to investigate the related system with minimum runs. Box-Behnken design (BBD) as a kind of RSM is generally chosen for operating conditions without fraction. It is mostly set with three of four explanatory variables with three levels, three replicates, and one duplicate. By this way, response variable(s) can be predicted by regression analyses, the effects of explanatory variables can be compared by ANOVA, and operating conditions can be optimized by numeric techniques. Considering the advantageous sides of BBD, incorporating ozone-based photocatalytic treatment of LPE with BBD can contribute to related literature significantly [11-14].

The purpose of the present study can be summarized considering the literature survey given above as follows: (1) investigation of performance of TiO_2–assisted photocatalytic-ozonation process in treatment of LPE, (2) quantification of the effects of catalyst dose, ozone dose, and aeration, (3) prediction of COD and turbidity removals using multiple non-linear regression models, and (4) optimization and validation of explanatory variables.

2. MATERIALS AND METHOD

2.1. Leather processing effluents

Leather processing effluents (LPE) were provided from the discharge point of a local leather processing plant in Gerede, Bolu, Turkey. Its properties were listed in Table 1. Any pretreatment procedure was not applied to the effluents and they were directly used in the experiments.

2.2. Photocatalytic ozonation process

This process was formed incorporating a cylindrical photoreactor made from stainless steel with an ozone generator coupled to an oxygen tube. Additionally, a UV lamb, an air pump and a magnetic stirrer with heater were also utilized. Photoreactor with a certain volume of 1.25 L was put onto magnetic stirrer vertically and UV-C lamb (235 nm, Philips, 20 cm, 11 W) was put in it. Air pump that could pump up to 50 mL min^{-1} was connected to process using a glass-tube. Detailed information on photocatalytic process could be reached from the related paper [14]. By this way, air was sent to system from below to above. Likewise, ozone generator that could produce an ozone amount from 8 mg L^{-1} to 32 mg L^{-1} by decreasing flow rates from 5 mL min^{-1} to 0.5 mL min^{-1} was adopted to photoreactor. Schematic illustration of the related process was given in Fig 1.

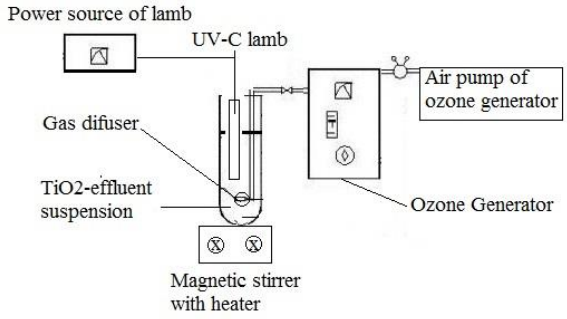


Fig 1. Schematic presentation of photocatalytic-ozonation process.

2.3. Catalyst

Although TiO_2 could be synthesized by various simple ways, it was purchased from Merck in anatase form with a purity of 99% and it was used in the experiments without any purification. Because, synthesis of a novel catalyst and characterization and/or comparison of it with other catalysts were out of scopes of the present study.

2.4. Response surface methodology

Box-Behnken design (BBD) as a kind of response surface methodology (RSM) was used to decrease both error probability and cost, and to predict both the COD and turbidity removals. It was set up with three explanatory variables of ozone dose (OD, mg L^{-1}), catalyst dose (CD, g L^{-1}), and aeration (A, mL min^{-1}) with three replicates and one duplicate. This approach suggested 15 experiments to investigate the variations in response variables. Levels of explanatory variables and the experimental schedule were concurrently given in Table 2. For all statistical approaches, Design Expert 9.0.6 (Statease) software was utilized. Additionally, Minitab 17 (Minitab, PA) was used to correlation calculations.

2.5. Turbidity and COD analyses

A similar procedure for COD analysis was followed that Buyukada (2017) performed [14]. COD removal was analyzed using COD measuring kits (Hach LCI 400, 0-1000 mg L^{-1} O_2). 2 mL of effluent was added into kit and then it was heated at 150oC for 2 hours in a digester (Hach 200). After it, it was left to get cool at room temperature. Blank sample was obtained by following the same procedure with 2 mL of destile water and it was used to calibrate UV-spectrophotometer. Finally, a UV spectrophotometer (Hach 2000) based on a barcode system was utilized to determine the COD values of each samples. Difference between the COD values of initial and treated samples were divided to initial COD values for converting the results to percentage. Turbidity (T, NTU) was analyzed using a turbidimeters (Micro TPI, Scientific Inc.) and the same percentage procedure that was used for COD was applied to data.

3. RESULTS AND DISCUSSION

3.1. Effects of operating parameters

3.1.1. Effect of catalyst dose (CD, g L^{-1} TiO_2)

A positive correlation between CD and COD removal ($p = 0.007$; $r = 0.120$; $n = 15$) and turbidity removal ($p = 0.005$; $r = 0.762$; $n = 15$) was determined according to results. Thus, increasing CD resulted an increase in both COD and T removals. Increasing CD from 1 g L^{-1} to 3 g L^{-1} increased COD and T removal from 52% to 63% and 40% to 48%, respectively under the experimental conditions of 15 mg L^{-1} of OD and 20 mL min^{-1} of A. These results showed the positive effect of CD on both COD and turbidity removals. The effect of CD on removal of COD and turbidity was visually given in Fig 2. Similarly, oxidation of a drug with ozone in aqueous media was studied in related literature and removal efficiency of 85% was obtained [17]. Furthermore, diclofenac removal was aimed in another study using photocatalytic ozonation and 89% was obtained as COD removal efficacy [15]. These findings were in good agreement with related literature [15-18].

Table 1. Chemical properties of leather effluents

COD (mg L^{-1} O_2)	TNb (mg L^{-1})	TOC (mg L^{-1})	Abs (IU)	pH	Conductivity (µS cm^{-1})	Turbidity (NTU)	Color (m^{-1})
384.3	12.1	216.5	0.968	6.8	1265	9.6	452

Table 2. Levels of explanatory variables and experimental schedule

	Levels of variables	Explanatory variables			Response variables	
		OD (mg L^{-1})	CD (g L^{-1})	A (mL min^{-1})	COD removal (%)	Turbidity removal (%)
	Min. (-1)	10	1	0	0	0
	Med. (0)	15	2	5	-	-
	Max. (+1)	20	3	10	100	100
Standard run	Randomly run	OD (mg L^{-1})	CD (g L^{-1})	A (mL min^{-1})	COD removal (%)	Turbidity removal (%)
8	1	20	2	20	58.81	47.27
3	2	10	3	10	90.85	78.76
15	3	15	2	10	93.53	76.43
11	4	15	1	20	52.09	40.01
5	5	10	2	0	94.45	88.86
4	6	20	3	10	93.58	81.99
14	7	15	2	10	93.40	76.41
12	8	15	3	20	62.63	48.26
1	9	10	1	10	85.00	73.90
7	10	10	2	20	55.19	45.69
9	11	15	1	0	96.03	89.86
6	12	20	2	0	96.77	95.37
13	13	15	2	10	93.49	76.39
2	14	20	1	10	88.61	78.78
10	15	15	3	0	95.90	89.96

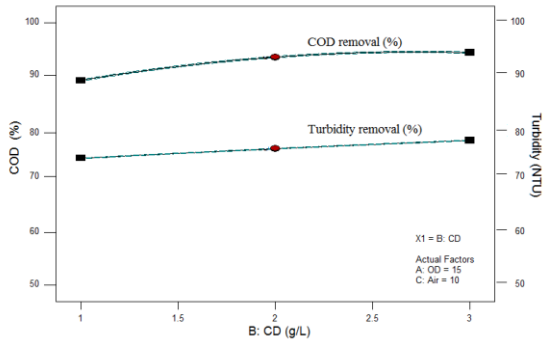


Fig 2. The effect of CD on COD and turbidity removal

3.1.2. Effect of ozone dose (OD, mg L^{-1} O_3)

Similar findings of CD were obtained for the effect of OD on removal of COD and turbidity. A positive correlation between OD and COD removal ($p = 0.009$; $r = 0.806$; $n = 15$) and turbidity removal ($p = 0.004$; $r = 0.765$; $n = 15$) was determined according to results. Thus, increasing OD triggered an increase in both COD and turbidity removals. Increasing OD from 10 g/L to 20 g L^{-1} increased COD and turbidity removal from 90% to 94% and 78% to 81.8%, respectively under operating conditions of 3 g L^{-1} of CD and 10 mL min^{-1} of A. These results showed the positive effect of OD on both COD and turbidity removal. This synergistic effect was figured out in Fig 3. In a similar study, ultrasound assisted ozonation was utilized for wastewater treatment and COD removal of 70% was obtained [19]. Additionally, UV–assisted hydrogen peroxide was used for the treatment of pharmaceutical effluents and an approximate COD removal of 80% was obtained [20]. Results of related literature showed a fairly similarity with the results of present study [19, 20].

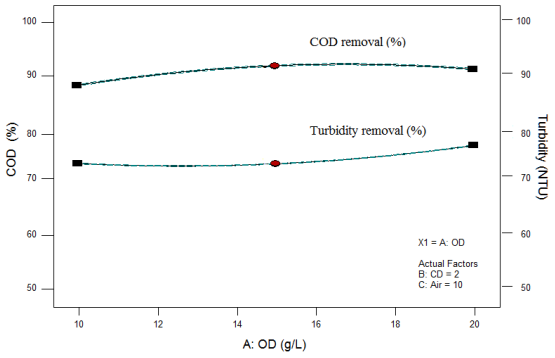


Fig 3. The effect of OD on COD and turbidity removal

3.1.3. Effect of aeration (A, mL min^{-1})

A powerful and also negative correlation between A and COD removal ($p < 0.001$; $r = -0.872$; $n = 15$), and turbidity removal ($p < 0.001$; $r = -0.952$; $n = 15$) were obtained according to experimental results. These findings pointed out a certain decrease in COD and turbidity removals while A was increasing. A decrease from 94.5% to 55.2% in COD removal and from 88.9% to 45.7% in turbidity removal were obtained by increasing A from 0 mL min^{-1} to 20 mL min^{-1} under 10 mg L^{-1} of OD and 2 g L^{-1} of CD. These results were also illustrated in Fig 4. Fenton process was utilized in related literature for diclofenac removal and this resulted in terms of COD removal of 70% [21]. A similar study of [21], photo–assisted Fenton process was utilized for the same aim and 80% of COD removal was obtained [22]. Similar results were obtained by various studies [21-23].

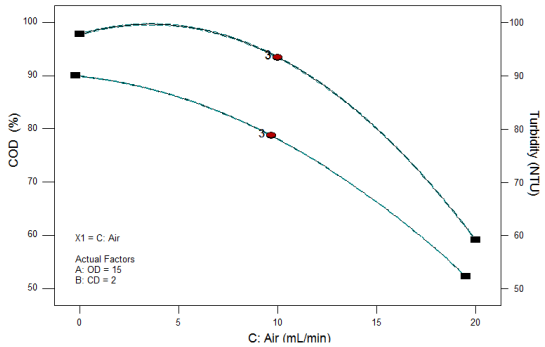


Fig 4. The effect of A on COD and turbidity removal

3.2. Characteristic findings on Box Behnken design (BBD)

To determine the optimum model type, sequential model sum of squares, lack of fit test, and model summary statistics were concurrently incorporated. All the obtained results were given in Table 3. Model type showed that the quadratic model was the best way to predict the response variables considering the choosing criteria of p [11]. As much as lower p could be stated as a better p. Thus, quadratic model was firstly suggested by the results of sequential model findings (Table 3) [12]. Lack of fit could be stated as an indicator that showed the sustainability and it demonstrated the reasonable and significant sides of proposed model. To meet this criteria, lack of fit must be greater than 0.05, in another terms it must be insignificant [13]. It was totally clear that only quadratic model had a lower p value than 0.05 (Table 3). Summary statistics were generally used to take general information about predictive power of suggested models. The highest regression coefficients could guide for selection of the optimum model type. Table 3 showed that the highest regression coefficient of 99.99% was obtained for quadratic model. Thus, quadratic model was selected to identify the variation in response variables and also to predict the response variables [11-13].

3.3. Diagnostic findings based on ANOVA results

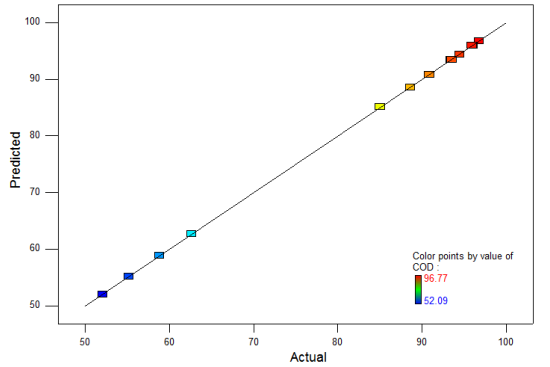
Some assumption such as there was no autocorrelation and data had a normal probability were also tested before statistical modeling. To test these criteria, externally studentized predicted vs. actual graph (Fig 5) and normal probability plot (Fig 6) were drawn, respectively [13, 14]. As seen from Fig 5 and 6, there was no autocorrelation and experimental data showed a normal distribution.

Table 3. Characteristic findings on Box Behnken design

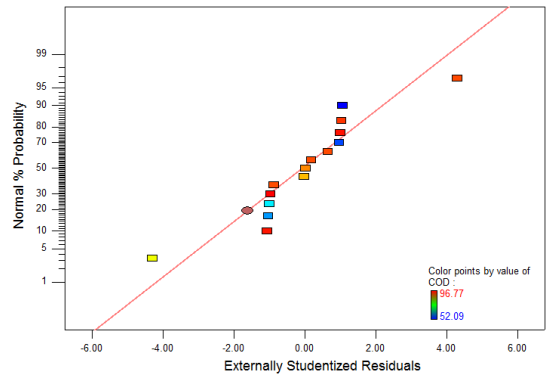
Sequential model sum of squares for COD removal						
Source	Squares	df	Square	Value	Prob > F	Decision
Mean vs. Total	104,200,000	1	104,200,000			
Linear vs. Mean	3056.27	3	1018.76	12.94	0.0006	
2FI vs. Linear	29.08	3	9.69	0.093	0.9620	
Quadratic vs. 2FI	836.65	3	278.88	27948.77	< 0.0001	Suggested
Cubic vs. Quadratic	0.041	3	0.014	3.08	0.2544	Aliased
Residual	0.008867	2	0.004433			
Total	108,100,000	15	7209.58			
Lack of fit tests for COD removal						
Source	Squares	df	Square	Value	Prob > F	
Linear	865.77	9	96.20	21698.39	< 0.0001	
2FI	836.69	6	139.45	31454.41	< 0.0001	
Quadratic	0.041	3	0.014	3.08	0.2544	Suggested
Cubic	0.000	0				Aliased
Pure Error	0.008867	2	0.004433			
Model summary statistics for COD removal						
Source	Std. Dev.	R2	R2adj	R2pred	PRESS	
Linear	8.87	0.7793	0.7191	0.6051	1548.96	
2FI	10.23	0.7867	0.6267	0.1910	3172.75	
Quadratic	0.100	1.0000	0.9999	0.9998	0.68	Suggested
Cubic	0.067	1.0000	0.9999			Aliased
Sequential model sum of squares for turbidity removal						
Source	Squares	df	Square	Value	Prob > F	
Mean vs. Total	78907.56	1	78907.56			
Linear vs. Mean	4244.40	3	1414.80	42.35	< 0.0001	
2FI vs. Linear	23.36	3	7.79	0.18	0.9063	
Quadratic vs. 2FI	344.13	3	114.71	28046.35	< 0.0001	Suggested
Cubic vs. Quadratic	0.020	3	0.006550	16.38	0.0581	Aliased
Residual	0.0008	2	0.0004			
Total	83519.48	15	5567.97			
Lack of fit tests for turbidity removal						
Source	Squares	df	Square	Value	Prob > F	
Linear	367.51	9	40.83	102,100,000	< 0.0001	
2FI	344.15	6	57.36	143,400,000	< 0.0001	
Quadratic	0.020	3	0.0006550	16.38	0.0581	Suggested
Cubic	0.000	0				Aliased
Pure Error	0.0008	2	0.0004			
Model summary statistics for turbidity removal						
Source	Std. Dev.	R2	R2adj	R2pred	PRESS	
Linear	5.78	0.9203	0.8986	0.8391	742.16	
2FI	6.56	0.9254	0.8694	0.6435	1644.01	
Quadratic	0.064	0.9999	0.9999	0.9999	0.32	Suggested
Cubic	0.020	0.9999	0.9999			Aliased

ANOVA results were given in Table 4. According to Table 4, all the linear effects of CD, A, and OD were found significantly effective on both COD and turbidity removals ($p < 0.001$). Additionally quadratic effects of all explanatory variables were also significantly effective on COD removal ($p < 0.001$) and turbidity removal ($p < 0.0044$). Furthermore, three significant binary interaction between A and OD ($p = 0.0013$ for COD and $p < 0.001$ for turbidity), A and CD ($p < 0.001$ for COD and $p < 0.001$ for turbidity), and OD and CD ($p < 0.0070$ for COD and $p < 0.001$ for turbidity) were found as significantly effective parameters. The visual presentation of these binary interactions were given in Fig 7 and Fig 8 for COD and turbidity removals, respectively.

Finally, proposed multiple non-linear regression models were given in Table 5. Adjusted and predicted regression coefficients of 99.99% for COD and turbidity removals demonstrated the powerful side of proposed model in statement of variation and in prediction.



(a)

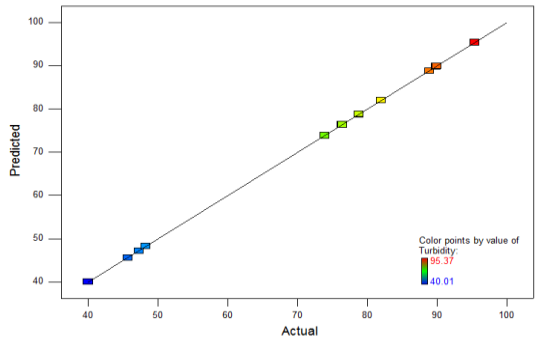


(b)

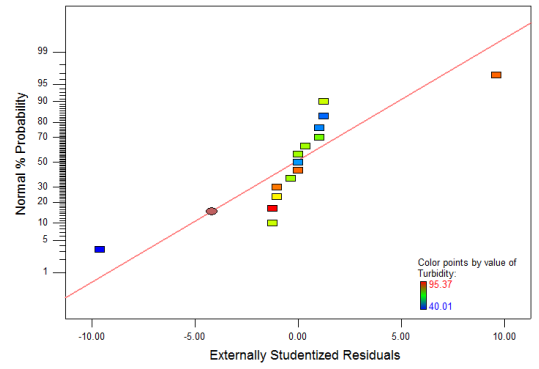
Fig 5. Externally studentized graph for (a) COD removal (b) turbidity removal

3.4. Optimization and validation

To maximize the COD and turbidity removals, a numeric optimization procedure was followed. Considering the results obtained for linear effects of explanatory variables, "in range" section was selected for OD and CD unless "minimize" was selected for A. At the same time "maximize" function was also selected for both COD and turbidity removal considering interpolation (not extrapolation of experimental results). 19.99 mg L^{-1} of OD, 2.95 g L^{-1} of CD, and 1.63 mL min^{-1} of A were determined as RSM-optimized operating conditions. RSM suggested COD removal of 96.77% and turbidity removal of 94.03% at this conditions.



(a)



(b)

Fig 6. Normal probability plot of (a) COD removal (b) turbidity removal

Validation experiments were performed under RSM-optimized conditions for three times to prevent experimental error and also to calculate standard deviation. 95.52%±1.28 for COD removal and 94.36%±2.52 for turbidity removal were obtained. The findings of this part of present study seemed to be in good accordance with related literature [11-14]. These results demonstrated that RSM was a successful method for optimization of operating parameters of TiO_2-assisted photocatalytic ozonation process. Good accordance between predicted values and experimental results justified the accuracy of RSM in optimization.

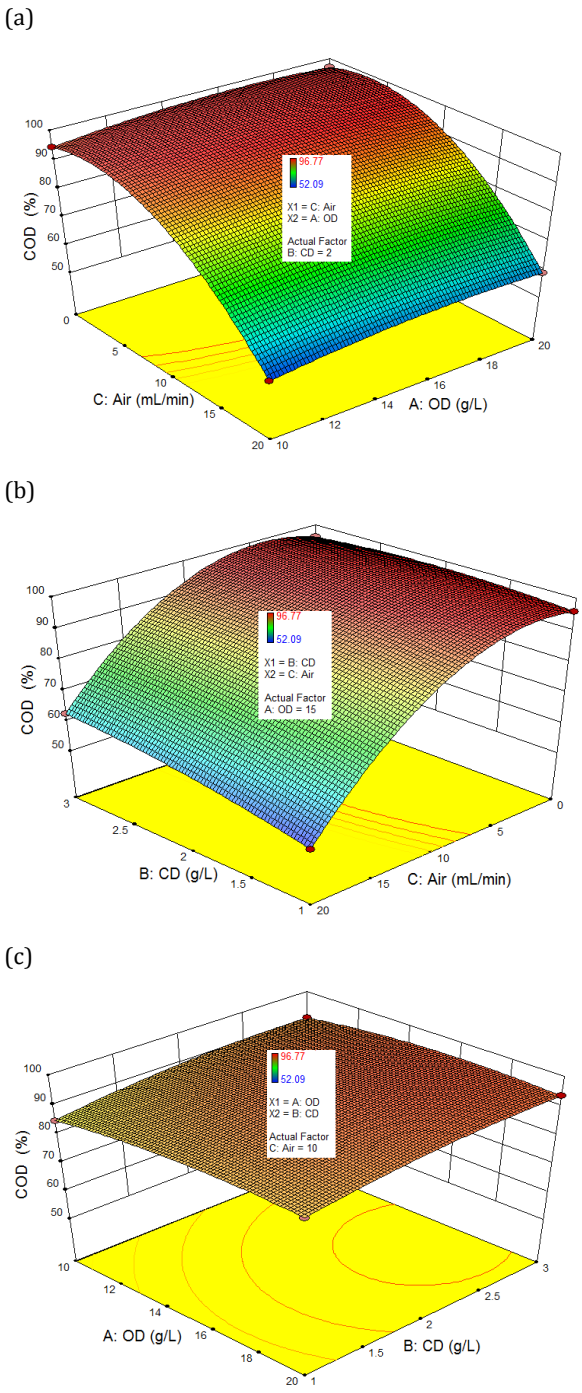


Fig 7. Binary interactive effects of (a) A and OD, (b) A and CD, and (c) OD and CD on COD removal

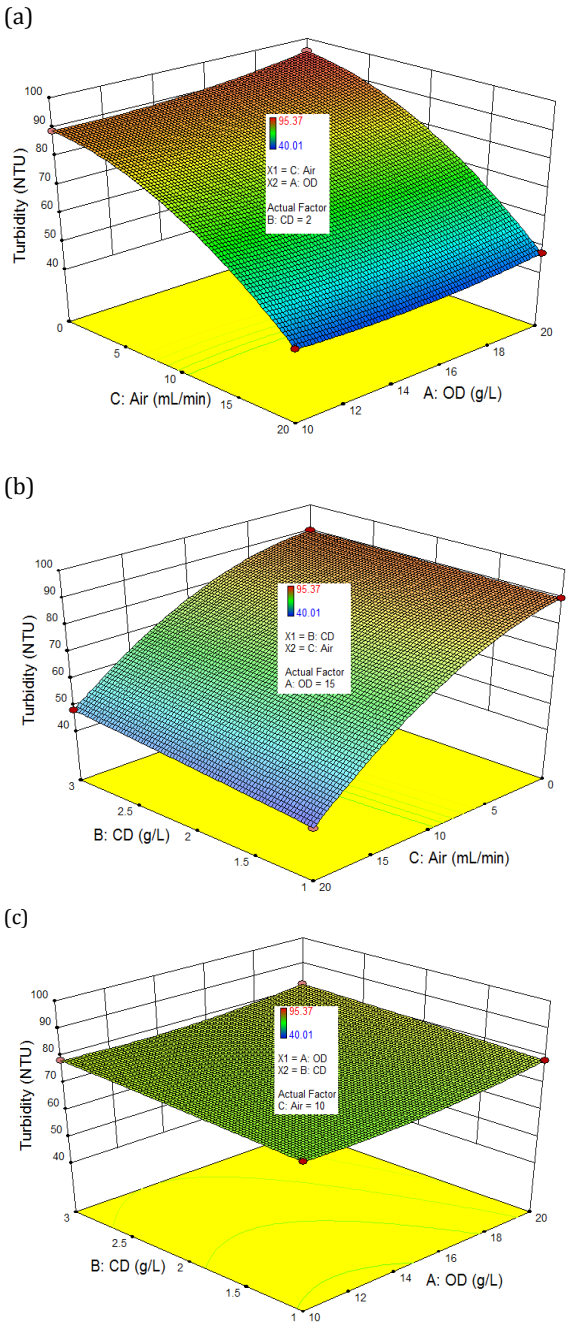


Fig 8. Binary interactive effects of (a) A and OD, (b) A and CD, and (c) OD and CD on turbidity removal

Table 4. ANOVA results based on Box Behnken design

Source	Squares	df	Square	Value	Prob > F	
COD removal						
Model	3921.99	9	435.78	43672.31	< 0.0001	significant
A-OD	18.85	1	18.85	1889.07	< 0.0001	
B-CD	56.34	1	56.34	5646.14	< 0.0001	
C-Air	2981.08	1	2981.08	298,800,000	< 0.0001	
AB	0.19	1	0.19	19.40	0.0070	
AC	0.42	1	0.42	42.34	0.0013	
BC	28.46	1	28.46	2852.40	< 0.0001	
A^2	17.23	1	17.23	1727.09	< 0.0001	
B^2	12.00	1	12.00	1202.79	< 0.0001	
C^2	831.65	1	831.65	83345.22	< 0.0001	
Residual	0.050	5	0.009978			
Lack of Fit	0.041	3	0.014	3.08	0.2544	not significant
Pure Error	0.008867	2	0.004433			
Cor Total	3922.04	14				
Turbidity removal						
Model	4611.89	9	512.43	125,300,000	< 0.0001	significant
A-OD	32.80	1	32.80	8020.78	< 0.0001	
B-CD	33.70	1	33.70	8240.11	< 0.0001	
C-Air	4177.89	1	4177.89	1,021,000,000	< 0.0001	
AB	0.68	1	0.68	166.41	< 0.0001	
AC	6.08	1	6.08	1485.63	< 0.0001	
BC	16.61	1	16.61	4060.06	< 0.0001	
A^2	16.46	1	16.46	4023.96	< 0.0001	
B^2	0.099	1	0.099	24.21	0.0044	
C^2	314.13	1	314.13	76805.02	< 0.0001	
Residual	0.020	5	0.00409			
Lack of Fit	0.020	3	0.00655	16.38	0.0581	not significant
Cor Total	4611.91	14				

Table 5. Predictors of proposed MNLR models

Predictors	COD removal		Turbidity removal	
	Coded	Actual	Coded	Actual
Intercept	93.47	66.19	96.11	76.41
A-OD	1.53	2.92	2.02	1.72
B-CD	2.65	7.86	2.05	1.91
C-Air	-19.30	-0.44	-22.85	-0.48
AB	-0.22	-0.04	-0.41	-0.083
AC	-0.33	-0.007	-1.23	-0.025
BC	2.67	0.267	2.04	0.20
A^2	-2.16	-0.086	-2.11	-0.084
B^2	-1.80	-1.80	-0.16	-0.16
C^2	-15.01	-0.15	-9.22	-0.092

4. CONCLUSIONS

TiO_2-assisted photocatalytic ozonation process was used to remove COD and turbidity from LPE. Maximum COD removal of 96.77% and turbidity removal of 95.37% were obtained under the experimental conditions of 2 g L^{-1} TiO_2, 20 mg L^{-1} of O_3 and no aeration. These findings showed that this process was efficient for treatment of LPE. MNLR models predicted COD removal and turbidity removal with a regression coefficient of 99.99%. This demonstrated the powerful side of proposed models in predictions of removal efficiencies. Accuracy of RSM–based optimization process was justified by the results of validation experiments. RSM was found significantly effective in optimization of operating variables.

5. ACKNOWLEDGEMENT

The author would like to present him special thanks to Dr. Fatih Evrendilek and Dr. Nusret Karakaya, the supervisors of Hydrology and Limnology Laboratory, where the experimental parts of the present study were performed. Ersin Abanuz was gratefully acknowledged by the author for him invaluable helps in running experiments.

REFERENCES

[1]. S.K. Khetan and T.J. Collins, "Human pharmaceuticals in the aquatic environment: a challenge to green chemistry," *Chemical Reviews*, Vol. 107, pp. 2319-2364, 2007.

[2]. N. Laville, S. Ait-Aissa, E. Gomez, C. Casellas and J.M. Porcher, "Effects of human pharmaceuticals on cytotoxicity, EROD activity and ROS production in fish hepatocytes," *Toxicology,* Vol. 196, pp. 41-55, 2004.

[3]. B.T. Ferrari, N. Paxéus, R.L. Giudice, A. Pollio and J. Garric, "Ecotoxicological impact of pharmaceuticals found in treated wastewaters: study of carbamazepine, clofibric acid, and diclofenac," *Ecotoxicological Environmental Safety*, Vol. 55, pp. 359-370, 2003.

[4]. J. Schwaiger, H. Ferling, U. Mallow, H. Wintermayr and R.D. Negele, "Toxic effects of the non-steroidal anti-inflammatory drug diclofenac: Part I: histopathological alterations and bioaccumulation in rainbow trout," *Aquatic Toxicology,* Vol. 68, pp. 141-150, 2004.

[5]. R.R. Giri, H. Ozaki, T. Ishida, R. Takanami and S. Taniguchi, "Synergy of ozonation and photocatalysis to mineralize low concentration 2,4-dichlorophenoxyacetic acid in aqueous solution," *Chemosphere*, Vol. 66, pp. 1610-1617, 2007.

[6]. V. Naddeo, V. Belgiorno, D. Kassinos, D. Mantzavinos and S. Meric, "Ultrasonic degradation, mineralization and detoxification of diclofenac in water: optimization of operating parameters," *Ultrasonics Sonochemistry,* Vol. 17, pp. 179-185, 2010.

[7]. T. Kosjek, E. Heath and A. Krbavčič, "Determination of non-steroidal anti-inflammatory drug (NSAIDs) residues in water samples," *Environmental Intermediate,* Vol. 31, pp. 679-685, 2005.

[8]. M. Cleuvers, "Mixture toxicity of the anti-inflammatory drugs diclofenac, ibuprofen, naproxen, and acetylsalicylic acid," *Ecotoxicological Environmental Safety,* Vol. 59, pp. 309-315, 2004.

[9]. M. Hijosa-Valsero, R. Molina, H. Schikora, M. Müller and J.M. Bayona, "Removal of priority pollutants from water by means of dielectric barrier discharge atmospheric plasma," *Journal of Hazardous Materials*, Vol. 262, pp. 664-673, 2013.

[10]. G.T. Güyer and N.H. Ince, "Degradation of diclofenac in water by homogeneous and heterogeneous sonolysis," *Ultrasonics Sonochemistry*, Vol. 18, pp. 114-119, 2011.

[11]. M. Buyukada, "Modeling of decolorization of synthetic reactive dyestuff solutions with response surface methodology by a rapid and efficient process of ultrasound-assisted ozone oxidation," *Desalination and Water Treatment,* Vol. 57, pp. 14973–14985, 2016.

[12]. M. Buyukada, "Prediction of Photocatalytic Degradation and Mineralization Efficiencies of Basic Blue 3 Using TiO2 by Nonlinear Modeling Based on Box–Behnken Design," *Arabian Journal for Science and Engineering,* Vol. 41, pp. 2631-2646, 2017.

[13]. M. Buyukada and F. Evrendilek "Color and cod removals by photocatalytic degradation: an experimental design approach and cost analysis," *Sigma Journal of Engineering and Architecture*, Vol. 8, pp. 217-226, 2017.

[14]. Buyukada, M. "Advanced treatment of poultry slaughterhouse effluents using photocatalytic degradation: modeling, optimization, and cost analysis," Env. Eng. PhD thesis, *Abant Izzet Baysal University Institute of Science,* Bolu, Turkey, Nov. 2017.

[15]. J.F. García-Araya, F.J. Beltrán and A. Aguinaco, "Diclofenac removal from water by ozone and photolytic TiO2 catalysed processes," *Journal of Chemical Technology and Biotechnology,* Vol. 85, pp. 798-804, 2010.

[16]. J. Hartmann, P. Bartels, U. Mau, M. Witter, W.V. Tümpling, J. Hofmann and E. Nietzschmann, "Degradation of the drug diclofenac in water by sonolysis in presence of catalysts," *Chemosphere*, Vol. 70, pp. 453-461, 2008.

[17]. M.M. Sein, M. Zedda, J. Tuerk, T.C. Schmidt, A. Golloch and C.V. Sonntag, "Oxidation of diclofenac with ozone in aqueous solution," *Environmental Science and Technology,* Vol. 42, pp. 6656-6662, 2008.

[18]. S. He, J. Wang, L. Ye, Y. Zhang and J. Yu, "Removal of diclofenac from surface water by electron beam irradiation combined with a biological aerated filter," *Radiate Physical Chemistry,* Vol. 105, pp. 104-108, 2014.

[19]. V. Naddeo, V. Belgiorno, D. Ricco and D. Kassinos, "Degradation of diclofenac during sonolysis, ozonation and their simultaneous application," *Ultrasonics Sonochemistry,* Vol. 16, pp. 790-794, 2009.

[20]. D. Vogna, R. Marotta, A. Napolitano, R. Andreozzi and M. d'Ischia, "Advanced oxidation of the pharmaceutical drug diclofenac with UV/H2O2 and ozone," *Water Research,* Vol. 38, pp. 414-422, 2004.

[21]. B. M. Mahamood, "Degradation kinetics of diclofenac in water by Fenton's oxidation," *Journal of Sustainable Energy Environment,* Vol. 3, pp. 173-176, 2012.

[22]. L.A. Pérez-Estrada, S. Malato, W. Gernjak, A. Agüera, E.M. Thurman, I. Ferrer and A.R. Fernández-Alba, "Photo-Fenton degradation of diclofenac: identification of main intermediates and degradation pathway," *Environmental Science and Technology,* Vol. 39, pp. 8300-8306, 2005.

[23]. J. Hofmann, U. Freier, M. Wecks and S. Hohmann, "Degradation of diclofenac in water by heterogeneous catalytic oxidation with H2O2," *Applied Catalyst B,* Vol. 70, pp. 447-451, 2007.

Environmental Research & Technology, Vol. 1(3), pp. 11-18, 2018

Environmental Research & Technology

http://dergipark.gov.tr/ert

RESEARCH ARTICLE

Dissolution behavior of metallic zinc in organic acid

Ikram Boukerche[1], Souad Djerad[1]*, Rima Larba[1], Leila Benmansour[1], Lakhdar Tifouti[1]

[1] Laboratory of Environmental Engineering, Department of Process Engineering, Badji Mokhtar – Annaba University, P. O. Box 12, 23000 Annaba, ALGERIA

ABSTRACT

A series of experiments were conducted to examine the effect of citric acid on the dissolution of zerovalent zinc. The effects of citric acid concentration, the presence of anions and temperature were studied. The results have shown that zinc dissolution registered a maximum of 34% with 0.5M citric acid after 270 min and that the nature of anions present with citric acid affected differently the dissolution rate. In fact, the presence of 2M nitrates with 0.5M citric acid dissolved totally zinc after 30min while 91.85% and 13.15% were dissolved in the presence of 2M chlorides and sulfates respectively after 270min. SEM analyses have shown that the morphology of the corroded surface depended on the composition of the solution. The kinetic study has shown that zinc dissolution was controlled by the chemical reaction in all cases and that the activation energy was 39.3 kJ mol^{-1}.

Keywords: Zinc, citric acid, dissolution, concentrated conditions, nitrates, pollution

1. INTRODUCTION

The improper disposal of industrial, agricultural and municipal wastes is the major cause for soil contamination in developing countries [1]. In fact, population growth, the lack of awareness regarding the consequences of municipal solid wastes disposal and under-founded governments to prevent the efficient management of wastes participate in increasing the environmental pollution. Landfilling of municipal solid wastes is the most used method because of its simplicity and its low cost [2]. However, when huge amounts of organic wastes are daily placed in landfills as it is the case in Algeria "Mediterranean diet based essentially on the consumption of vegetables", then the anaerobic fermentation of the organic products occurred continuously leading to form leachates rich with organic acids such as formic, acetic, oxalic, citric and malic acids [3]. On the other hand, metals such as Fe, Pb, Cu, Zn, Mn, Cd, Ni and Cr are also found in landfills in Algeria [4]. This is problematic because various reactions can be occurring when these metals come into contact with these leachates enough acid to initiate the dissolution reactions and contaminate soil and groundwater [5] while they can be recovered in order to be reused as secondary raw materials [6-8]. In the literature, the dissolution of zinc by citric acid was studied in framework of its bioavailability in soils for agriculture. In fact, in soil plant system citric acid is often used because of its high efficiency in binding zinc cations (micronutrient) facilitating their absorption by the roots [9-11]. For this task only diluted citric acid is used (in mM). However, in landfills other conditions prevail where huge amounts of organic wastes continuously feed the discharge leading to increase the amount of the organic acids formed by anaerobic-digestion [12,13]. Citric acid is one of the most studied organic acids present in anaerobically-digested biosolids [14]. However, in the literature, the experimental data about the dissolution reaction of metallic zinc in concentrated citric acid is not available. The aim of this study is to investigate the extent of the dissolution process of zinc when exposed to highly concentrated citric acid. The effects of citric acid concentration, temperature, and the presence of anions were studied. The effect of the operation conditions on the resultant morphology was also investigated by SEM analysis and the kinetic parameters and the controlling step of the dissolution process were determined by using a heterogeneous model.

Corresponding Author: s_djerad@hotmail.com (Souad Djerad)
Received 12 January 2018; Received in revised form 17 May 2018; Accepted 22 May 2018
Available Online 1 July 2018
Doi: ISSN: 2636-8498

2. MATERIALS AND METHOD

Zn (metal) (99.99% purity) in the form of spheres (3 mm of diameter) was supplied by Sigma-Aldrich. The composition of zinc is given in Table 1. The specimens were degreased in acetone and rinsed with deonized water, and were used without polishing as shown in Fig 1. Citric acid monohydrate (99.5 %, Riedel de Haën), NaCl (99.5 %, Biochem), $NaNO_3$ (99 %, Fluka) and Na_2SO_4 (99 %, Sigma-Aldrich) were used as received. Deonized water was used to prepare all aqueous solutions. Tests of Zn dissolution were performed in a Pyrex glass reactor heated in a water bath and equipped with a return-flow cooler. The experiments were performed by contacting 0.2 g of Zn with 200 mL of citric acid solution. After the leaching process, the reaction mixture was filtered and the Zn^{2+} specie was analyzed by complexometric titration with ethylenediamine tetraacetic acid disodium salt (EDTA), using NET as indicator [15]. The data presented are an average of three test replicates with an error of 5%. The percentage of dissolution was calculated from the following equation:

$$\frac{mol\ number\ of\ zinc\ in\ the\ solution}{mol\ number\ of\ zinc\ in\ the\ metal}\ X\ 100 \quad (1)$$

SEM images were taken with the Environmental Scanning Microscopy instrument (XL 30, Philips, Netherlands). All analyses were performed in duplicate with an error of 5%. In this study, the results of zinc dissolution were analyzed using the shrinking core model. In this model the reactant is considered to be nonporous and is initially surrounded by a fluid film through which mass transfer occurs between the solid and the bulk of the fluid. This model used the following expressions to describe the dissolution kinetics of the process [16]:

For liquid film diffusion control:

$$x = kt \quad (2)$$

For film diffusion control through product layer:

$$1 - 3(1 - x)^{2/3} + 2(1 - x) = kt \quad (3)$$

For surface chemical reaction control:

$$1 - (1 - x)^{1/3} = kt \quad (4)$$

where x is the fractional conversion of zinc at time t and k is the apparent rate constant (min^{-1}). The overall rate of dissolution is controlled by the slowest of these sequential steps.

Table 1. Composition of Zn used in this study

Element	As	Cd	Cu	Fe	Pb	Sn	Zn
%	0.0005	0.0005	0.001	0.002	0.005	0.001	99.99

3. RESULTS

3.1 Effect of citric acid concentration and temperature

The dissolution of zinc by citric acid may be written as follows:

$$3Zn + 2C_6H_8O_{7(aq)} \rightarrow 3Zn^{2+} + 3H_{2(g)} + 2C_6H_5O_7^{3-}{}_{(aq)} \quad (5)$$

Preliminary test was conducted with citric acid solution at 2M, ambient temperature, and without agitation. No dissolution of zinc was observed after 24h. The temperature was thus increased to 80°C and the solution was stirred under 350rpm to decrease the reaction time. Zinc was contacted with citric acid solution at different concentrations (0.2, 0.5, 1 and 2M) (Fig 2a). The results show that the dissolution of Zn passed through a maximum in the acid concentration range studied. In fact, 9.5% of zinc was dissolved with 0.2M citric acid after 270 min. It increased to 34% with 0.5M after the same period of time and decreased thereafter at higher citric acid concentration (1 and 2M) registering 31 and 16% respectively.

The effect of temperature was studied in range 30-80°C with 0.5M citric acid at 350rpm (Fig 2b). The results show that the dissolution of Zn increased with increasing temperature attaining 4.22-11.37-14.67 and 34% at 30-40-60 and 80°C respectively after 270min of reaction. The dissolution of Zn in citric acid was thus, thermally activated.

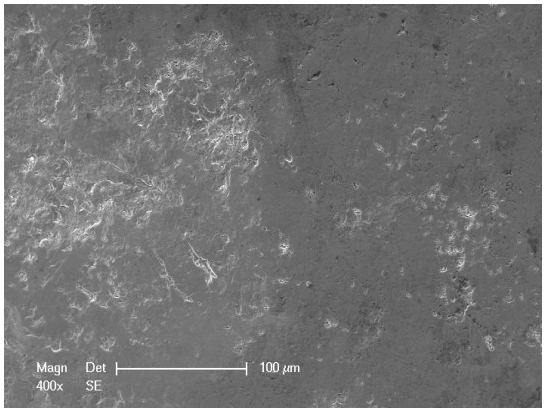


Fig 1. SEM analysis of Zn metal before dissolution experiments by citric acid

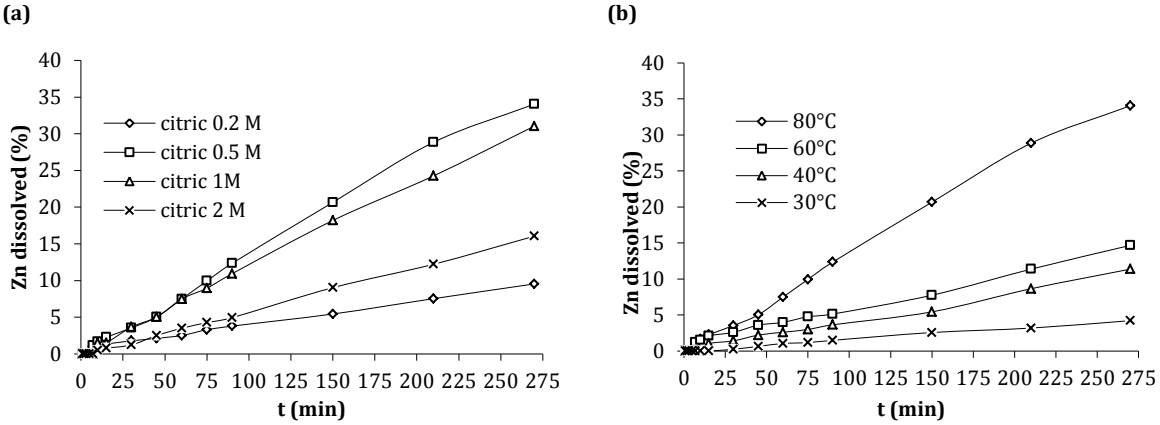


Fig 2. Effect of citric acid concentration (a) and temperature (b) on Zn dissolution

3.2 Effect of the presence of anions

The experiments were carried out in order to investigate the effect of nitrates, sulfates and chlorides on Zn dissolution by citric acid. Two concentrations of citric acid were used (0.5 and 2M) with the presence of NaCl, $NaNO_3$ and Na_2SO_4 at 2M (Fig 3a-c). The experiments were carried out at 80°C and 350rpm. The results show that zinc dissolution was greatly enhanced with both citric acid concentrations in the presence of nitrates (Fig 3a). In fact, the dissolution attained in both cases 100% after 90 min of contact with nitrates while with chlorides the results of dissolution depended on citric acid concentration. In fact, with 0.5M citric acid (Fig 3b) the dissolution attained 91.8% after 270min while with 2M citric acid the dissolution registered 16.5% after the same period of time. Zinc dissolution in the presence of sulfates was slight in both cases registering 13.15% with citric acid at 0.5M and 7.56% with citric acid at 2M after 270 min. Thus, the nature of the ions present with the organic acid may drastically affect the progress of the dissolution.

In order to determine the activation energy, Zn dissolution by citric acid at different temperatures was analyzed by using the shrinking core model. To determine the controlling step, the three expressions $[(x), (1 - 3(1 - x)^{2/3} + 2(1 - x)]$ and $[(1 - (1 - x)^{1/3})]$ were reported on the y axis as a function of time (t) which is reported on the x axis. The fit of the experimental data was tested by calculating the regression coefficients (R^2) for the three expressions. The equation $1 - (1 - x)^{1/3} = kt$ gave good linear fit as confirmed by the values of R^2 close to the unity (Table 2) indicating that the reaction was chemically controlled. The apparent rate constant is the slope of each line plotted. To determine the activation energy, Arrhenius equation $k = A \cdot e - Ea/RT$ was plotted as lnk vs. $1/T$ for each temperature and the activation energie was calculated from the slope $-Ea/R$. Ea value was determined to be 39.3kJ mol^{-1} corroborating the chemical reaction control. A chemically controlled reaction is generally a temperature dependent process and has an activation energy equal or higher than 40 kJ mol^{-1}.

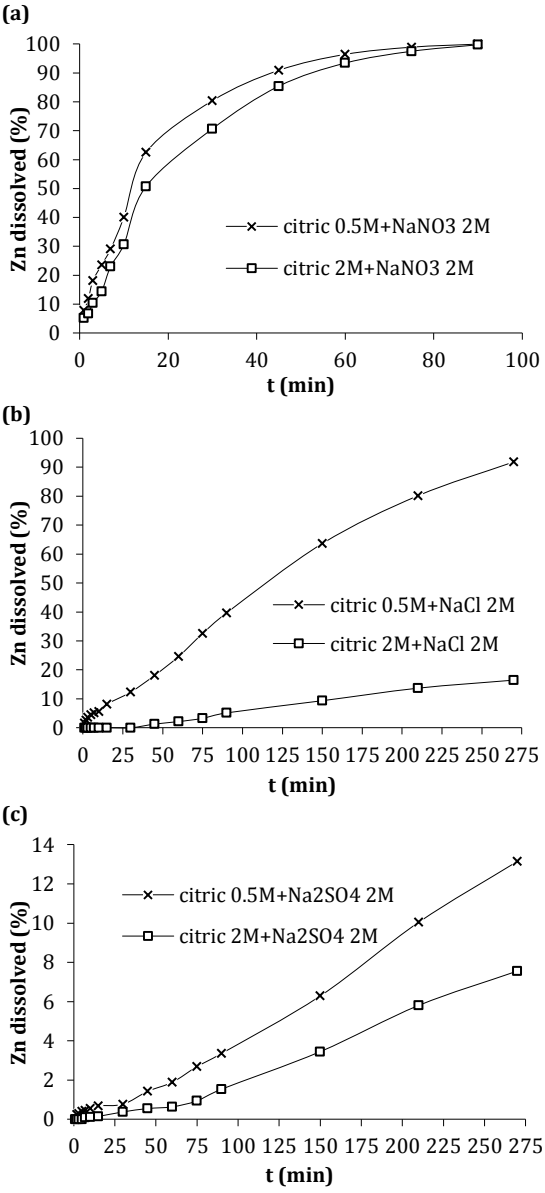


Fig 3. Effect of the presence of nitrates (a), chlorides (b) and sulfates (c) on Zn dissolution by citric acid

3.3 Special case of nitrates

Because of the remarkable effect of nitrates compared to those of chlorides and sulfates and in order to provide a better understanding of their role during zinc dissolution, other experiments were carried out in which Zn was contacted with citric acid at 0.5M to which nitrates were added at two concentrations (0.5 and 2M) at 80°C and 350rpm. The results (Fig. 4a) show a great effect of nitrates on Zn dissolution. In fact, citric acid alone at 0.5M dissolved 34% of Zn after 270 min while when mixed with nitrates at 0.5M i.e. (citric 0.5M + $NaNO_3$ 0.5M) it attained 100% after 30 min. At higher nitrates concentration i.e. (citric 0.5M + $NaNO_3$ 2M) the time needed to attain 100% was longer (90min). To assess the enhancing effect of nitrates on zinc dissolution, the temperature was lowered to 30°C and the dissolution was carried out with the mixtures (citric 0.5M + $NaNO_3$ 0.5M) and (citric 0.5M + $NaNO_3$ 0.2M) as shown in figure 4b. The dissolution of zinc at 30°C was still important since both mixtures dissolved respectively 95.4% and 83.4% of Zn after 60 min. Thus, the solubility of metallic zinc is increased in the presence of nitrates and the impact of temperature in this case was lowered.

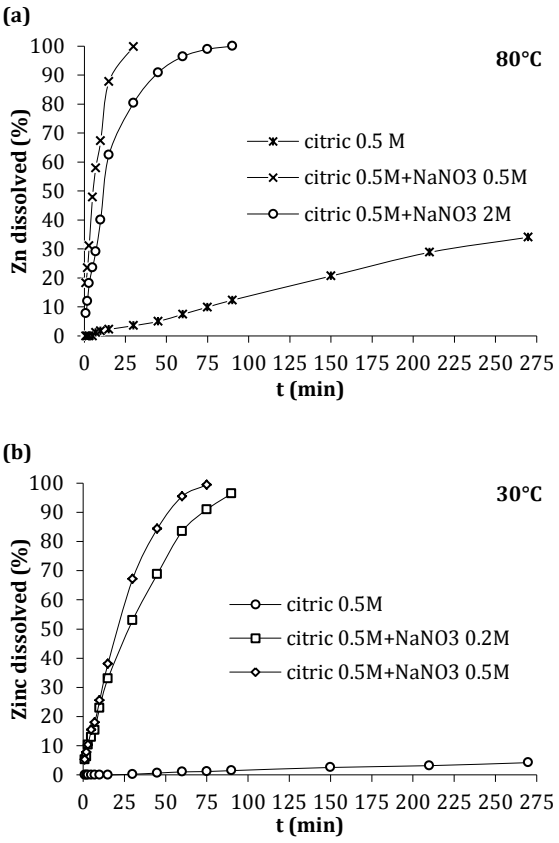


Fig 4. Effect of the presence of nitrates on Zn dissolution

3.4 SEM analysis

The surface of zinc was examined by scanning electron microscopy (SEM) analysis. The morphology of Zn surface obtained after contacting 0.5M citric acid at ambient temperature for 8 days and without agitation shows closed perpendicular sheets (Fig 5a). When Zn was contacted with the same solution heated at 80°C and stirred at 350rpm for 270 min, hexagonal pits (~5µm of size) were formed (Fig 5b). Thus, when the conditions are varied with the same solution the morphology of the pitted surface radically changed. The morphology of zinc surface was also studied in the presence of two nitrate concentrations. Figures 5c and d show Zn surfaces after contacting for 5 min the solutions (citric 0.5M + $NaNO_3$ 0.5M) and (citric 0.5M + $NaNO_3$ 2M) at 350rpm and 80°C. The images show that with the first solution a start of the corrosion was clearly observed while with the second one the surface was not pitted. Thus, increasing nitrate amount does not necessary increase the corrosion of Zn. Zinc surface was also analyzed after contacting the solutions (citric 0.5M + NaCl 2M) for 60 min and (citric 0.5M + Na_2SO_4 2M) for 270 min at 80°C and 350rpm. Figure 5f shows that despite the high temperature and the presence of stirring the corrosion of zinc in the presence of sulfates was very weak. In fact, small pits (~1-2µm of size) not uniformly dispersed on the surface were observed while with citric acid alone and under the same conditions the surface was clearly pitted (Fig 5b). This indicates that sulfates were greatly involved in the inhibition of Zn dissolution. On the contrary, clear corrosion was observed in the presence of chlorides (Fig 5e). In this case the crystallographic cubic shaped pits which are characteristics of chlorides attack were replaced by hexagonal pits (~5-10µm of size) already observed with citric acid alone. Thus, the presence of anions may have a decisive effect on the kinetic of zinc dissolution and the morphology of the pitted surface.

4. DISCUSSION

In this study it was found that among the 3 anions tested, nitrates increased remarkably Zn dissolution compared to chlorides and sulfates. In fact, the facility by which the dissolution of Zn occurred in the presence of nitrates regardless of the conditions used and the fact that it does not need high temperature to be initiated in their presence (as it was the case with citric acid alone) indicated that the mechanism involving nitrates during Zn release is different from those involving chlorides and sulfates.

In the literature there is a lack in details about the reactivity of metallic zinc in the presence of concentrated citric acid and nitrates. However, studies dealing with its solubility in diluted organic acids were found in framework of phytoremediation of contaminated soil by metals. These studies were conducted on plants species such as Thalspi caerulescens and Arabidopsis halleri that have the ability to survive and reproduce on soils containing high concentration of zinc [17,18]. Mosant et al. for example added nitrogen in the form of NO_3^- and NH_4^+ to EDDS (Ethylenediaminedisuccinic acid) to study their effect on Zn phytoextraction by Thalspi caerulescens [17]. They observed that Zn phytoextraction was enhanced more with NO_3^- than with NH_4^+. They suggested that this uptake may be the consequence of physiology of NO_3^- assimilation by the plant which favors Zn uptake more than NH_4^+ or the variation of rhizosphere pH due to cellular cation-

anion balance (NO_3^- uptake causes H^+ influx or OH^- efflux which may increase the pH of rhizosphere) leading to a favorable pH for Zn uptake. Other studies were also found dealing with the mixture nitrates+metal but in framework of water denitrification. In fact, it was reported that the presence of zerovalent metals with nitrates in an acidified medium leads to a reductive denitrification as follows [19,20]:

$$Zn + NO_3^- + H^+ \rightarrow Zn^{2+} + NO_2^- + OH^- \quad (6)$$

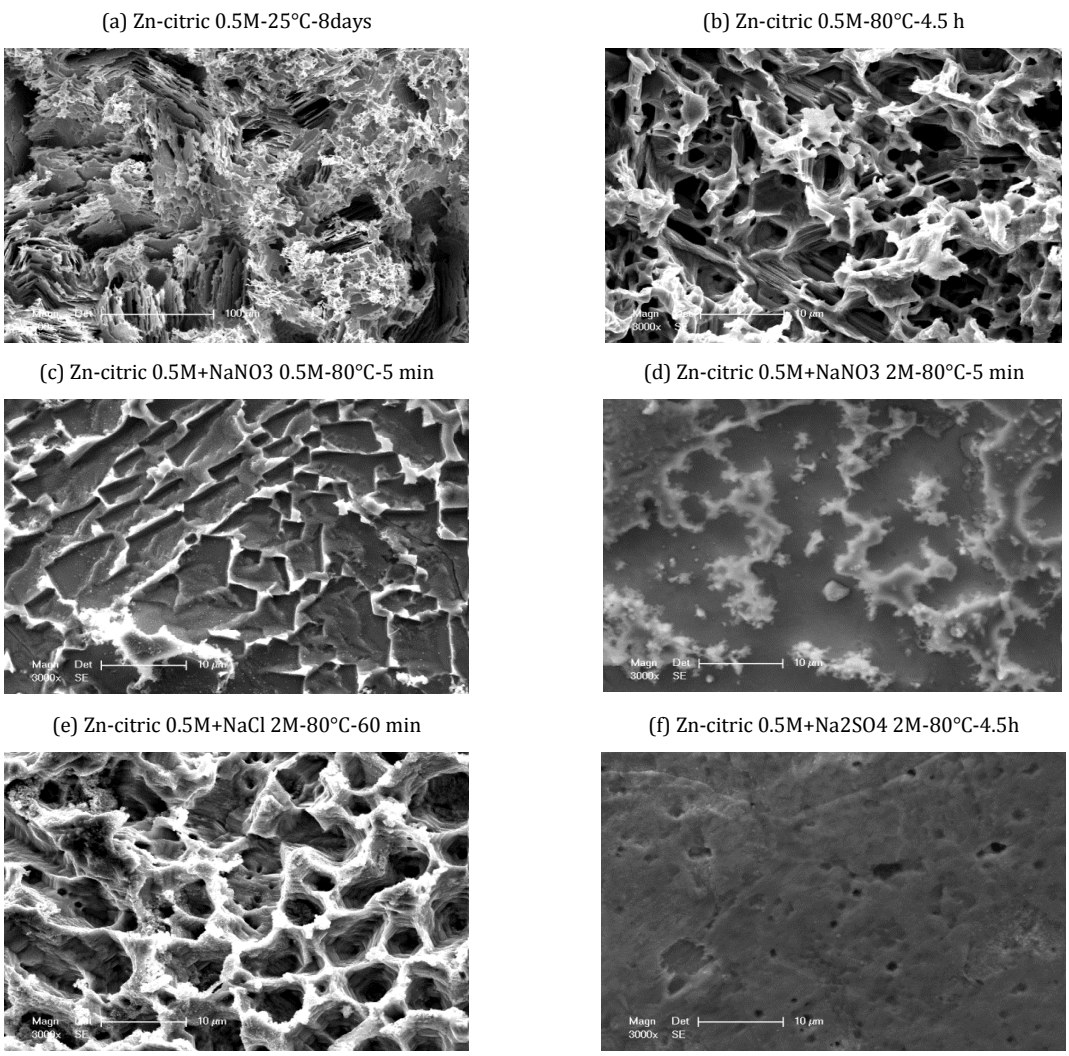


Fig 5. SEM analyses of zinc metal after contacting citric acid under different conditions

This denitrification is accompanied by the dissolution of the metal and the increase in pH of the medium. Alongside with the reaction (5) the dissolution of zinc in an acidified medium also occurs according to:

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_{2(g)} \quad (7)$$

Thus, in our study the enhanced dissolution rate observed in the presence of nitrates was due to the occurrence of the reactions (6) and (7) simultaneously. This may explain also the finding reported by Mosant et al. [17]. In fact, since plants can extract Zn from soil only in soluble form, the enhancing Zn uptake by plants observed when nitrates were added was likely due to the reaction (6) leading to solubilize the metal. In this study another behavior was also observed when nitrates concentration was increased from 0.5M to 2M in the presence of citric acid. In fact, the dissolution of metallic zinc was lower at 2M NO_3^- than at 0.5M NO_3^- (Fig 4a).

In the literature it was reported that nitrates acted as oxidant that forms a protective oxide layer leading to decrease the corrosion of zinc [21]. Thus, when NO_3^- and H^+ are present, a competition between oxide film growth and metal dissolution occurred [22]. This was observed in our previous study [23]. Thus, at 2M NO_3^- it can be supposed that the oxide film growth on zinc surface was more important that at 0.5M NO_3^- leading to decrease Zn dissolution. On the other hand, the high dissolution rate observed in the presence of nitrates regardless of the conditions used may suggest that their involvement in zinc dissolution was mainly through the reaction (6) and when their concentration increased up to a certain value a part of them participates in developing the protective oxide film leading to decrease the dissolution rate of Zn.

The concentrations of citric acid used in this study (0.2-0.5-1 and 2M) corresponded to molar ratios (nca:nZn) of 13.5-33-66 and 132 respectively. Thus, in all cases the acid was in excess relative to zinc. However, the dissolution passed through a maximum

located at 0.5M beyond which zinc dissolution decreased. This behavior is not usually observed; generally increasing the concentration of a leaching reagent leads to increase the dissolution of metals. In the literature, it was reported that citrate and protons are expected to react with metal surfaces [24]. Thus, the dissolution of zinc may be due to both the complexing action of citrate anions and the dissolution properties of protons released from citric acid.

Furrer and Stumm [25] explained the dissolution process by low molecular weight organic acids as follows: the adsorption of chelating anion (citrate in our case) will transfer a considerable electron density into the coordination sphere of the metal cation (citrate contains several donor atoms that are able of forming mononuclear bi- and polydentate surface chelates). As a result, the metal-oxygen bonds are polarized and weakened lowering consequently the energy barrier for the dissolution of the metal atom.

The explanation given above indicates clearly the importance of the anionic specie of organic acid (ligand) in the dissolution process. However the decrease in dissolution rate observed at 2M citric acid is not easy to explain since this organic acid is known as an enhanced-dissolution compound. One study was found dealing with the inhibiting effect of a dissolution-promoting chelating agent when its concentration increased. In fact, it was reported that increasing the concentration of maleate beyond a certain value caused a decrease in the dissolution rate of corundum [26]. This behavior was explained by the fact that at high concentration the strong adsorption of this anion sterically protects corundum surface sites against attack by dissolution promoting species such as protons at low pH. The results obtained in our study may be due to the same phenomenon. Thus, the adsorption strength of the ligand -which is dependent on the organic acid concentration- occurring prior to detachment process of the metal from the surface, orients toward a retarding dissolution process in the case of concentrated acid.

Table 2 shows the rate constants (k) calculated with the equation (4) for all the operation conditions tested in this work.

The rate constant of Zn dissolved at 30°C by 0.5M citric acid was 5.10^{-5} min^{-1}. The same solution but containing nitrates (citric 0.5M + $NaNO_3$ 0.5M) at 30°C increased the dissolution rate to 0.0107 min^{-1} which represents ~214 times the value obtained with citric acid alone while increasing the temperature to 80°C with citric acid alone increased the dissolution rate to 0.0005 min^{-1} which represents only 10 times the rate constant obtained at 30°C. Thus, Zn dissolution was more sensitive to the presence of nitrates than to temperature.

It is known that when several anions contacted a solid in aqueous solutions they compete for the adsorption on surface sites [27]. The initial pH values of acid solutions at 2-1-0.5 and 0.2M were 1.09- 1.39- 1.61 and 1.89. In these cases the metal was positively charged attracting electrostatically the anions present in the solution. Thus, two kinds of positive species (protons and the positively charged surface of zinc) and two negative species (citrates and anions (Cl^-, NO_3^- and SO_4^{2-})) may react together and simultaneously in several ways: 1)- H^+ attack (protons with zinc surface species), 2)- Anions reactions (Cl^- , NO_3^-, SO_4^{2-} with zinc surface species), 3)- Citrate complexation with zinc surface species, 4)- H^+ combination with citrates to form molecular citric acid. This shows the complexity of the system studied.

Chlorides were involved remarkably in the dissolution process when used with 0.5M citric acid (Fig 3b) while with 2M citric acid they had no effect. It should be noted that citric acid alone dissolved 34% of Zn when used at 0.5M and 16.05% when its concentration increased to 2M after 270 min (Fig 2a). In the presence of chlorides Zn dissolution registered 91.85% with the solution (citric 0.5M+NaCl 2M) and 16.46% with the solution (citric 2M+ NaCl 2M) after 270min. The high dissolution rate obtained in the first case was probably due to chlorides attack favored by the presence of the suitable acid concentration [28,29]. This behavior indicated that chlorides favored the dissolution when the latter is already initiated. The absence of their effect when present with 2M citric acid may confirm the fact that pitting process of chlorides - which begins generally with their adsorption on the solid surface - was absent because of the saturation of zinc surface with citrates forming strongly bonded complexes and avoiding consequently chlorides attack. This is in accordance with the explanation given by Johnson et al. [26]. In this study sulfates were found to inhibit the dissolution of Zn registering 13.15% with the solution (citric 0.5M+Na_2SO_4 2M) and 5.81% with the solution (citric 2M+ Na_2SO_4 2M) after 270min. In both cases the dissolution percentages were lower than those obtained with citric acid alone at both concentrations. This behavior was reported to be due to the strong adsorptive affinity of sulfates (doubly charged) on solid surfaces that may hinder the progress of the dissolution [30].

On the contrary, Zn release was less parameter dependent in the presence of nitrates and a strong accelerating effect on the dissolution was observed regardless of the conditions used. This indicates their involvement in the dissolution of zinc through a chemical reaction. However, another reaction may also occur in their presence. In fact, Fanning [19] reported that nitrates may react with H_2 formed during zinc dissolution according to:

$$NO_3^- + 4H_2 \rightarrow NH_3 + 2H_2O + OH^- \quad (8)$$

The reactions (7) is related to be the mechanism involving direct electron transfer between the metal and nitrates, whereas the reaction (8) is considered as an indirect electron transfer mechanism via H_2. Although there are controversies in the literature about the dominant process, the high dissolution rate of zinc obtained in this study in the presence of nitrates indicated that the reaction involving the direct exchange of electrons between Zn and NO_3^- was the dominant process.

Table 2. Kinetic parameters for Zn dissolution by citric acid

Parameters studied	$1-(1-x)^{1/3}=kt\pm b$	R^2
Effect of citric acid concentration		
Operations conditions : 80 °C, 350rpm, Zn=0.2 g, V=200 mL		
Citric acid 0.2M	0.0001t+0.0013	0.9858
Citric acid 0.5M	0.0005t-0.0015	0.9971
Citric acid 1M	0.0004t-0.0012	0.9992
Citric acid 2M	0.0002t-0.0010	0.9985
Effect of temperature		
Operation conditions: 0.5 M-350 rpm, Zn=0.2 g, V=200 mL		
30°C	0.00005t-0.0003	0.9935
40°C	0.0001t-0.00008	0.9895
60°C	0.0002t+0.0017	0.9912
80°C	0.0005t-0.0015	0.9971
Effect of the presence of anions		
Operation conditions: 80 °C-350 rpm, Zn=0.2 g, V=200 mL		
Citric acid 0.5M+$NaNO_3$ 2M	0.0101t+0.0543	0.9853
Citric acid 0.5M+ NaCl 2M	0.002t-0.0083	0.9913
Citric acid 0.5M+ Na_2SO_4 2M	0.0002t-0.0042	0.9973
Citric acid 2M+$NaNO_3$ 2M	0.0095t+0.022	0.9943
Citric acid 2M+ NaCl 2M	0.0002t-0.0065	0.9933
Citric acid 2M+ Na_2SO_4 2M	0.0001t-0.0037	0.9871
Presence of nitrates		
Operation conditions: 80 °C-350 rpm, Zn=0.2 g, V=200 mL		
Citric acid 0.5M+$NaNO_3$ 0.5M	0.0284t+0.0414	0.9956
Citric acid 0.5M+$NaNO_3$ 2M	0.0101t+0.0543	0.9853
Operation conditions: 30 °C-350 rpm, Zn=0.2 g, V=200 mL		
Citric acid 0.5M+$NaNO_3$ 0.2M	0.0073t+0.0085	0.9993
Citric acid 0.5M+$NaNO_3$ 0.5M	0.0107t-0.0046	0.9985

5. CONCLUSION

The results revealed that the mechanism through which zinc metal is dissolved by citric acid is complex. In this system several ionic species seem to interfere together leading to decrease or increase zinc dissolution. It was observed that increasing citric acid concentration up to 0.5M increased the dissolution of Zn to a maximum of 34% beyond which the dissolution decreased at higher citric acid concentrations. This can be interpreted in terms of sorption capacity of the solid surface where high amount of citrate anions may sterically protect the solid surface from proton attack and hinder the dissolution rate. The moderate conditions in which strong dissolution of zinc was observed in the presence of nitrates indicated that they were chemically involved in the reaction. The dissolution of zinc was accelerated when chlorides were present with 0.5M citric acid and was not impacted with 2M citric acid, while sulfate inhibited the dissolution of zinc in all cases. The kinetic study revealed that the dissolution process of Zn was chemically controlled and this was corroborated with the value of the activation energy which was found to be equal to 39.3kJ/mol.

Organic acids such as citric acid are prevalent in many natural settings and in discharges. Understanding the mechanism of metals dissolution in their presence alone or with mineral substances at a fundamental level is important in order to predict the environmental pollution risk.

ACKNOWLEDGEMENTS

This work was financially supported by the Ministry of Higher Education and Scientifc Research of Algeria (CNEPRU Project No. J0101120110047).

REFERENCES

[1]. B.O. Clarke, T. Anumol, M. Barlaz, S. A. Snyder, "Investigating landfill leachate as a source of trace organic pollutants," *Chemosphere,* Vol. 127, pp. 269-275, 2015

[2]. L. Rong, C. Zhang, D. Jin, Z. Dai, "Assessment of the potential utilization of municipal solid waste from a closed irregular landfill", *Journal of Cleaner Production* Vol. 142, pp. 413-419, 2017.

[3]. S. Bendebane, L. Tifouti and S. Djerad, "The effect of the nature of organic acids and the hydrodynamic conditions on the dissolution of Pb particles", *RSC Advances* Vol. 7, pp. 77-86, 2017

[4]. Inventory of wild discharges, National Center of Discharges (NCD), *Ministry of Environmental Management*, Algiers, 2011.

[5]. S. Xie, Y. Ma, P.J. Strong, W.P. Clarke, "Fluctuation of dissolved heavy metal concentrations in the leachate from anaerobic digestion of municipal solid

waste in commercial scale landfill bioreactors: The effect of pH and associated mechanisms", *Journal of Hazardous Materials* Vol. 299, pp. 577-583, 2015

[6]. I. Boukerche, N. Habbache, N. Alane, S. Djerad, L. Tifouti, "Dissolution of Cobalt from CoO/Al_2O_3 Catalyst with Mineral Acids", *Industrial Engineering and Chemistry Research* Vol. 49, pp. 6514–6520, 2010.

[7]. N. Habbache, S. Djerad, L. Tifouti, "Optimization of the operation conditions for NiO dissolution with different leachants"*, Process Engineering Journal* Vol. 1, pp. 59–67, 2017

[8]. S. Djerad, "Pyrometallurgical method for the recovery of aluminum from Fe_2O_3/α-Al_2O_3 catalyst", *International Journal of Science and Technology* Vol. 3, pp. 210-223, 2017

[9]. Y. Tapia, E. Eymar, A. Garate, A. Masaguer, "Effect of citric acid on metals mobility in pruning wastes and biosolids compost and metals uptake in Atriplex halimus and Rosmarinus officinalis", *Environmental Monitoring and Assessment,* Vol. 185, pp. 4221-4229, 2013.

[10]. S.G. Moreira, L.I. Prochnow, J. de Castro Kiehl, V. Pauletti, L. Martin-Neto, "Chemical forms in soil and availability of manganese and zinc to soybean in soil under different tillage systems", *Soil and Tillage Research*, Vol. 163, pp. 41-53, 2016

[11]. C. Kaur, G. Selvakumar, A.N. Ganeshamurthy, Organic acids in the rhizosphere: their Role in phosphate dissolution, In: D. Singh, H. Singh, R. Prabha (eds), Microbial Inoculants In Sustainable Agricultural Productivity. Springer, New Delhi, 2016

[12]. S. Legros, C. Levard, C.E. Marcato-Romain, M. Guiresse, E. Doelsch, "Anaerobic digestion alters copper and zinc speciation", *Environmental Science and Technology* Vol. 51, pp. 10326–10334, 2017

[13]. P.M. Thanh, B. Ketheesan, Z. Yan, D. Stuckey, "Trace metal speciation and bioavailability in anaerobic digestion: A review", *Biotechnology Advances* Vol. 34, pp. 122-136, 2016

[14]. P.A.W. Van Hees, D.L. Jones, D.L. Godbold, "Biodegradation of low molecular weight organic acids in coniferous forest podzolic soils", *Soil Biology and Biochemistry* Vol. 34, pp. 1261-1272, 2002

[15] A.I. Vogel, "A Textbook of Quantitative Inorganic Analysis, Chapter IV: Complexometric Titrations", third ed., Longmans, London, 1962.

[16]. O. Levenspiel, "Chemical Reaction Engineering", 3rd ed., John Wiley & Sons, New York 1999.

[17]. A.C. Mosant, C. Tang, A.J.M. Baker, "The effect of nitrogen form on rhizosphere soil pH and zinc phytoextraction by Thlaspi caerulescens", *Chemosphere* Vol. 73, pp. 635-642, 2008

[18]. G. Sarret, P. Saumitou-Laprade, V. bert, O. Proux, J.L. Hazemann, A.Traverse, M.A. Marcus, A. Manceau, "Forms of zinc accumulated in the hyperaccumulator Arabidopsis helleri, Plant Physiology" Vol. 130, pp. 1815-1826, 2002

[19]. J.C. Fanning, "The chemical reduction of nitrate in aqueous solution", *Coordination Chemistry Reviews* Vol. 199, pp. 159-179, 2000.

[20]. Y.H. Liou, C.J. Lin, I.C. Hung, S.Y. Chen, S.L. Lo, "Selective reduction of NO_3- to N_2 with bimetallic particles of Zn coupled with palladium, platinum, and copper", *Chemical Engineering Journal* pp. 181-182, pp. 236-242, 2012

[21]. R. Lindström, L.G. Johansson, J.E. Svensson, "The Influence of $NaNO_3$ on the Atmospheric Corrosion of Zinc", *Journal of The Electrochemical Society* Vol. 150, pp. B583-B588, 2003

[22]. E.A. Abd El Aal, S. Abd El Wanees, A. Farouk, S.M. Abd El Haleem, "Factors affecting the corrosion behaviour of aluminium in acid solutions. II. Inorganic additives as corrosion inhibitors for Al in HCl solutions", *Corrosion Science* Vol. 68, pp. 14-24, 2013

[23]. I. Boukerche, S. Djerad, L. Benmansour , L. Tifouti, K. Saleh, "Degradability of aluminum in acidic and alkaline solutions", *Corrosion Science* Vol. 78, pp. 343–352, 2014

[24]. G. Sposito, The Chemistry of Soil. Oxford University Press, Oxford, New York, 1989

[25] G. Furrer, W. Stumm, "The coordination chemistry of weathering: I. Dissolution kinetics of δ-Al_2O_3 and BeO*", Geochimica et Cosmochimica Acta* Vol. 50, pp. 1847-1860, 1986.

[26]. S.B. Johnston, T.H. Yoon, B.D. Kocar, G.E. Brown Jr, "Adsorption of Organic Matter at Mineral/Water Interfaces. 2. Outer-Sphere Adsorption of Maleate and Implications for Dissolution Processes", *Langmuir* Vol. 20, pp. 4996-5006, 2004.

[27]. S.S. Kim, W.J. Lee, S.I. Pyun, D.R. Kim, "Effects of applied potential and solution temperature on the pitting corrosion of pure aluminum in sulfate ion-containing chloride solution", *Metals and Materials* Vol. 5, pp. 583-588, 1999

[28]. A. Aït Aghzzaf, B. Rhouta, E. Rocca, A. Khalil, J. Steinmetz, "Corrosion inhibition of zinc by calcium exchanged beidellite clay mineral: A new smart corrosion inhibitor", *Corrosion Science* Vol. 80, pp. 46-52, 2014

[29]. X. Zhang, T.N. Vu, P. Volovitch, C. Leygraf, K. Ogle, I. Odnevall Wallinder, "The initial release of zinc and aluminum from non-treated Galvalume and the formation of corrosion products in chloride containing media", *Applied Surface Science* Vol. 258, pp. 4351-4359, 2012

[30]. A.A.Yu, I.I. Reformatskaya, A.N. Podobaev, "The effect of chloride and sulfate anions on the iron dissolution rate in neutral and nearly neutral media", *Protection of Metals* Vol. 43, pp. 125–128, 2007

Environmental Research & Technology, Vol. 1(3), pp. 19-24, 2018

Environmental Research & Technology

http://dergipark.gov.tr/ert

RESEARCH ARTICLE

Synthesis of Fe_3O_4/humic acid/silver nanoparticles and their application in Cu and Cd adsorption

F. Ayca Ozdemir Olgun[1,*], Gozde Mediha Kamer[1], Birsen Demirata Ozturk[1]

[1] Department of Chemistry, Faculty of Science and Letters, Istanbul Technical University, 34469 Maslak, Istanbul, TURKEY.

ABSTRACT

Nanoparticle technology developed rapidly due to the multifunctional utilization of nanoparticles in many disciplines such as medicine, drug delivery, environmental chemistry, food chemistry and analytical chemistry. In concept of this study, magnetic nanoparticles with a core-shell structure were synthesized and applied to the adsorption of copper and cadmium. The synthesis procedure consists of two steps. In the first step a core-shell structure was formed with Fe_3O_4 and humic acid. In the second step, the coating of synthesized core/shell structure with silver occurs. The characterization of synthesized nanoparticles was performed with the aid of Scanning Electron Microscope (SEM) images combined with an elemental distribution image (EDX mapping), Zeta Potential, and Dynamic Light Scattering (DLS) analyses. Adsorption isotherms of copper and cadmium on Fe_3O_4/HA/Ag multi-component structure were studied. The optimum adsorption conditions in aqueous solutions were fixed at pH 9 and at 300 K. As a result, the Fe_3O_4/HA/Ag multi-component structure showed excellent adsorption capacity for both copper and cadmium ions with removal percentages of 92% and 97% after the calculations were performed using the absorbance values measured by Flame Atomic Absorption Spectrometer (FAAS) respectively. Langmuir isotherm, which describes the monolayer adsorption was found to be the most adequate to fit the overall procedure.

Keywords: Nanocomposites, magnetic nanoparticles, humic acid, metal removal, Langmuir isotherm

1. INTRODUCTION

There are two different types of pollutants in industrial waters as organic and inorganic pollutants. Inorganic pollutants mostly consist of heavy metal ions that result from industrial metal coating processes [1, 2]. Toxic heavy metal pollution is a global problem and new environmental regulations are required to control the release of heavy metal ion concentrations to the environment. Earlier, various types of materials and techniques were used for the removal of toxic ions, such as ultra-filtration, ion exchange chromatography, or precipitation [3 - 5]. However, adsorption on a magnetic surface is an easy technique to enrich or clean aqueous solutions when they have very low ion concentrations [6]. During magnetic separation a coated or modified surface first adsorbs the analyte and then an external magnetic field removes the particle with the analyte from the solution. The removed particles can be re-used after cleaning to repeat the adsorption process [7 - 9]. In this method, magnetic nano-sized particles form a core/shell structure. Magnetic separation with these particles is a very fast, and eminently selective method. It is also very popular in environmental applications, mining, food & steel industries and biotechnology due to their practical industrial utilization. The magnetic property of nanoparticles depends on the surface coating, size and composition of the particles. Moreover, coating the synthesized nanoparticles with polymers or surfactants prevent the oxidation and agglomeration providing long-time stability within composites [10, 11].

In soil, the end product of microbiological decomposition of animals and plants are humic acids. These are large natural acidic organic polymers that are able to interact with cations and herbicides in soil. Cation binding mostly occurs because of carboxyl (COOH), carbonyl (C=O), hydroxyl (OH) or hydrophobic aliphatic and aromatic groups [12]. Some studies show the efficiency of calcium humate for the removal of some metals from wastewater such as iron, mercury, cadmium, and copper [13, 14]. Further studies show that humus based filters or humate can

Corresponding Author: ozdemirfa@itu.edu.tr (F. Ayca Ozdemir Olgun)
Received 4 May 2018; Received in revised form 11 July 2018; Accepted 12 July 2018
Available Online: 16 July 2018
Doi: ISSN: 2636-8498

remove hydrogen sulfide, mercaptan, and sulfur dioxide [15]. Moreover, HA has high affinity for magnetic nanoparticles and a Fe_3O_4/HA, core/shell, structure is able to remove heavy metal ions with a 93% yield [16 - 18]. Although there are many studies using core/shell structures in the literature, to our knowledge there are few that focus on multiple component systems [19]. Humic acid which itself is a biodegradable substance can easily be used as an ecology friendly material. The aim of this study is to coat magnetite nanoparticles with humic acid and silver, forming a multicomponent nanostructure for the removal of heavy metal and bacterial pollution in water. In this part of the study only the synthesis of multicomponent nanoparticles and their synthetic heavy metal applications is reported. The combination of Fe_3O_4, HA and Ag for the synthesis of magnetic nanoparticles occurs for the first time in concept of this study bringing novelty in literature.

2. MATERIALS AND METHOD

2.1 Instrumentation

Varian Flame Atomic Absorption Spectrometer (FAAS) was used to measure the absorbance values of standard metal solutions and synthetic mixture solutions to observe the adsorption characteristics of synthesized composite particles. For an equal and homogeneous sorption process, an Edmund Bühler 7.400 Tubingen shaker was used. The Shaker period was adjusted to $300 min^{-1}$. A JOEL JSM-7600F Scanning Electron Microscope and FEI Quanta 250 FEG was used for the SEM analysis. Zeta potential analyses were made using ZetaPals Zeta potential Analyzer BIC (Brookhaven Inst. Corp.). A Chiltelrn Hotplate Magnetic Stirrer was used to achieve homogeneous heating during the co-precipitation process of nanoparticles. A regular magnet was used to collect particles from the sample solution. For successful coating at all stages of synthesis BANDELIN RK100H ultrasonic bath was used.

2.2 Chemicals and reagents

All reagents and standards were of analytical grade and were used without any further purification. All dilutions have been carried out with milliQ pure deionized water. The chemical reagents used in this procedure were Fluka ferrous chloride hexa hydrate (98% pure), Merck Ammonium iron(II)sulfate hexa hydrate, Aldrich Humic acid sodium salt, Merck Ammonia (%25), Merck Tin(II)chloride, Merck Hydrochloric acid, Fluka Silver nitrate, Fluka Sodium Hydroxide, Merck Copper(II) and Cadmium(II) standard solutions.

2.3 Synthesis Procedure of Magnetite Nanoparticles

Particles were prepared using co-precipitation process. A stochiometric mixture of $FeCl_3.6H_2O$ and $NH_4FeSO_4.6H_2O$ (molar ratio 1.5:1) was heated to 90^0C for 45 minutes on Chiltelrn hot plate magnetic stirrer. For this purpose, 6.1 g $FeCl_3.6H_2O$ and 4.2 g $NH_4FeSO_4.6H_2O$ were weighed and dissolved in 100 mL pure water separately. Once the heating is over 10.0 mL of 1.0 mg L^{-1} humic acid sodium salt solution was mixed along with iron(III) chloride and iron(II) chloride solutions and 10.0 mL 25% ammonia solution was appended immediately to precipitate HA coated magnetite nanoparticles. For a complete reduction and coating, heating was carried out in 90^0C for an hour. Particles were washed with milliQ pure water twice and sonicated for 30 minutes. A simple magnet easily worked for the collection of particles from the bottom of the beaker, and a Pasteur pipette was used to collect supernatant from the surface. Very small particles with a very weak magnetic property were observed in supernatant liquid. These particles were discarded with the supernatant liquid.

After several trials, a redox reaction between Sn^{2+} ions and silver ions was found useful to coat the particles with silver [20]. Therefore, the coating of Fe_3O_4/HA particles with silver resulted in two steps and ultrasonication was used at the end of each. It is known that Sn^{2+} ions can reduce Ag^+ to Ag^0 and can be adsorbed on the HA surface through negatively charged groups. A 0.063 M acidic Tin(II) chloride solution was mixed with Fe_3O_4/HA particles and the mixture was sonicated for 30 minutes. Hence, Sn^{2+} ions were adsorbed on the surface of core/shell structure. After sonication, the mixture was cleaned with milliQ water twice. The second part of silver coating process consisted of the electrochemical plating of silver on the core/shell structure. The suspension was mixed with freshly made 0.13 M Tollen's reagent (ammonium silver nitrate), sonicated for 30 minutes and washed twice with milliQ water. At the end Fe_3O_4/HA/Ag magnetic particles were separated from the suspension by using a magnet and then dried at 60^0C in air. Fig 1 below shows the schematic illustration of the formation of Fe_3O_4/HA/Ag multi-component structure.

2.4 Characterization of Synthesized Particles

The characterization of synthesized Fe_3O_4/HA/Ag composite structure was made using SEM and Zeta potential analysis. For each selected area on SEM, an EDX mapping analyses were made for surface elemental analysis. Sample preparation was carried out mechanically on dried samples. These samples were Fe_3O_4, Fe_3O_4/HA as the intermediates, and Fe_3O_4/HA/Ag as the final product.

The DLS experiments were conducted at a 90^0 angle using 35 mW solid state laser detectors operating at 658 nm. The change in the particle size in response to pH was also determined by DLS measurements, adjusting the pH with 0.1M HCl and 0.1M NaOH in 10^{-2} M KNO_3 aqueous solution.

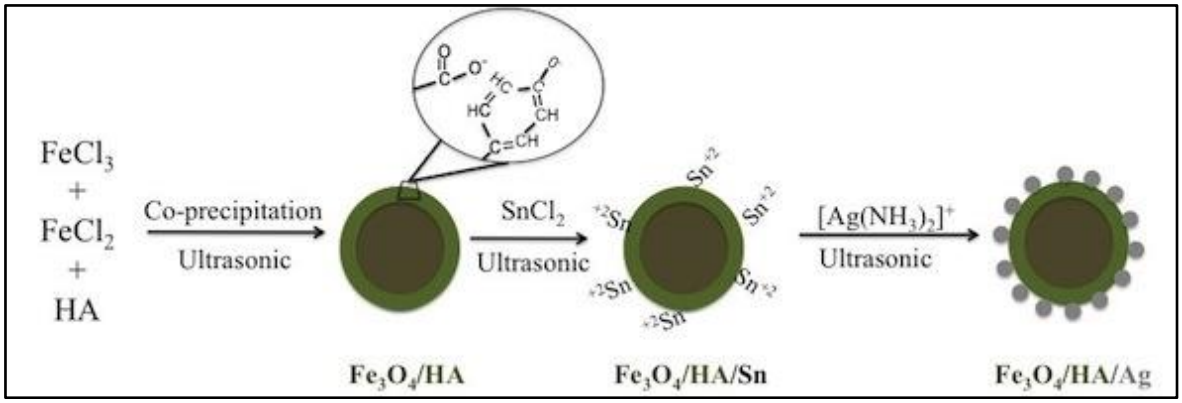


Fig 1. Schematic illustration of the formation of Fe_3O_4/HA/Ag multi-component structure

A diluted aqueous solution of particles was prepared for the zeta measurements, which were carried out in triplicate, as were the DLS measurements. The first sample was diluted (portions were 1/50 and 1/100) with 10 mL KNO_3 in sonicator for 5 minutes. The second and third samples diluted in 10 mL KNO_3 and sonicated for 5 minutes. Only then, zeta potentials were measured.

2.5 Procedure of Heavy Metal Adsorption

The adsorption of copper and cadmium was investigated by batch adsorption method using FAAS. The initial concentrations of copper and cadmium were prepared in the concentration range of 1.0-3.0 mg L^{-1} for copper and 0.5- 2.0 mg L^{-1} for cadmium, respectively. Particles were collected with a magnet after the adsorption process has reached to the equilibrium. Adsorption parameters as pH value, sorption time, and particle mass on heavy metal removal were optimized in separate sets of experiments. pH value adjustments were made using 0.01 M NaOH and 0.001 M HCl solutions and values were varied to 3.0, 5.0, 7.0, and 9.0. In order to obtain the optimum pH value, the particle mass was set constant at 0.01 g with a 10 min. of contact time. On these conditions, the optimum metal removal was obtained at pH 9.0. All adsorption experiments were performed at pH 9.0 except those in which the effects of particle mass and contact time was investigated. Finally, three different trials were made with these optimized values and a mixture of cadmium and copper solutions were prepared to understand the selectivity of magnetic nanoparticle between two metal ions.

The adsorbed heavy metal amount (q_e) per unit absorbent mass was calculated as follows;

$$q_e=(C_o-C_e)V/m \quad (1)$$

where C_o is the initial heavy metal concentration, C_e is the concentration of heavy metal at equilibrium (mg L^{-1}), m is the magnetite mass (mg) and V is the solution volume (L). Calculations were made using these data and adsorption curves of copper and cadmium on magnetic nanoparticles were obtained.

3. RESULTS & DISCUSSION

3.1 Characterization of Fe_3O_4/HA/Ag Particles

A JOEL JSM-7600F and FEI Quanta 250 FEG SEM were used for the characterization. EDX mapping was performed for the surface elemental analysis. On the SEM images, the bright particles represent silver, the gray parts represent humic acid coated magnetite particles and the black parts represent empty spaces. Fig 2 and Fig 3 below show the SEM images of the intermediates and final products respectively. The most suitable closest image was obtained with ×50.000 magnifications. The dispersion of silver particles was not uniform on the surface but EDX mapping proved the existence of silver shown in Fig 4. On EDX mapping, there was no sign of tin (II) which shows the efficiency of ultrasonication and repeated particle cleaning after each step.

The Zeta potential was used to prove negative charge of double layer and DLS analysis was used to procure the mean diameter size of particles. Since HA has negatively charged large groups on the surface, it was easy to predict that zeta potential of the particles had a negative value. Results showed that this value was -23.09 mV. According to Zeta potential data, synthesized multi-component structure can be accepted to have incipient stability. The DLS analysis showed that in the given conditions the mean diameter of the particles was as 291.0 nm. This results from large structure of humic acid and aggregation of particles during DLS measurement.

3.2 Optimization of Adsorption Parameters

3.2.1 Effect of pH

In the pH study, adsorption of ions investigated at varying pH values of 3.0, 5.0, 7.0 and 9.0. The particle mass was fixed 0.01 g with a contact time of 10 minutes. Adsorption percentages were calculated to compare the results and as it is seen on Fig 5-a, the maximum adsorption percentage was recorded at pH value 9.0 for the removal of copper and cadmium with 89.92% and 94.26% removal percentages, respectively.

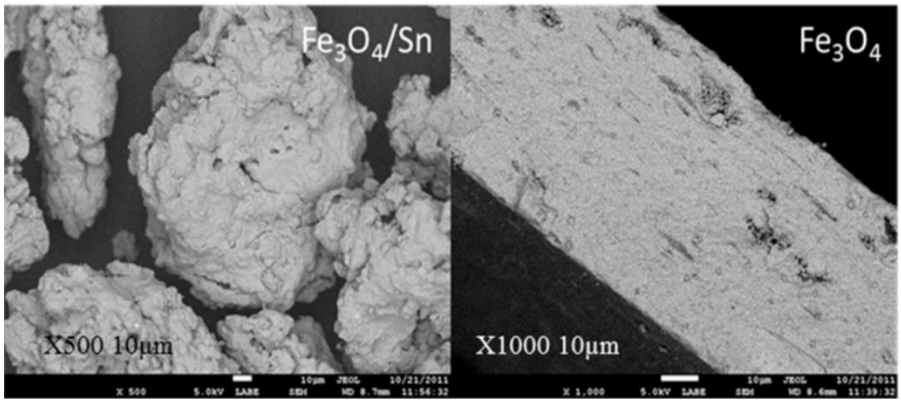


Fig 2. SEM images of intermediates a) in Fe_3O_4/HA nanoparticles after the dispersion of Sn^{+2} solution ×500

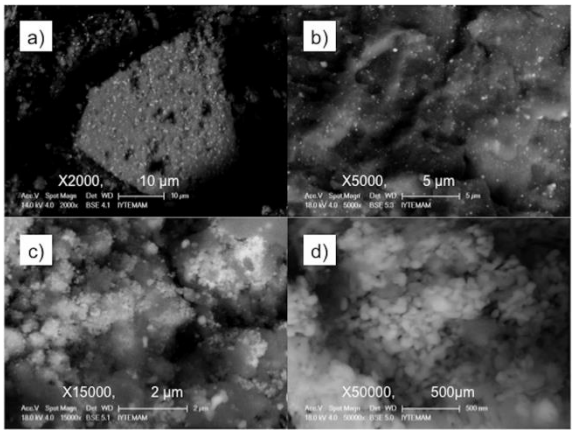


Fig 3. SEM images of the prepared Fe_3O_4/HA/Ag particles at different magnification ranges a) ×2.000 b) ×5.000 c) ×15.000 d) ×50.000

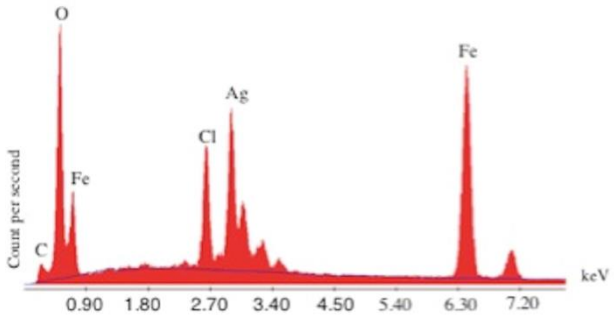


Fig 4. EDX mapping of the surface labeled as b on Fig 2

According to the studies reported in the literature, many different pH values were maintained due to the maximum adsorption of copper and cadmium. When compared to the other studies where pH value was kept at 9.0 removal percentage obtained in our study was found to be the highest.

3.2.2 Effect of Contact Time

During the investigation of contact time, adsorption process was performed using 0.01 g particles at a pH value of 9.0. The absorbance values were measured at time intervals of 5, 10, 20, 25, and 30 minutes and adsorption percentages were calculated. Adsorption of copper and cadmium was found to be 90.25% and 94.37% respectively. Although there were small fluctuations between 20 and 30 minutes contact time for copper and cadmium, the highest removal percentage was accepted at 20 minutes for both metals. Fig 5-c found below, represents the removal percentages of cadmium and copper ions in the given conditions. This data related with the physical character of adsorption also gives clue about the favorability of increased surface area of the sorbent.

3.2.3 Adsorption Isotherms

For the design and analysis of adsorption process, adsorption isotherms should be well understood. Langmuir isotherm stands as the simplest theoretical model for the monolayer. By modeling single coating layer on adsorption surface it supposes that the adsorption takes place at a specific adsorption surface and as it gets further from the adsorption surface the attraction between molecules decrease [21].

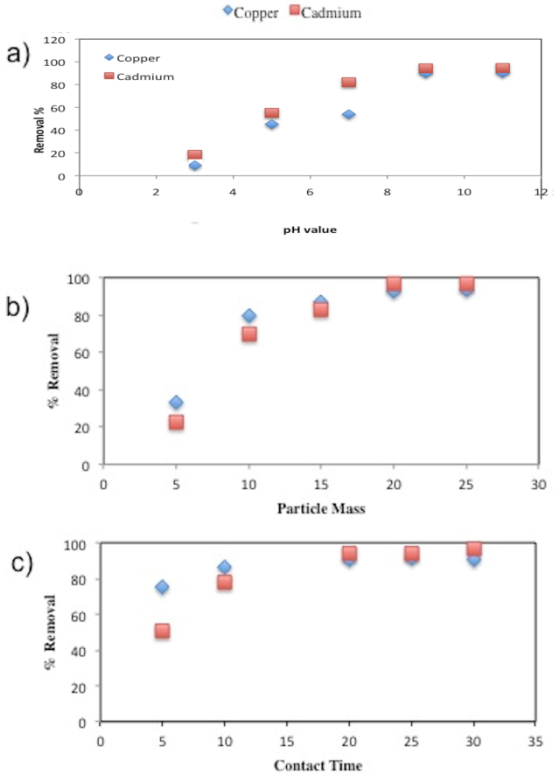


Fig 5. Influence of a) pH, b) particle mass and c) contact time on the removal of copper and cadmium by prepared Fe_3O_4/HA/Ag particles to aqueous solution containing Cd and Cu and 2 mg L^{-1} respectively

The following formulas related to Langmuir isotherm are given below;

$$q_e=V_mkC_e/(1+kC_e) \quad (2)$$

where q_e is the amount of adsorbed heavy metal per unit magnetite mass (mg g^{-1}), V_m is the monolayer capacity, k is the equilibrium constant and C_e is the equilibrium concentration of the solution (mg L^{-1}).

Eq. (2) can be linearized as follows:

$$C_e/q_e=1/kV_m+C_e/V_m \quad (3)$$

The results obtained from the empirical studies were applied to Langmuir isotherm.

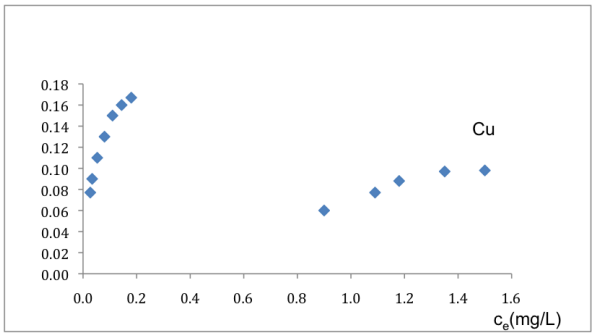


Fig 6. Adsorption isotherm of Cu and Cd on magnetic nanoparticle fits of Langmuir Model

The dependence of Ce/qe from C_e was obtained by using empirical results. The linear form of Langmuir equation for copper and cadmium adsorption on magnetites are calculated with the aid of adsorption graph shown in Fig 7 and found as;

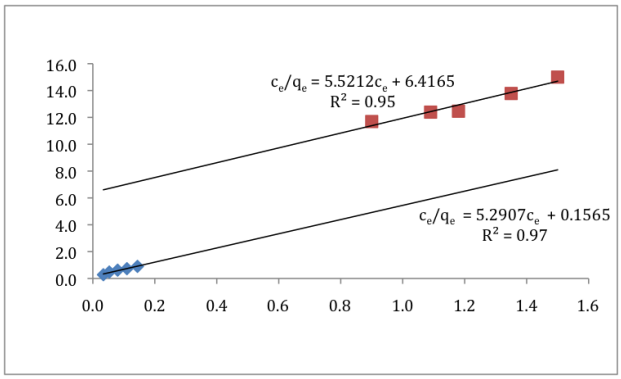


Fig 7. Linearized adsorption isotherm of Cu and Cd fits of Langmuir Model at 300 K

$$C_e/q_e=5.2907C_e+0.1565, R^2=0.97 \text{ for Cd} \quad (4)$$

$$C_e/q_e=5.5212C_e+6.4165, R^2=0.95 \text{ for Cu} \quad (5)$$

As it can be seen from Table 1, the Langmuir model can represent the actual adsorption data. Adsorption (q_e) reaches a plateau region (possibly corresponding to monolayer coverage) with respect to equilibrium concentration of the aqueous phase (C_e) beyond a limiting concentration, which is a characteristic property of the Langmuir isotherm.

Table 1. Parameters of Langmuir Isotherm

Name of metal adsorbed	Isotherm Equation	Slope	K_L	R^2
Cu	$C_e/q_e=5.5212C_e+6.4165$	5.5212	92.54	R2= 0.9
Cd	$C_e/q_e=5.2907C_e+0.1565$	5.2907	0.87	R2= 0.97

4. CONCLUSIONS

The Fe_3O_4/HA/Ag multi-component structure was synthesized using co-precipitation and electroplating methods. In order to build a multi-component system with three components, a redox reaction between Tin (II) chloride and Tollen's reagent is required otherwise it is not possible to coat the particles with silver. Hence, there are two intermediates obtained during the process. Ultrasonication and cleaning of the suspension after each step is very important because it allows a homogeneous core/shell structure to form. The SEM images supported with EDX mapping showed the existence of silver and humic acid in the structure and the mean diameter of synthesized particles were found as 291 nm in DLS analysis when their zeta potential was -23.09 mV. Between 92% and 98%, of the heavy metal ions were removed from the solution at optimum conditions. The optimum conditions were a pH value of 9.0, a 20 mg particle mass and 20 minutes of sorption time. The adsorption characteristics of magnetic nanoparticles were defined by Langmuir isotherm giving an adsorption capacity of 33.63 mg g^{-1} for Cd and 0.87 mg g^{-1} for Cu.

As an addition to this study, the antibacterial property of the synthesized particles, which were derived from the silver component, were observed but will be reported at a later date.

REFERENCES

[1]. M. Faraji, Y. Yamini, M. Razaee, "Magnetic nanoparticles: Synthesis, Stabilization, Functionalization, Characterization and its applications," *Journal of the Iranian Chemical Society*, Vol. 7. doi: 10.1007/BF03245856, 2010

[2]. W. Z. Zhang, "Nanoscale iron particles for environmental remediation: An overview," *Journal of Nanoparticle Research*, Vol. 5, pp. 323-332, 2003.

[3]. Y. C. Chang, D. H. Chen, "Preparation and adsorption properties of monodisperse chitosan-bound Fe3O4 magnetic nanoparticles for removal of Cu(II) ions," *Journal of Colloid and Interface Science*, Vol. 283, pp. 446-451, 2005.

[4]. N. Savage, M. S. Diallo , "Nanomaterials and water purification: oppurtunities and challenges," *Journal of Nanoparticle Research*, Vol 7, pp. 331-342, 2005.

[5]. E. Erdem , N. Karapınar, R. Donat, "The removal of heavy metal cations by natural zeolites," *Journal of Colloid and Interface Science*, Vol 280, pp. 309-314, 2004.

[6]. Y. G. Ko, U. S. Choi, "Diverse applications of fibers surface-functionalized with nano- and microparticles," *Composites Science and Technology*, vol. 79, pp. 77-86, 2013.

[7]. K. Aguilar-Artega, J. A. Rodriguez, E. Barroda, "Magnetic solids in analytical chemistry: A review," *Analytica Chimica Acta*., vol. 674, pp. 157-165, 2010.

[8]. B. H. Jun, M. S. Noh, G. Kim, H. Kang, J. H. Kim, W. J. Chung, M. S. Kim, Y. K. Kim, M. H. Cho, D. H. Jeong, Y. S. Lee, "Protein separation and identification using magnetic beads encoded with surface enhanced Raman spectroscopy," *Analytical Biochemistry,* Vol. 391, pp. 24-30, 2009.

[9]. S. Yean, L. Cong, J. T. Yavuz, M. Yu, "Effect of Material Particle Size on Adsorption and Desorption of Arsenite and Arsenate," *Journal of Materials Research*, Vol. 20, pp. 3255-3264, 2005.

[10]. M. Rong, M. Q. Zhang, H. Liu, H. Zeng, "Synthesis of silver nanoparticles and their self-organization behavior in epoxy resin," *Polymer*, vol. 40, pp. 6169-6177, 1999.

[11]. M. Z. Rong, M. Q. Zhang, H. B. Wang, H. M. Zeng, "Surface modification of magnetic metal nanoparticles through irradiation graft polymerization," *Applied Surface Science*, Vol. 200, pp. 76-93, 2002.

[12]. S. T. Dubas, V. Pimpan, "Humic acid assisted synthesis of silver nanoparticles and its application on herbicide detection," *Materials Letters* , Vol. 62, pp. 2661-2663, 2008.

[13]. E. Pena-Mendez, J. Havel, J. Patocka, "Humic substances- compounds of still unknown structure: applications in agriculture, industry, environment and biomedicine," *Journal of Applied Biomedicine*, Vol. 3, pp. 13-24, 2004.

[14]. E. A. Ghabbour, G. Davies, N. K. Ghali, M. D. Mulligan, "The effect of temperature on tight metal binding by peat and soil derived solid humic acids," *Canadian Journal of Soil Science*, Vol. 81, pp. 331-336, 2001.

[15]. J. B. Green, S. E. Manahan, "Absorption of sulphur dioxide by sodium humates," *Fuel*, Vol. 60, pp. 488-494, 1981.

[16]. A. Oehmen, Z. Yuan, L. L. Blackall, J. Keller, "Short-term effects of carbon source on the competition of polyphosphate accumulating organisms and glycogen accumulating organisms," *Water Science and Technology*, Vol 50, pp. 139-146, 2004.

[17]. E. lls, E. Tombacz, "The role of variable surface charge and surface complexation in the adsorption of humic acid on magnetite," *Colloids and Surface*, Vol. 230, pp. 99-109, 2003.

[18]. J. F. Liu, Z. S. Zhao, G. B. Jiang, "Coating Fe3O4 magnetic nanoparticles with Humic acid for high efficient removal of heavy metals in water," *Environmental Science and Technology*, Vol. 42, pp. 6949-6954, 2008.

[19]. B. Lv, Y. Xu, H. Tian, D. Wu, Y. Sun, "Synthesis of Fe3O4/ SiO2/Ag nanoparticles and its application on surface enhanced Raman scattering," *Journal of Solid State Chemistry*, Vol.18, pp. 2968-2973, 2010.

[20]. C. Wangab, Z. Rongh, J. Wang, N. Jiang, Y. Pang, R. Xiao, S. Wang, "Seed-mediated synthesis of high-performance silver-coated magnetic nanoparticles and their use as effective SERS substrates," Colloids and Surfaces A: *Physicochemical and Engineering Aspects*, Vol. 506, pp. 393-401, 2016.

[21]. N. Unlu, M. Ersoz, "Adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions," *Journal of Hazardous Materials*, Vol. 136, pp. 272-280, 2006.

Environmental Research & Technology, Vol. 1(3), pp. 25-34, 2018

Environmental Research & Technology

http://dergipark.gov.tr/ert

RESEARCH ARTICLE

Energy self-sufficiency and its significance: Japan's potential and some take-away lessons from Germany

Philipp Konstantin Huehn[1], Davar Pishva[1,*]

Faculty of Asia Pacific Studies, Ritsumeikan Asia Pacific University, Beppu, JAPAN

ABSTRACT

Fossil fuels have traditionally powered modern societies since the Industrial Revolution and our present day well-being have been achieved through such fuels. They are, however, finite in nature and quite harmful to the environment since they are the main source of global warming. Japan, Germany as well as many other countries are highly dependent on the import of oil, gas or coal and have to pay the world market price. Unsustainable extractions have brought fossil fuels under constraint and countries which want to (partly) mitigate this issue, should start investing in renewable energies and re-arrange their energy generation sector to a more sustainable system. A functional mix of renewable and conventional power plants can reduce the need for fossil fuels in the electricity generation sector, thus lessen the carbon dioxide emission while securing supplies and stability. The main aim of this study is to investigate Japan's potential for renewable energies and how to influence its energy generation sector with some take-away lessons from Germany. Qualitative and quantitative research designs were adopted to provide reasonable arguments to support the hypothesis that a fair share of its total (electric) energy demand could be achieved by capitalizing on renewable energy sources, while phasing out some old thermal power plants. A significant take-away lesson from Germany turns out to be adoption of more innovative energy policies and their constant upgrades. Patience with higher price of renewable energy sources during times that world oil prices significantly drops through political manipulation is another consideration.

Keywords: Fossil fuels, renewable energies, sustainability, policies, Japan, Germany

1. INTRODUCTION

At the outset, the authors would like to mention that this work was initially conducted as a master's thesis by the first author under the guidance and supervision of the corresponding author as part of the requirements of the German-Japanese dual degree program in International Material Flow Management (IMAT) [1]. After its initial success, the authors decided to collaboratively enhance and improve the work and transform it into a reputable journal article for its wider access. Considering that the first author comes from Germany and raised after the 1970's oil crises; corresponding author comes from a major oil producing country, have spent his entire professional career in Japan while observing how world politics have affected both major oil producing and consuming countries, we would like to share our findings in a sincere and scientific manner. In our modern world, energy is considered our lifeline and after observing how superiority complexes have used numerous gimmicks and politics to manipulate and control such lifeline, we would like to emphasize the importance of energy self-sufficiency and propose practical ways for its attainment. Japan's achievement of energy self-sufficiency using some take-away lessons from Germany will encourage other countries to pursue similar path, prepare the world for the complete depletion of fossil fuel in the near future, help prevent global warming and eventually enable each nation to control and manage their lifeline independently and without forced submission to tricks or dirty politics.

There are certain similarities between Germany and Japan in the sense that both are highly industrialized nations, have only scarce fossil fuel deposits (excluding Germany's access to lignite) and are thus dependent on fossil fuel imports to meet their energy demands. Such dependency on fossil fuel imports got

Corresponding Author: dpishva@apu.ac.jp (Davar Pishva)
Received 11 April 2018; Received in revised form 18 July 2018; Accepted 18 July 2018
Available Online 6 August 2018
Doi: ISSN: 2636-8498

tangible with the oil crises in the 70's for the first time. Since then Germany and Japan have diversified the energy sources of their electricity generation sectors. In 2011, the Great East Japan Earthquake and its follow up tsunami created a nuclear disaster at Fukushima Daiichi power plant. This accident led to a chain reaction of consequences after which the Japanese government decided to shut all of Japan's 54 nuclear reactors down for revision and suspend all plans related to nuclear power plant set up. The German government even passed a slow phase out of all nuclear power plants as a direct reaction to Fukushima incident [2]. Both countries have used different approaches to solve the discontinuation of nuclear power. Although Germany had already successfully implemented a feed-in-tariff (FIT) system and other policies, which have been carefully analyzed by governments around the world, prior to the nuclear phase-out, the newly decided phase-out puts more stress on the electricity generation system. In Japan's electricity generation strategy, compensation for electricity share of the shutdown nuclear power plants mainly come from obsolete – fossil fuel driven power plants, something which has led to increased spending on fossil fuel imports and higher CO2 - emissions [3]. Despite world market prices for fossil fuels being low in recent years [4], the additional spending has resulted in a negative trade balance and with the prices slowly recovering, such deficits could become worse. Given the finiteness of fossil fuels, the prices are likely to increase to even higher than prior peaks. Therefore, it would be a big mistake to rely on fossil fuels for too long, especially for countries that have no or limited fossil fuels resources.

In this paper we have analyzed the potential of renewable energies in Japan. The investigated energy sources are wind, water, solar, geothermal and biomass. With focus on national energy resources, Japan could reduce fossil fuel imports and simultaneously increase its independence from suppliers. Furthermore, CO_2 - emissions could be reduced as well. The above mentioned similarities with Germany are seen as opportunity to look at Germany's measures to restructure its energy generation sector. Some measure could be implemented in Japan in order to nourish the development of Japan's renewable energy sector and mitigate fossil fuel imports. Therefore, the main questions that we try to answer are: Where does Japan's renewable energy potentials lie and what measures which have been implemented by Germany could be applied in Japan in order to support the development of renewable energies?

2. HISTORICAL PERSPECTIVES AND TRANSFORMATION PROCESSES

Japan and Germany were among the list of countries which started to industrialize after the United Kingdom (UK) in the second half of the 19th century. In 1868, the Tokugawa Shogunate was overthrown, and with the emperor back in power, the Meiji Restoration put an end to the century long Japanese self-imposed isolation. This marks the starting point of the Japanese industrialization era [5]. In Germany some factories had been in operation since the early 19th century. However, first movements towards a broad industrialization era began to sprout after the pre-March revolution in 1848. After the German victory over France in 1870/71, the German Confederation was united under Prussia's lead to the second German Empire. With the unification and war reparations from France, the industrialization process was significantly nurtured. Areas of the empire with rich coal and iron ore deposits like the Ruhr area, the Saarland, Alsace-Lorraine and Silesia saw explosive growth rates in population and economic activity [6].

With the slowly upcoming electricity generation, water power plants were used to meet initial demand. However, due to steadily growing demand and the need of a water body for water power plants, larger power plants driven by coal, generated the main share of electricity. The energy and electricity demand continued to grow around the world, especially after the 2nd World War [7].

2.1 Expanding energy demand and diversification

Population growth and economic recovery in Germany and Japan lead to a constantly expanding energy demand which could no longer be satisfied by national resources as both countries are poor in fossil resources. Imported cheap mineral oil supplemented coal and slowly started replacing it as the main energy source in the second half of the 20th century [8]. Their low prices and wide availability led to an increasing dependence on the new fossil fuels, making them the driving force of global development. Thermal power plants generated the electricity needed for development by burning fossil fuels. Mineral oil was also crucial for transport and the chemical industries. This dependence became visible during the oil and energy crises of the 1970's.

A substantial mineral oil shortage during the first crisis in 1973 was caused by an oil embargo of the Organization of Arab Petroleum Exporting Countries (OAPEC) [9], which lead to a price increase from US$3 per barrel to nearly $12 per barrel globally by 1974 [10]. Price increase by four folds had many effects on industries and the global economy, one of which was greater interest in energy alternatives, namely renewable energy sources, nuclear power plants and national fossil fuel reserves.

Both countries diversified their energy generation sector and reduced their dependency on Middle Eastern mineral oil. Nuclear energy was seen as the most economical and useful solution, therefore governments prioritized the expansion of nuclear energy [11]. Despite the fact that dirty political manipulations lowered oil prices and many renewable energy projects which had been implemented during the height of the oil crisis were discontinued, the oil crisis increased awareness about the importance of energy self-sufficiency and generated incentives to develop energy efficient technologies for households and industries.

2.2 Impacts of the Fukushima Disaster

The Fukushima disaster refers to the nuclear meltdown in Fukushima Daiichi nuclear power plant which was caused by the Great East Japan Earthquake and its subsequent tsunami. This nuclear meltdown had major impact on Japanese and German energy policies. As a direct result of the Fukushima disaster, the previously cancelled German nuclear phase-out by the year 2022 was reconsidered and became a German law through strong public support [12].

Prior to the Great East Japan Earthquake in 2011, nuclear energy had an annual share of around 30% on Japan's electricity generation [13]. This share was scheduled to increase to around 40% in order to sustain energy supply security and mitigate carbon dioxide emissions [14].

However, most nuclear power stations in Japan were shut down after the accident. The share of nuclear energy on the annual electricity generation dropped to 2% in 2012 and to 0% in 2014 [13]. According to the Japanese Ministry of Economy, Trade and Industry (METI) only 3 of the 54 reactors are in operation [3]. The supply gap is mainly covered by thermal power plants which are fueled by mineral oil, coal or liquefied natural gas (LNG). But due to Japan's low self-sufficiency ratio of about 6% in 2014, the country heavily depends on fossil fuel imports. When electricity was also generated by nuclear power stations, the self-sufficiency level was at 19.9%. After the shut-down of all nuclear power stations, 88% of the energy carriers used for electricity generation in 2014 had to be imported, while only 9% of the electricity was generated by hydro power and 3.2% by renewable energies [3].

3. JAPAN'S ENERGY SECTOR AND ITS 2-GRID SYSTEMS

Japan has a rather unique electricity generation sector and grid systems. The country is split into 10 areas, each of which is managed by one company. Grid operation and electricity generation are both under the control of those companies. Up until recently, households had to purchase their electricity from the utility company in their area and were not able to choose their suppliers. However, since the liberalization of the electricity market in 2016 it has become possible for households to select their electricity provider [15].

Apart from its still inflexible electricity market, the electricity transmission network is split into two more or less independently operating grids. Its North-East grid which covers Tokyo metropolitan area operates at 50 Hz while its South-West grid runs at 60 Hz. Considering that transmission of electricity from one grid to another requires frequency conversion and there are only three frequency converting stations that connect the North-East grid to South-West grid, puts a limit on such transfer. Currently the Japanese frequency converting capacity is at 1.2 GW [16].

4. JAPAN'S RENEWABLE ENERGY POTENTIALS

Renewable energies (excluding large scale hydro power projects) were not part of Japan's energy source portfolio until 2011. In 2012, the share of renewable energies (excluding hydro) made up only 3% of its total national energy generation, just increasing by 1% compared to 1990 level [17]. A considerable large potential in national energy generation remains still untapped and Sovacool in 2011 concluded that a total of 324 GW renewable energies are feasible for Japan [18]. Onshore and offshore wind turbines account to 222 GW, geothermal power plants to 70 GW, additional hydro power plants (especially small scale ones) to 26.5 GW, solar energy to 4.8 GW and agricultural residue to 1.1 GW. Wakeyama and Ehara focused on the potentials of renewable energies in Northern Japan (Hokkaido, Aomori, Akita, Iwate, Niigata) which include wind, geothermal, micro-hydro power plants, biomass and solar power. Their results show that it is possible to generate enough energy in Northern Japan which not only can supply the need of the whole area sustainably but also have a surplus that can be transmitted to other parts of the country, especially to the densely populated Tokyo metropolitan area [19].

4.1 Wind power

Electricity generation is relatively new in the field of wind power. Although the first windmill used to generate electricity was built in 1887 in Scotland by Professor James Blyth, it took almost one century for the real potential of wind power to be acknowledged [20]. From small wind mills on top of buildings to large on- and offshore wind farms that are capable of generating hundreds of megawatts – even gigawatts in some cases – thus can feed vital electricity into the national grids. It is possible to build power stations with a power output of several MW (Offshore SIEMENS D-7 Platform 6-7 MW rated capacity). Although wind power is dependent on whether conditions, in the same manner that solar energy is, it has the advantage of being easier to predict. Hence, it is relatively easier to plan electricity supplementation with wind energy. With the Sovacool's estimated potential of Japan's wind power [18], this renewable source could contribute to the energy mix decisively.

Left side of Fig 1 shows Japan's onshore wind power potential and the right side indicates its offshore wind power potential. As can be observed, its onshore potential is limited, but the offshore is quite high. Although the onshore northern areas of Hokkaido and Tohoku can provide high enough wind speeds for large wind turbines, the southern part does not. On the other hand, the offshore potential is quite high, especially in the northern areas around Hokkaido and in front of the Izu peninsula (marked in red), where wind speeds of around 8.5 m/s or even higher have been recorded [21]. Some high yield zones are close to the mainland (lower right side, marked in red) and could supply electricity without long transmission lines. Except for a few cities, Hokkaido and Tohoku regions are not densely populated and areas around

the Izu peninsula could be used to generate electricity for the highly populated areas in and around Tokyo or Nagoya.

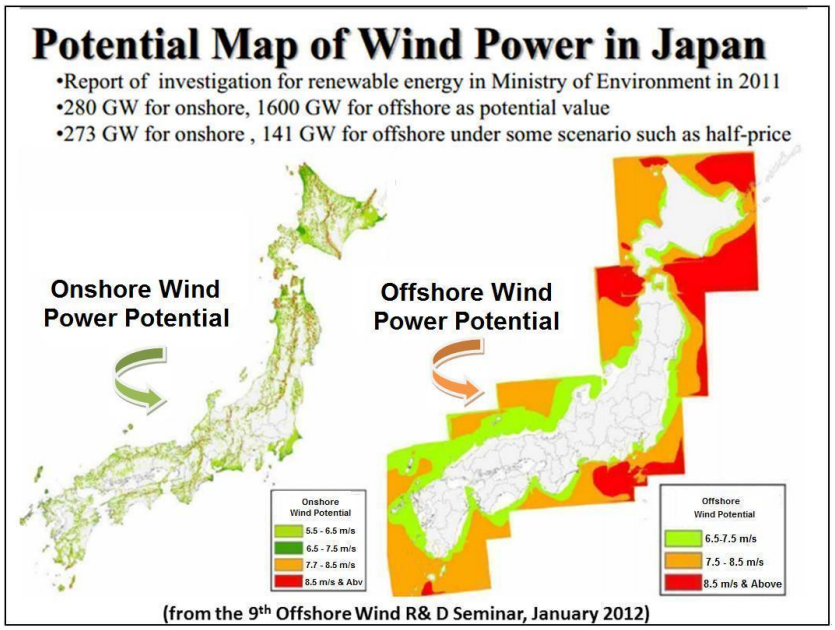


Fig 1. Potential Wind Power Map of Japan (Source: United Press International (2013) Japan plans biggest ocean wind farm)

4.2 Geothermal energy

Geothermal energy, defined as the heat from the earth, is a statute-recognized renewable source [22]. Originating from the earth's inner structures and radioactive decay, heat is generated and stored in the earth's crust. This energy can be used in direct and indirect ways. Direct usages are heating and cooling of private households or public buildings, greenhouse heating, relaxation and healthcare in spas, even cooking with the hot water or steam is possible. Electricity generation is an indirect use and can only be implemented when temperature and heat levels are high enough to run an attached steam turbine.

Japan is located right on top of the Pacific Ring of Fire. The tectonic activities not only cause constant earthquakes, but also contribute to a high volcanic activity. That is why geothermal energy in Japan is close to the surface, often even visible in form of hot springs, referred to as "Onsen" or steam rising up from crevices. Despite this, according to the IEA (International Energy Agency), geothermal energy with an installed capacity of 353 MW, contributed only 0.3% to Japan's electricity generation in 2013 [23].

Fig 2 shows all major geothermal power plants that were operated in 2012 by electric power companies. Majority of those plants are located in the northern area (Tohoku) and the southern island (Kyushu). There are just a few large ones, with the power plant Hatchobaru in Oita being the largest one (110 MWe). Compared to large conventional power plants, the power output is rather low, as most of those power plants can generate up to 500 MWe per block. However, the potential of geothermal energy is there and can be tapped.

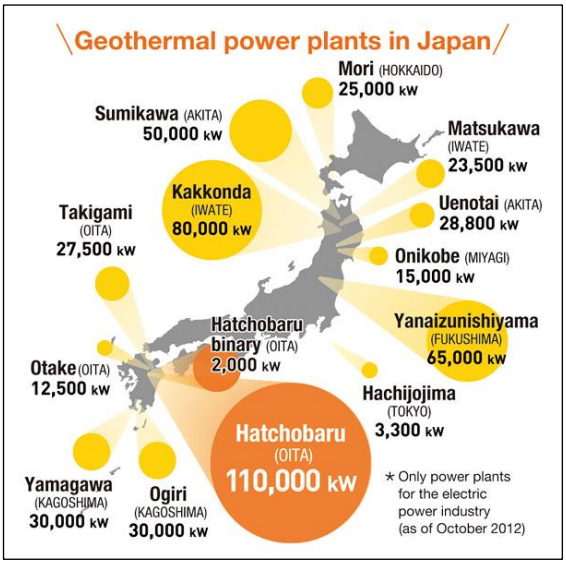


Fig 2. Geothermal Power Plants in Japan (Source: Mitsubishi Heavy Industries: Geothermal Power [2012])

4.3 Hydro power

Water power generates electricity through the transformation of kinetic energy of falling- or running water. Electricity can be generated by hydro power in various ways: conventional dams which store (usually) large amounts of water are able to generate large amounts of electricity. Run-to-the-river power plants, which use the speed of running water, are often found next to running waters, their sizes range from micro- to medium sized stations, depending on the amount of available water and flowing speed. Recent developments have led to pumped storage

plants which are used to store surplus electricity in form of potential energy in water during periods of overproduction, and release the water to generate electricity during peak demand.

Water power can generate electricity steadily. Though its amount may fluctuate through the year, it is possible to feed into the base load or store energy for peak demands. This adaptive capacity makes water power appealing for a well equilibrated energy mix. However, large dams change the ecosystem of the affected area and are not usually seen as sustainable thus leading to the conclusion that large scale projects have to be carefully evaluated in order to prove their sustainability.

Hydropower is currently Japan's main renewable energy source and constituted 9% of its total electricity generation in 2014 [3]. Fig 3 shows the potential number of station in various sizes and the resulting power output. Since most feasible sites for large scale power plants have been exploited already, the future potential has to be utilized by small-scale or even micro hydro power plants, as Japan still has many sites suitable for that purpose. As indicated in Fig 3, the largest potential in terms of power output is in the category 10-30 MW while the largest potential in terms of number of stations is in the category 1-3 MW.

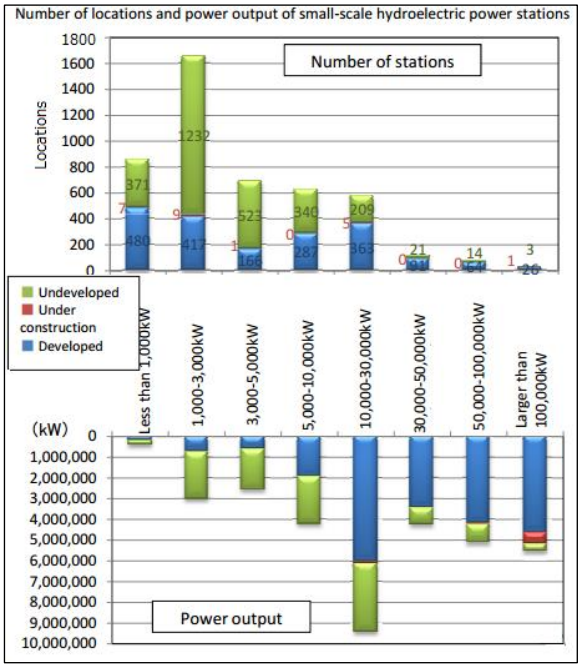


Fig 3. Locations and Power-Output of Hydropower in Japan(Source: METI (2012) Japan Renewable Energy)

4.4 Solar energy

Solar energy is radiant light and heat from the sun which are utilized by various technologies [24]. Solar heating, photovoltaic and solar thermal panels are used to generate electricity or heat, either in large-scale complexes or on the rooftop of private houses. The range of applicable solutions for solar technology is large.

Crucial for energy production, however, are optimal weather conditions and the intensity of the solar irradiation in the area. That means without sunlight, photovoltaic panels cannot generate electricity and solar thermal panels cannot heat up water. On the other hand, with provided sunlight, the panels can generate electricity and heat up water. Solar panels' performance, however, varies with changing weather conditions. Countries with a fairly large share of PV technology in their energy mix are highly vulnerable to fluctuations in their national electricity grid. Other power plant types are also needed so as to cushion sudden changes, keep the grid stable and ensure supply security. In general, weather-dependent renewable energy sources require other power plant types or energy storage systems since even their sudden surpluses of electricity may not necessarily be used at the time they are generated.

According to the IEA, Japan was the second largest market for solar growth in 2013 and 2014. During that time, 6.9 GW and 9.2 GW of nominal capacity were added to the already existing capacities, cumulating up to a total of 23.3 GW. With that notable amount of installed capacities, the country became the number three in terms of solar electricity generation in the world, behind China (28.2 GW) and Germany (38.2 GW). The currently installed capacity is estimated to be sufficient to supply up to 2.5% of the country's annual electricity demand [25].
The global horizontal irradiation map of Japan in Fig 4 shows the sun's average annual sum of irradiation between the years 2007 to 2012. As can be observed, the potential is high especially in its southern parts. The Ryukyu Islands (琉球諸島), Kyushu(九州), Shikoku (四国) and southern parts of the Japan's main island Honshu (本州) have high sun irradiation, between 1450 kWh/m^{2}and 1600 kWh/m annually (by comparison, Germany's average annual sun irradiation is around 1000 kWh/m). While Honshu's (本州) southern coast line is densely populated, other areas have vast unpopulated areas.

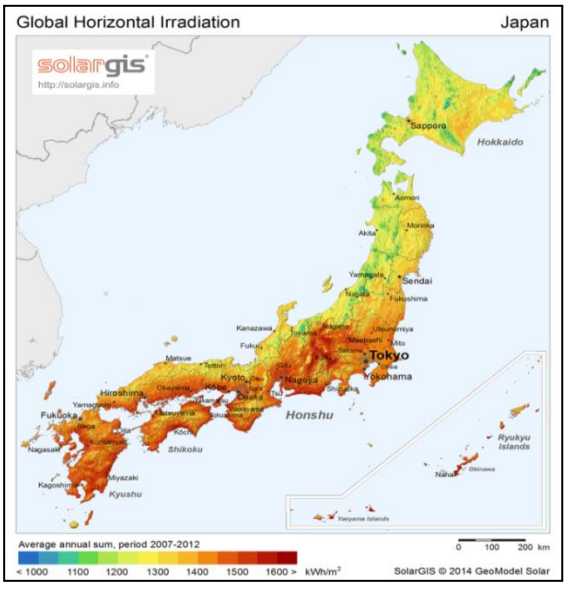


Fig 4. Horizontal Radiation of Japan(Source: Solar GIS Global Horizontal Irradiation Map: Japan)

Decline in production price (from over 980 Yen/Wp in 1993 to 380 Yen/Wp in 2011) and financial incentives offered the Japanese government made photovoltaic systems attractive for households [24]. Energy balance can be improved by placing solar panels on the currently unutilized rooftops, especially in urban areas.

4.5 Biomass

Biomass can be defined as any organic matter that can be renewed over time. In other words, biomass is stored energy. Through photosynthesis, sunlight, carbon dioxide and water, it can be turned into oxygen and simple sugars which are stored. Even though they emit carbon dioxide when burned they are considered to be carbon neutral. The main reason for biomass to be considered as carbon neutral is that fossil fuels are hydrocarbon deposits derived from organic materials of a previous geological time. They are fossilized biomass, and the containing carbon was removed from the atmosphere long time ago [26]. In other words, when burning new biomass it only emits the CO2 that it has recently absorbed from the atmosphere while fossil fuels release the stored carbon dioxide of previous geological time, implying a surplus to greenhouse gas particles of the atmosphere.

Biomass plants are versatile and almost anything can be used. Energy crops, food waste or human/animal residues contain a higher energy density and have been proved to be more efficient than simple greenery. Biomass can be utilized in form of gas (biogas plant) for heating, generating electricity or cooking, biofuel for transportation, chemical substitutes for fossil fuel based chemicals or in form of wood for heating. Its generation can be decentralized and operate completely independent from the electric grid. Its gas form can be used for either generating electricity or stored in the national gas grid or special containers and utilized when needed. The transportability and decentralized functionality makes it possible for biomass to be utilized almost anywhere in the world.

As shown in Fig 5, the potential for biomass utilization in Japan is enormous. In some areas, biomass is being utilized already while others require infrastructure before they can be utilized. According to the MAFF (Ministry of Agriculture, Forestry and Fisheries), forestry residue and agricultural residue are unused at the moment.

Possessing high potential for different renewable energy sources is a good opportunity for Japan to diversify its electricity generation sector and increase its independence from energy carrier imports. Wind and solar are fluctuating energy sources, dependent on the right weather conditions, they cannot be used for base load purposes. Geothermal power and hydro power are subject to seasonal change as well, but they can generate electricity day and night and therefore can be utilized for base load purposes. Agricultural residue and other biomass could be used for electricity generation, heat or gas production which can then be used for electricity generation or other purposes.

5. ENERGY POLICIES

Underlying renewable energy policies, their necessary fine tuning in response to the needs of the time and governmental commitments are extremely important for a successful renewable energy generation strategy. This section briefly examines German and Japanese energy policies.

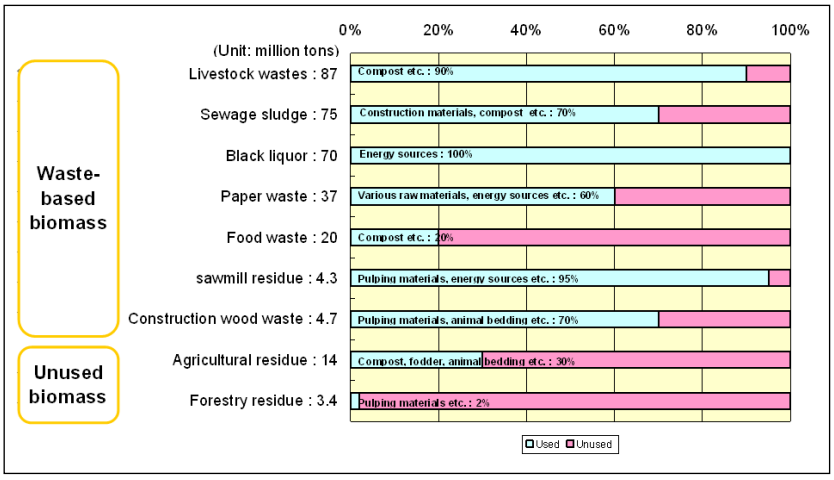


Fig 5. Japan's Biomass Usage and Potentials (Source: MAFF, basic plan for the promotion of biomass utilisation (2009))

5.1 German policies

The first pertinent German law which regulates the utilization of renewable energy in the German grid and adopted in 1990, is known as Electricity Feed-in Act and locally called the Stromeinspeisungsgesetz (StromEinspG). This law demands power utilities to connect renewable energy plants to the power grid and reimburse their owners for the generated electricity fed into the national power grid [27]. This regulation is still in place. With the liberalization of the electricity market, power utilities are no longer in control of the national power grid. Grid operators and power generators have to work together instead so as

to guarantee grid connection and preferred feed-in for renewable energies.

German Renewable-Energy-Sources Act, locally called Erneuerbare-Energien-Gesetz (EEG), is the follow up of the StromEinspG and came into effect in early 2000. With the EEG, the grid connection was once more guaranteed to renewable energy plant operators together with a fixed purchase price for all generated electricity during the next 20 years. This feed-in tariff scheme promoted the development for all major renewable energy sources, and led to a fast development of wind and solar power in the first years. After its initial successes, the EEG has been revised regularly (in 2004, 2009, 2012, 2014 and 2017) and undergone major changes.

While the EEG successfully promoted the growth of renewable energies, the German (or European) power grid was not capable of keeping up with the constant expansion. Additional electricity being generated in the northern parts and demand for extra electricity in the southern parts, required increase in power transmission capacity of the grid for a successful transmission of the generated electricity to the consumers. Hence, an auction system was introduced for the first time in the EEG 2014 [28]. This auction system was even further enhanced in the EEG 2017 which nominates the lowest bidder to build the advertised capacity. First offshore wind park projects were already auctioned with zero subsidies [29].

The next pertinent German law after the EEG is its Energy-Saving-Regulation, locally called Energiesparverordnung (EnEV) and adopted in 2002. The aim of this regulation is to enhance energy efficiency of buildings. The idea is to increase energy savings through insulation and efficiency measures. According to Chiarello, most of the energy consumed in households is for heating (75%) and warm water (12%) - share of electricity utilization for other purposes is only 13% [30]. The EnEv is therefore enforced to reduce energy consumption for heating. Steady increase in energy efficiency of newly built houses and renovated buildings are planned to ensure a consumption reduction.

5.2 Japanese policies

The first subsidy system for residential photovoltaic (PV) electricity generation in Japan started as early as 1992 [31]. The PV promotion program continued until 2007 but ended thereafter presumably due to the price drop of fossil fuel in the world market. In 2012, however, a feed-in tariff system based on the German system was created in order to promote the development of renewable energies in Japan. It is important to mention that Japan's style of annually revising tariffs for each type of subsidized technology, has generated even faster changes in its electricity generation sector than Germany.

Another policy of Japanese government is to improve energy efficiency of household appliances. The Top-Runners program is used to promote the development of more efficient machinery like air conditioners, freezers, etc. Japanese government is strongly promoting IoT (Internet of Thing) technology for both automation as well as energy efficiency purposes.

6. SUMMARY AND CONCLUSION

Several renewable energy sources are available in Japan, allowing the country to implement an energy mix that can help power utilities and the Japanese government to commit to their 3E+S (Energy Security, Economic Efficiency, Environment + Safety) policy. Renewable energy sources could fill the energy gap created by shut down of its nuclear power stations. Although energy saving policies and fossil fuel driven power plants have filled such gaps for now, the additional money spent on fossil fuel imports has in return led to a negative trade balance and an increase in GHG (Greenhouse gases) emissions [32]. Instead of continuing this vicious circle of import dependency, out flowing funds and growing GHG emissions, some of the money spent on fossil fuels could get invested in the development of renewable energies. This can subsequently lead to the self-sufficiency of Japan's electricity generation sector, reduce the outflow of money outside the country and cut GHG emissions. The diminishing nature of fossil fuel, its crucial role for the Industrial Revolution, and the panic that it generated in the 1970's oil crises should not be forgotten. The proposed approach can eventually enable Japan to control and manage its lifeline independently and without forced submission to international political games.

6.1 Summary analysis

On one side, there are small hydro power plants and geothermal power plants which can be used in large quantities regardless of weather conditions, but have limited available construction sites. On the other side, there are solar and wind power which can be installed more flexibly in terms of location, but are dependent on weather conditions. Biomass – when utilized for gas generation – can serve as a buffer technology, because gas is storable and transportable. Its decentralized and transportable nature makes biomass utilization possible at any time and in part of the country. In terms of regions, the northern parts offer better conditions for wind energy, while the southern areas are more attractive for solar panels due to the higher radiation of the region. Geothermal and hydro energy are spread across the country as well as biomass which can be collected / produced in both urban and rural areas.

A FIT scheme has been proved to be a good approach to promote renewable energies. It has worked well in Germany, leading to a steep increase in renewable energies. The FIT approach in Japan which started around 5 years ago, has incentivized investments into renewable energies. The approach has enabled to increase its installed renewable energy capacity from 25 GW in 2012 to more than 50 GW in 2016 [31]. In fact, Japan's style of annually revising tariffs for each type of subsidized technology, has generated even faster changes in its electricity generation sector than Germany.

However, one of the major short comings in Japanese energy policy is its unresolved grid connection and feed in problem. While in Germany renewable power plants have to be connected to the grid and can feed in their generated electricity by law (or get compensated otherwise), there is no such law in Japan. The local power utilities decide whether to allow the connection of power plants to the grid or not and as well dictate the necessary requirements that have to be fulfilled. While German approach enable investors to rely on prior estimations and subsequently create higher investment reliability, the Japanese approach does not and may even discourage / prevent constant feed in approach.

Moreover, its current mid-term strategy favors a return to nuclear energy rather than a move towards renewable energies in order to increase the self-sufficiency. The latest Japanese energy plan of 2015 consists of two main pillars: Energy Conservation Promotion and Balanced Energy Supply. The energy conservation policies aim to reduce the volume of total electricity generation demand. The planned strategy for the energy mix of its electricity generation sector by 2030 consists of 27% LNG, 26% coal, 22-24% renewable energy, 20-22% nuclear, and 3% oil. The 22-24% share of renewable energies is split into 7.0% solar, 1.7% wind, 3.7-4.6% biomass, 1.0-1.1% geothermal and 8.8-9.2% hydro [33]. This implies that the share of its renewable energies is envisioned to grow from 15% in 2016 [31] to 20-22% in 2030 [33]. Even if we set aside the role of energy efficiency measures, this is still a conservative approach considering Japan's potential for renewable energies. Currently hydropower already generates 9% of the total electricity supplied to the grid [3]. Wind power, despite its large on-and offshore potential, planned to constitute only 1.7% to the energy mix. Although solar power, biomass and geothermal energy are going to increase, the planned levels are far below their extractable potentials in Japan.

Supply security and technical concerns, like increased control dynamics through the utilization of weather dependent renewable energies might have led to this decision. Because the German power grid is part of the synchronous grid of Continental Europe, the control and dynamics in Germany have increased with the continuous growth of volatile energy sources like wind and solar thus requiring power utilities to keep conventional power plants as reserves. Since Japan is not connected to an intercontinental power grid, the projected share of renewable energies will keep the control dynamics low, especially because large hydro power stations are already being used for base load purposes. Therefore, it seems that the latest energy plan favors a return back to the status of prior to 2011 in combination with a moderate share of renewable energies. Activation of overhauled nuclear reactors will reduce the amount of fossil fuels which otherwise have to be imported. Thus with only minor changes, the self-sufficiency rate would increase. Nonetheless, a more ambitious strategy could increase Japan's self-sufficiency rate further than what the current plan aims for and the potentials are there. Aside from its widely available renewable energy sources, Japan can also utilize its technological capabilities and numerous patents in order to boost up its national renewable energy usage [21].

6.2 Conclusion and future research

Considering Japan's both technological know-how in the field and the vast accessible energy potentials, a more ambitious energy strategy could work significantly better. Its advantages of possessing temperate climate in the north with strong wind power, tropical climate in the south with high radiation, the world third largest geothermal energy, and blessed with huge amount of offshore energy potential for being an island country, could be better utilized. The fact that biomass energy is referred to as sleeping giant among renewable energy sources, Japan has large population and blessed with greenery, rain and tropical climate, should not also be ignored. Policies that regulate grid connection and feed in sequences are critical for a controlled development. A nationwide uniform approach can lead to successful changes, without necessarily abandoning nuclear energy, but increasing its independence from fossil fuel and eventually achieving energy self-sufficiency. Some take-away lessons from Germany to Japan could be more innovative policies along with their constant enhancements and upgrades, and patience with the higher price of renewable energy sources during the times that world oil prices significantly drops through political manipulation. Fossil fuel is going to diminish and the independent control and management of lifeline is much more important.

Future work along this research can investigate Japan's potential for tidal energy as Japan has also huge potential for tidal energy because of its geographical location and being an island country. Although tidal energy technology is not yet fully developed and still expensive, with vanishing nature of fossil fuel, having access to enough energy, and being energy self-sufficient is going to be far more important.

REFERENCES

[1]. Huehn, P. Konstantin, "Japan's Renewable Energy Potential: Possible Ways to Reduce the Dependency on Fossil Fuels", MS thesis, Ritsumeikan Asia Pacific University, Beppu, Japan, August 2017.

[2]. German Federal Government, Der Weg zur Energie der Zukunft - sicher, bezahlbar und umweltfreundlich - https://web.archive.org/web/20111116042621/http://www.bundesregierung.de/Content/DE/__Anlagen/2011/06/2011-06-06-energiekonzept-eckpunkte,property=publicationFile.pdf (Last access: 2018.1.9).

[3]. METI (2016 a), Japan's Energy 20 Questions to understand the current situation, METI, Tokyo http://www.enecho.meti.go.jp/en/category/brochures/pdf/japanenergy_2016.pdf (Last access: 2017.11.20) 2016.

[4]. Papandreou, A., Ruzzenenti, F., "On the effects of fossil fuel prices on the transition towards a low carbon energy system" Part A, FESSUD FINANCIALISATION, ECONOMY, SOCIETY AND SUSTAINABLE DEVELOPMENT Working Paper Series No 89, http://fessud.eu/wp-content/uploads/2015/03/ Papandreou_Ruzzeneti_Effects-of-fossil-fuel-prices-on-transition-to-low-carbon-energy-part-A-working-paper-89.v2.pdf (Last access: 2018.1.9). 2015.

[5]. Honda, G., "Differential Structure, Differential Health: Industrialization in Japan", 1868-1 940, pp. 251 - 284 Health and Welfare during Industrialization, University of Chicago Press ISBN: 0-226-77156-3, 1997

[6]. Scriba, A., Kaiserreich "Industrie und Wirtschaft, LeMo Lebendiges Museum Online", Deutsches Historisches Museum, Berlin, https://www.dhm.de/lemo/kapitel/kaiserreich/industrie-und-wirtschaft.html (Last access: 2017.1.9), 2014.

[7]. Danilevich, Y.B.; Kirichenko, B.E.; Tikhodeev, N.N.,"History of Electric Energy Systems and New Evolution, UNESCOEOLSS", ELECTRICAL ENERGY SYSTEMS, http://www.eolss.net/outlinecomponents/Electrical-Energy-Systems.aspx (Last access: 2018.1.9), 2016.

[8]. Auer, J., "Energiemix in Deutschland im Wandel Treiber sind Energiewende und internationale Trends", Deutsche Bank Research, Aktuelle Themen Natürliche Ressourcen, ISSN 1435-0734, https://www.dbresearch.de/PROD/RPS_DE-PROD/PROD0000000000444456/Energiemix_in_Deutschland_im_Wandel%3A_Treiber_sind_.PDF (Last access: 2018.1.9), 2014.

[9]. Painter, D.S., "Oil and Geopolitics: The Oil Crises of the 1970s and the Cold War", Historical Social Research. Band Vol. 39, Nr. 4. GESIS – Leibniz Institute for the SocialSciences, Köln, pp. 190, 2014

[10]. Corbett, M., "Oil Shock of 1973–74", Federal Reserve History, https://www.federalreservehistory.org/essays/oil_shock_of_1973_74 (Last access: 2018.1.9), 2013.

[11]. Schiffer, H.-W., "Energiepolitische Programme der Bundesregierung 1973 bis 2017; Energiewirtschaftliche Tagesfragen Year 67", Issue 11 http://www.et-energie-online.de/Portals/0/PDF/zukunftsfragen_2017_11_schiffer.pdf (Last access: 2017.11.20) 2017.

[12]. BMU, "The Federal Government's energy concept of 2010 and the transformation of the energy system of 2011". Bonn, Germany: Federal Ministry for the Environment, Nature Conservation, and Nuclear Safety (BMU), October 2011.

[13]. FECP, "Results and Prospects of Power Generation Volume by Source", Historical Trend of Power Generation Volume by Source in Japan, https://www.fepc.or.jp/english/nuclear/necessary/sw_necessary_02/index.html (Last access: 2017.11.20), 2014

[14]. World Nuclear Association, "Nuclear Power in Japan", http://www.world-nucle"ar.org/information-library/country-profiles/countries-g-/japan-nuclear-power.aspx (Last access: 2017.11.20), 2017.

[15]. METI (2016 b), "What does the liberalization of the electricity market mean? METI; Tokyo" http://www.enecho.meti.go.jp/en/category/electricity_and_gas/electric/electricity_liberalization/what/ (Last access: 20181.10), 2016.

[16]. EIA, "Country Analysis Brief: Japan; U.S. Energy Information Administration", https://www.eia.gov/beta/international/analysis_includes/countries_long/Japan/japan.pdf (Last access: 2017.11.20), 2015.

[17]. Kingdom of Netherlands, "Wind Energy Japan, Embassy of the Netherlands, Japan", https://www.rvo.nl/sites/default/files/Wind%20Energy%20Japan.pdf (Last Access: 2018.1.10), 2012.

[18]. Sovacool, B. K.. "Contesting the Future of Nuclear Power: A Critical Global Assessment of Atomic Energy", World Scientific, pp. 287, 2011.

[19]. Wakeyama, T., Ehara, S.. "Estimation of Renewable Energy Potential and Use-A Case Study of Hokkaido, Northern-Tohoku Area and Tokyo Metropolitan, Japan Sustainable Cities and Regions (SRC)", World Renewable Energy Congress 8-13 May 2011, Linköpping, Sweden http://www.ep.liu.se/ecp/057/vol12/012/ecp57vol12_012.pdf (Last access: 2017.11.20), 2011.

[20]. Price, T. J.. "James Blyth — Britain's First Modern Wind Power Pioneer, Wind Engineering" Volume: 29 issue: 3, pp. 191-200 Issue published: May 1, https://doi.org/10.1260/030952405774354921 (Last access: 2018.1.10), 2005.

[21]. Kojima, T., "How is 100% Renewable Energy Possible in Japan by 2020?" Global Energy Network Institute, https://www.geni.org/globalenergy/research/renewable-energy-potential-of japan/renewable_energy_potential_of_Japan_by_2020.pdf (Last access: 2017.11.20), 2012.

[22]. Kagel, A; Bates, D; Gawell, K, "A Guide to Geothermal Energy and the Environment, Geothermal Energy Association Washington D.C.", http://www.geo-energy.org/reports/Environmental%20Guide.pdf (Last access: 2018.1.9), 2007.

[23]. Oishi Takayuki, Kado Yasuyuki. "IEA Geothermal Implementing Agreement Japan Country Report"http://ieagia.org/wpcontent/uploads/2015/11/ IEAGIA-2014-Japan-Country- (Last access: 2018.1.9), 2014.

[24]. IEA, "Solar Energy Perspectives: Executive Summary"https://www.iea.org/publications/freepublications/publication/Solar_Energy_Perspectives2011.pdf (Last access: 2018.1.11), 2011.

[25]. IEA, "Photovoltaic Power Systems Programme Snapshot of Global PV 1992-2014", 2015.

[26]. Ashton, Sarah; McDonell, Lauren; Barnes Kiley; Longholtz Mattew, "Woody Biomass Desk Guide & Toolkit", National Association of Conservation Districts, http://www.nacdnet.org/policy/woody-biomass-desk-guide-and-toolkit?highlight=WyJiaW9tYXNzIl0= (Last access: 2017.1.9), 2015.

[27]. Salje, P.. Stromeinspeisungsgesetz. "Gesetz über die Einspeisung von Strom aus erneuerbaren Energien in das öffentliche Netz. Kommentar", Carl Heymanns, Köln, Berlin, Bonn, München, ISBN 3-452-24158-0, 1999.

[28]. Bartholl, C., "Auktionsverfahren im EEG – Was kommt Neues nach dem neuen EEG? Newsletter 1/2014" | Erneuerbare Energien, pp.10-11, https://unitedkingdom.taylorwessing.com/fileadmin/files/docs/pdf-german/Beitrag_Bartholl.pdf (Last access: 2018.1.9), 2014.

[29]. Wetzel, Stefan, "WELT Die brutale Kostenwahrheit über die Windkraft Branche", https://www.welt.de/wirtschaft/article163681001/Die-brutale-Kostenwahrheit-ueber-die-Windkraft-Branche.html (Last access: 2018.1.9), 2017.

[30]. Chiarello, G., "Energiesparen im Haushalt Energiespar- Tipps, BBZ Biel", https://www.energie-klimawerkstatt.ch/fileadmin/projects_EKW/2016_17/p_2943/ubungs_va_energie_sparen.pdf (Last access: 2018.1.11), 2017.

[31]. ISEP, "Status of Renewable Energies in Japan (August, 2017), Institute for Sustainable Energy Policies", Tokyo, Japan http://www.isep.or.jp/en/wp/wp-content/uploads/2017/08/ISEP20170827JapanStatus-EN.pdf (Last access: 2017.12.30), 2017.

[32]. Nakanishi, H., "Japan's Energy Situation and Policy, Ministry of Economy, Trade and Industry Agency for Natural Resources and Energy", Tokyo, http://www.pl.emb-japan.go.jp/keizai/documents/E0_2%20METI%20Nakanishi.pdf (Last access: 2018.1.11), 2014.

[33]. METI, "Japan's Energy Plan", METI, Tokyo, Japan, http://www.enecho.meti.go.jp/en/category/brochures/pdf/energy_plan_2015.pdf (Last access: 2017.12.30), 2015.

Environmental Research & Technology, Vol. 1(3), pp. 35-40, 2018

Environmental Research & Technology

http://dergipark.gov.tr/ert

RESEARCH ARTICLE

Investigation of variation of the recyclable solid waste amounts in Küçükçekmece district of Istanbul

Emine Elmaslar Ozbas[1*], Selda Yigit Hunce[1], Huseyin Kurtulus Ozcan[1], Atakan Ongen[1], Sedat Gazi[2]

[1] Istanbul University-Cerrahpaşa, Faculty of Engineering, Environmental Engineering Department, Avcilar, Istanbul, TURKEY
[2] Küçükçekmece Municipality Information Technologies Department, Küçükçekmece, Istanbul, TURKEY

ABSTRACT

It is known that the amount of solid waste changes depending on the economical and cultural living conditions and also seasonal changes. In this study, the variation of recyclable solid waste amounts was investigated for the Istanbul Küçükçekmece district which has a high density of population and industrial activity. The recyclable solid wastes generated in study area were categorized as packaging wastes, waste batteries, waste vegetable oils and electronic waste and the variation of the amounts of these waste groups was investigated based on time between 2010-2015 years. When the amounts of recyclable and recycled packaging wastes were investigated, it showed a significant increase by years. While the amount of recycled packaging wastes was 3,876 tons for the year 2010, it reached to 77,601 tons in the year 2015 with a 20 fold increase. In the period of the study, it is seen that packaging wastes form a large amount of the total wastes by analyzing the percent distribution of examined waste groups. The reason of that could be the simplicity of the recycling and reuse opportunities of packaging wastes. Recycling and reuse opportunities of the waste vegetable oils and e-wastes are new developing applications for this district. It is thought that the recycling ratio of this type of wastes will increase with the developments and improvements on waste management and collection systems.

Keywords: Küçükçekmece, Recycle, Reuse, Solid waste management

1. INTRODUCTION

The amount of waste generated in cities increase with population growth, urbanization and rapid economic development [1- 4]. In addition to the continuous increase in organic waste production, one of the biggest challenges facing the world recently is the effective use of organic wastes as well as recyclable wastes including plastics, tires and other recyclable municipal solid wastes [5]. Although the recycling of such waste has the primary priority, it is also a requirement to reduce the volume of these wastes [6,7]. Recycling is the process of converting wastes to secondary raw materials following physical and chemical processes. It is also called as the conversion of the recyclable materials such as cardboard, plastic, paper, glass and metal to a raw material or product after passing through multiple processes. Prior to conversion process, the separation of wastes is needed according to their types [8]. Energy production from recyclable wastes is significant in terms of economic benefits [9].

Packaging is any material used to contain, protect, handle, transport and present raw materials or goods. Packaging waste includes all the materials including the wastes defined in Regulation on the Management of Packaging Waste and the other non-recyclable materials. Packaging waste includes boxes, pallets, crates, bags, sacks, tapes, disposable foodservice packaging and also items being used to handle or support the products being sold or to be sold [10]. Reducing landfilling of plastics is one of the important priorities of The European Circular Economy package [11]. It was achieved largely by the legislations on recycling of postconsumer plastic packaging waste [12,13]. However, the rates of recycled plastics are still much lower than the production. The amount of annually traded waste plastics in the world in 2012 was about 15 million tons which is lower than 5% of globally produced plastics goods [14,15]. Landfilling

Corresponding Author: elmaslar@istanbul.edu.tr (Emine Elmaslar Ozbas)
Received 18 June 2018; Received in revised form 27 July 2018; Accepted 27 July 2018
Available Online 6 August 2018
Doi: ISSN: 2636-8498

and incineration processes can take place to reduce the environmental effects of such wastes, on the other hand unsanitary disposal or uncontrolled burning of plastics can lead to serious environmental issues [16].

Waste battery is called as battery which has completed its useful lifetime or unusable as a result of damage. Waste batteries should never be mixed with household waste. Therefore, waste batteries should not be disposed to the household trash [17]. The outer cover of waste batteries corrodes by time and the chemical materials and metals inside the battery spreads to soil and then into water. Heavy metals such as mercury and cadmium which is forming environmental pollution, damage living creatures consuming these contaminated foods. Different types of waste batteries should be separated according to their chemical structure [18,19, 20]. There are no waste battery recycling facility yet in use in Turkey. 'Regulation on the Management of Waste Batteries and Accumulators' was published by the Ministry of Environment and Forestry for the collection of waste batteries and accumulators on August 31, 2004. The responsibilities of battery manufacturers and importers and product distributors were defined by the Regulation [17].

Vegetable oil wastes when they are discharged to sewage or water bodies, cover the water surface and damage the water system. It accelarates the oxygen depletion in water by blocking the oxygen transfer from air to water. It leads to cloggings in pipes and increase in operational costs in waste water treatment plants. Vegetable oil wastes is responsible from the 25 % of total water pollution. The oil waste reaching to water bodies (sea, lake and river), harms fish, birds and the other creatures [21]. The used oils must be collected separately from other wastes. It also should not be discharged to the receiving environment such as sewage, soil and sea.

Electronic waste (e-waste) is the type of waste generated from the completing of the life of electronic instruments and finishing the duration of use. E-wastes are commonly composed from computers, printers, phones, fax and photocopy machines, wires and medical equipments [22]. The quick consumption of electric and electronic equipments to catch the technological innovations escalates the trade of these goods and it results in increase in the amount of electronic waste [23, 24, 25]. The rapid development of technology today provides alternative materials and low cost recycling methods. The electronic instruments renewed by developing technology is defined as waste and they are used as secondary raw materials with the higher order compliance for recycling. Almost all of the E-wastes can be recovered with available recycling methods in order to prevent to cause major problems because of their toxic composition [22, 25].

In this study, the variation of the amount of recoverable waste collected in Küçükçekmece province for 5 years period was examined. It is requested to collect and recycle the recoverable wastes separately from municipal solid wastes within the scope of the regulations applied in our country. With this study, it was tried to understand whether the waste collection policy observed after the regulations came into effect is effective.

2. MATERIALS AND METHOD

2.1 Study area

Küçükçekmece district is located on the western side of Istanbul province. Küçükçekmece district having 37.75 km2 area and 47.33 km perimeter, is located on major highways as Transit European Motorway (TEM-E80) and D100 (E5) that provide the Asia-Europe connection, as well as is located on the railway network which is centered in Sirkeci and extending to Europe. Istanbul Küçükçekmece district which has a high density of population and industrial activity. According to population data of 2015, 761,064 people live in the Küçükçekmece district [26]. The location of Küçükçekmece district in Istanbul province is shown in Fig 1.

Fig 1. Location of Küçükçekmece district in Istanbul

2.2 Collection of the data

The data of this study was formed by the arrangement of the data of domestic and industrial waste amounts reported regularly by the relevant units of the municipality on daily, weekly, monthly and yearly basis. In order to interpret the changes, the life styles of the population, the indoor and outdoor events held in the district, guest population of the district and the use of recreational areas are evaluated meticuolusly depending on the dates

3. RESULTS & DISCUSSION

The amount of packaging wastes collected by municipality shows large increases by the years in Küçükçekmece district boundaries (Fig 2). While the amount of recycled packaging waste amount is 3876 tons for the year of 2010, it is reached to 77601 tons with a 20 fold increase in the year 2015. The reason for this increase in the amount of packaging waste collected is thought to be the development of packaging waste collection policies for municipalities within the scope of the "Packaging Waste Control Regulation", which was enacted in 2011. For this purpose, district municipalities have placed recycle bins in many places of the city. In addition, public awareness-raising activities have begun to be implemented. When the collected packaging waste quantities were evaluated, an average of 35180 tons of packaging waste was collected during the 6-year period. The amount of packaging waste collected per

person, which was 5.56 kg capita^{-1} yr^{-1} in 2010, has reached 102 kg/capita/yr value in 2015. In Fig 3, the composition of collected packaging wastes is displayed. It is composed from %12 plastics, %1 metals and %87 paper and cardboards. In a study held in Eskisehir which is one of the metropolitan city of Turkey, the percent weight distribution of recyclable packaging wastes have been found as 50% paper and cardboard, 6.3% metal, 12.45% glass, and 28.1% plastics [27]. In another study conducted in Turkey basis, it is stated that the amount of recyclable wastes (as % weight) consist of 40–65% organics, 11.6-51.4% paper-cardboard, 8.3-40 % plastics, 1.6-17.1% metal and 3.3-17.1% glass [28]. Compared to the values in literature, the amount of paper as a component of packaging wastes collected in Küçükçekmece appears to be above the average of Turkey.

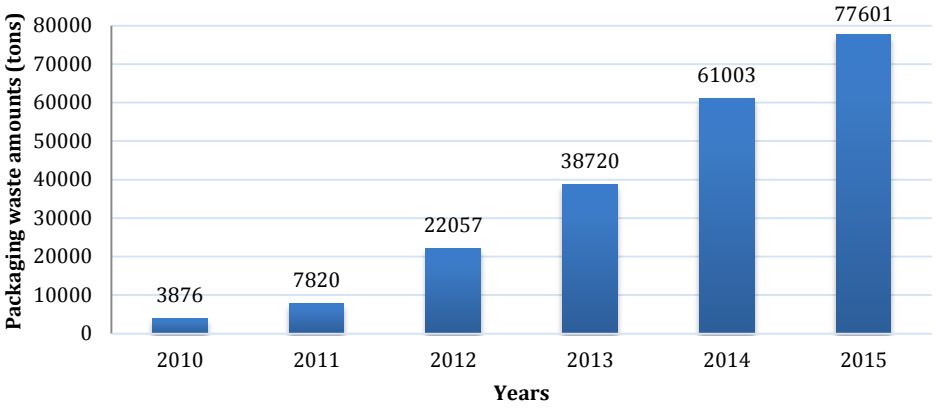


Fig 2. Recycled packaging waste amounts

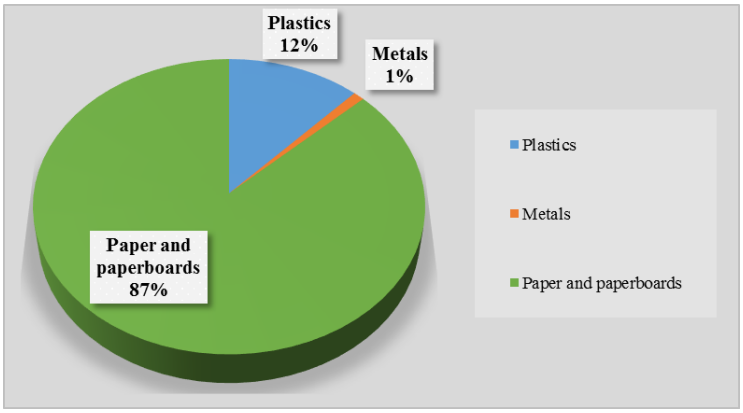


Fig 3. Material based distribution of collected packaging wastes

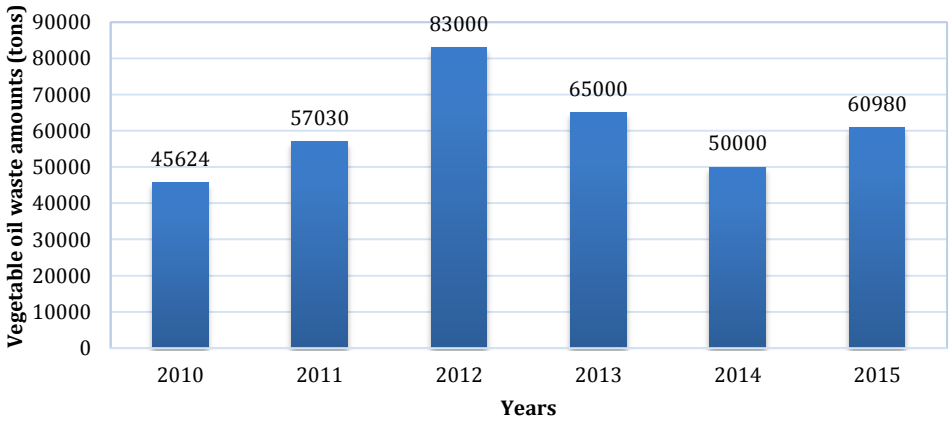


Fig 4. Recycled vegetable oil waste amounts

The amount of vegetable oil waste collected in Küçükçekmece district boundaries is showed fluctuations by the years (Fig 4). It has an increasing trend between the years 2010 and 2012, and it is reached to the highest value of the last six years in the 2012 year. There has been a decline in the years 2012-2014, then it is increased to 60,980 tons value in 2015. The regulation on "Control of Vegetable Waste Oils" was published in 2015. Prior to this regulation, it is considered that the amount of waste oil collected varies from year to year because there is no legal obligation to collect vegetable waste oils. As a legislative regulation on the collection of vegetable waste oils has started to be implemented by the year 2015, it is conceived that the amount of vegetable waste oil collected in 2015 is increased compared to the previous year. According to data of the 6 year period, the average amount of vegetable waste oil collected is 60.27 tons yr^{-1}. It is seen that the amount of vegetable waste oil collected in 2010 is 65 kg $capita^{-1}$ yr^{-1} and it reaches 80 kg $capita^{-1}$ yr^{-1} value in 2015.

As seen from the Fig 5, the amount of waste batteries collected in the Küçükçekmece district boundary was followed by a scattered trend by the years. It has the lowest value in 2009 with 3660 kg and the highest in 2013 with 7635 kg. The average annual amount of waste batteries collected was determined as 5333 tons for the 7 years period between 2009-2015. It is observed that the amount of waste batteries collected, which was 5.4 kg $capita^{-1}$ yr^{-1} in 2009, increased to 6.95 kg $capita^{-1}$ yr^{-1} in 2015. The lack of forceful regulations and efficient recycling applications leads to lower recycling amounts of wastes, for instance only about 2 percent of waste batteries were recycled in China [29-31]. Although it is estimated that the amount of waste batteries collected in the Küçükçekmece district is considerably less than the amount of waste batteries used, it is seen that the amount of waste batteries recovered in years is increasing gradually.

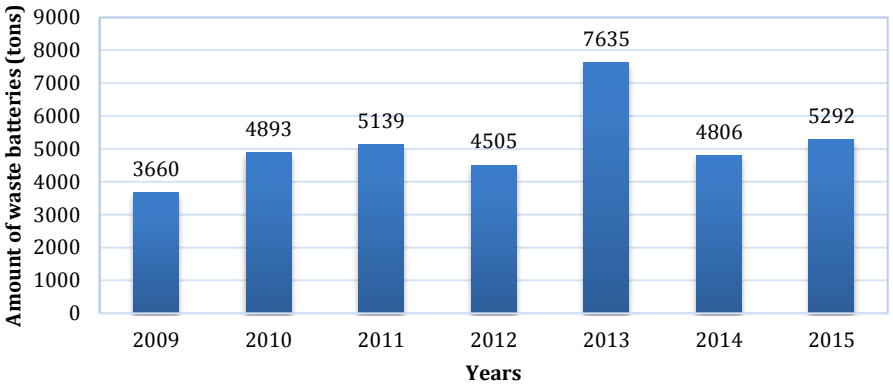


Fig 5. Amounts of recycled waste batteries

In Fig 6, the amount of electronic waste collected in the Küçükçekmece district, has followed a trend of ups and downs by the years. It is observed that an average of 1028 tons of electronic waste are collected annually over a period of 5 years between 2011 and 2015. While it has the lowest value as 600 tons in 2011, and it reached the highest value as 1,838 tons in the year of 2014. To put it another way the amount of collected electronic waste, which was 0.84 kg $capita^{-1}$ yr^{-1} in 2011, increased to 1.44 kg $capita^{-1}$ yr^{-1} in 2015. The largest producer of e-waste is the United States of America (USA) and the People's Republic of China (PRC), however when the per-capita electronic waste is calculated, Norway has the highest e-waste generation value with 28.3 kg. The waste production of Turkey with 503,000 tonnes ranks 17th place among other countries [32]. According to these values, it can be seen that the amount of e-waste recovered in Küçükçekmece is quite low.

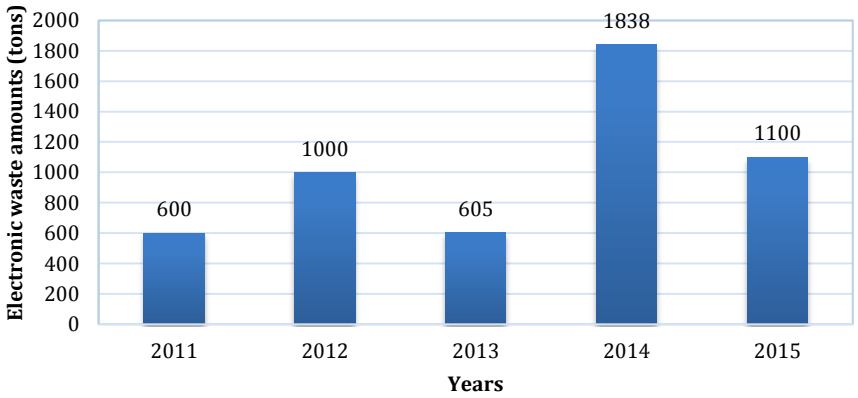


Fig 6. Amounts of recycled electronic wastes

The percent distribution of recycled waste quantities collected is shown in Table 1. From Table 1, it can be seen that the collected amount of waste vegetable oil has the lowest percentage of total recoverable waste. The amount of packaging waste collected increases over the years. The amount of packaging waste in recyclable wastes collected in 2010 was 44.0 % while it reached 92.3 % in 2015.

Table 1. Percent distribution of collected recyclable waste groups between years 2010-2015

Years	Packaging wastes (%)	Waste batteries (%)	Waste vegetable oils (%)	Electronic waste (%)
2010	44.0	55.5	0.5	0.00
2011	57.4	37.8	0.4	4.4
2012	79.8	16.3	0.3	3.6
2013	82.4	16.2	0.1	1.3
2014	90.1	7.1	0.1	2.7
2015	92.3	6.3	0.1	1.3

4. CONCLUSIONS

Examining the results, it can be said that a fairly stable and successful waste collection policy has been applied to the collection of packaging waste for Küçükçekmece-Istanbul. However, for the other types of recyclable wastes examined in this study, the amount of waste collected was found to be fluctuating around years. In the years that Küçükçekmece Municipality has organized training programs in order to raise public awareness, a significant increase is seen in the amount of recycled packaging waste, waste batteries, electronic waste and vegetable oil waste. It is thought that recycling awareness will be enhanced and lead to concrete results with periodical training programs in primary and secondary education institutions located in the district. In the period of this study, it is revealed that the amount of packaging wastes constitutes the major part of the examined waste groups according the percent distribution of total recyclable wastes. The possible cause of that could be the separation and collection of packaging wastes is easier and the recycling and reuse opportunities are more common. Recycling and reuse applications for the other examined waste groups like vegetable oils and e-wastes are not well known in this district. Therefore it is expected that the recycling rate of such waste will drastically increase with the innovations on waste management and collection.

REFERENCES

[1] K.O. Boadi, M. Kuitunen, "Environmental and health impact of household solid waste handling and disposal practices in third world cities: the case of the Accra Metropolitan Area, Ghana", *Journal of Environmental Health*, Vol. 68 (4), pp. 32-36, 2005.

[2] G.N.K. Rockson, F. Kemausuor, R. Seassey, E. Yanful, "Activities of scavengers and itinerant buyers in Greater Accra, Ghana", *Habitat International*, Vol. 39, pp. 148-155, 2013.

[3] B. Xue, X. Chen, Y. Geng, X. Guo, C. Lu, Z. Zhang, C. Lu, "Survey of officials' awareness on circular economy development in China: based on municipal and county level", *Resources, Conservation and Recycling – Journal*, Vol. 54 (12), pp. 1296-1302, 2010.

[4] P. Zheng, K. Zhang, S. Zhang, R. Wang, H. Wang, "The door-to-door recycling scheme of household solid wastes in urban areas: a case study from Nagoya, Japan", *Journal of Cleaner Production*, Vol. 163, pp. 366-373, 2017.

[5] J. Haydary, D. Susa, J. Dudáš, "Pyrolysis of aseptic packages (tetrapak) in a laboratory screw type reactor and secondary thermal/catalytic tar decomposition", *Waste Management*, Vol. 33 (5), pp. 1136–1141, 2013.

[6] A. Solak, P., Rutkowski, "The effect of clay catalyst on the chemical composition of bio-oil obtained by co-pyrolysis of cellulose and polyethylene", *Waste Management*, Vol. 34 (2), pp. 504–512, 2014.

[7] J.E. Rodríguez-Gómez. Y.Q. Silva-Reynoso, V. Varela-Guerrero, A. Núñez-Pineda, C.E. Barrera-Díaz, "Development of a process using waste vegetable oil for separation of aluminum and polyethylene from Tetra Pak", *Fuel*, Vol. 149, pp. 90–94, 2015.

[8] Ministry of Environment and Urban Planning, Recycling Applications on Waste Management, 2012.

[9] C. Guler, Z. Cobanoglu, Katı atiklar, 1st ed., Ankara, 1994.

[10] Regulation on the Management of Packaging Waste, Ministry of Environment and Urban Planning, 2011.

[11] European Commission, Communication from the commission to the *European parliament*, COM 614 December 2nd, 2015.

[12] European Parliament, European Parliament and Council Directive 94/62/EC, 1994.

[13] M.T. Brouwer, E.U.T. van Velzen, A. Augustinus, H. Soethoudt, S. De Meester, K. Ragaert, "Predictive model for the Dutch post-consumer plastic packaging recycling system and implications for the circular economy", *Waste Management*, Vol. 71, pp. 62–85, 2018.

[14] C.A. Veilis, "Global recycling markets - plastic waste: a story for one player – China", Report prepared by FUELogy and formatted by D-waste on behalf of International Solid Waste Association - Globalisation and Waste Management Task Force, *ISWA*, Vienna, 2014.

[15] H. Dahlbo, V. Poliakova, V. Mylläri, O., Sahimaa, R. Anderson, "Recycling potential of post-consumer plastic packaging waste in Finland", *Waste Management*, Vol. 71, pp. 52–61, 2018.

[16] G. Song, H. Zhang, H. Duan, M. Xu, "Packaging waste from food delivery in China's mega cities", *Resources, Conservation & Recycling*, Vol. 130, pp. 226–227, 2018.

[17] http://www.tap.org.tr, Avaliable:(2018)

[18] A. Agarwal, P. Pathak, D. Mishra, K.K. Sahu, "Solvent mediated interactions for the selective recovery of cadmium from Ni-Cd battery waste", *Journal of Molecular Liquids*, Vol. 173, pp.77-84, 2012.

[19] K. Provazi, B.A. Campos, D.C.R. Espinosa, J.A.S. Tenorio, "Metal separation from mixed types of batteries using selective precipitation and liquideliquid extraction techniques", *Waste Management*, Vol. 31 (1), pp. 59-64, 2011.

[20] H. Mahandra, R. Singh, B. Gupta, "Recycling of Zn-C and Ni-Cd spent batteries using Cyphos IL 104 via hydrometallurgical route", *Journal of Cleaner Production*, Vol. 172, pp.133-142, 2018.

[21] http://cevreonline.com, Avaliable: (2018)

[22] L. Zhang, Z. Xu, "A review of current progress of recycling technologies for metals from waste electrical and electronic equipment", *Journal of Cleaner Production*, Vol.127, pp.19-36, 2016.

[23] A. Kumar, M. Holuszko, D.C.R. Espinosa, "E-waste: an overview on generation, collection, legislation and recycling practices", *Resources, Conservation and Recycling – Journal*, Vol. 122, pp. 32-42, 2017.

[24] C.R. de Oliveira, A.M. Bernardes, A.E. Gerbase, "Collection and recycling of electronic scrap: a worldwide overview and comparison with the Brazilian situation", *Waste Management*, Vol. 32 (8), pp. 1592-1610, 2012.

[25] P. Dias, A. Machado, N. Huda, A.M. Bernardes, "Waste electric and electronic equipment (WEEE) management: A study on the Brazilian recycling routes", *Journal of Cleaner Production*, Vol. 174, pp. 7-16, 2018.

[26] TURKSTAT, 2015, http://www.tuik.gov.tr, Available: (2018)

[27] M. Banar, Z. Çokaygil, A. Ozkan, "Life cycle assessment of solid waste management options for Eskisehir, Turkey" , *Waste Management*, Vol. 29 (1), pp. 54–62, 2009.

[28] N.G. Turan, S. Çoruh, A. Akdemir, O.N. Ergun, "Municipal solid waste management strategies in Turkey", *Waste Management*, Vol. 29 (1), pp. 465–469, 2009.

[29] K. Huang, J. Li, Z. Xu, "Enhancement of the recycling of waste Ni–Cd and Ni–MH batteries by mechanical treatment", *Waste Management*, Vol. 31 (6), pp. 1292-1299, 2011.

[30] W. Yang, "Problems exposed in the domain of recycling and using of battery in China", *Environment*, Vol. 1, pp. 68–71, 2007.

[31] M. Zhang, J. Peng, Y. Cao,"Technological development of waste battery recovery and treatment", *Environmental Sanitation Engineering*, Vol. 16, pp. 18–21, 2008.

[32] A.A. Gunduzalp, S. Guven, "Atık, çeşitleri, atık yönetimi, geri dönüşüm ve tüketici: Çankaya belediyesi ve semt tüketicileri örneği", *Hacettepe University E-Journal of Sociological Research*, (http://www.sdergi.hacettepe.edu.tr/makaleler/Atik-Cesitleri-Yonetimi-GeriDonusumVeTuketici.pdf), pp. 1-19, 2016.

Environmental Research & Technology, Vol. 1(3), pp. 41-49, 2018

Environmental Research & Technology

http://dergipark.gov.tr/ert

RESEARCH ARTICLE

Assessment of waste management practice in hostel buildings in Ile-Ife, Osun State, Nigeria

Akeem B. Wahab[1,*], Oladeji A. Olabode[1]

[1] Department of Building, Obafemi Awolowo University, Ile-Ife, NIGERIA

ABSTRACT

The rise in the construction of hostel buildings to take care of accommodation needs of students in higher institutions of learning has been having effects on waste generation and its management practices. The study was carried out to assess waste generated and adequacy of facilities used in managing streams of waste in privately owned hostel buildings with a view to providing information to enhancing its management practice. This study was carried out in privately owned hostel buildings in Ife Central Local Government Area of Ile-Ife, Osun State, Nigeria. A multi-stage sampling process involving stratification and systematic random sampling technique of the hostels and occupants was used. Preliminary survey was carried out to determine types of hostel facilities, its occupancy pattern and personnel involved in its waste management. Eighteen (18%) out of the 858 occupants of the hostel buildings and eleven (11) waste management personnel were selected during the study. A total of 154 questionnaire was administered on the occupants of the hostel buildings and waste audit exercise was carried out to determine quantities of waste generated by using weighing instrument. The data collected were analyzed with descriptive and inferential methods such as cross tabulation, frequency distribution and mean score analysis. The study found that there was significant variation in the streams of waste generated in the types of hostel buildings sampled. It was found that nylon/polythene bags, covered refuse bin and bucket without cover with mean score value of 3.50, 2.89 and 2.78 respectively were used to collect waste generated. The study also showed variation in the alertness of occupants of the hostels to the severity of environmental conditions of waste generated. It was recommended that waste audit be taken as an integral part of waste management practice with the provision of waste collecting, transporting, disposal facilities and protective equipment in order to prevent environmental hazards associated with waste management.

Keywords: Adequacy, effect, facilities, hostel buildings, waste audit, waste streams

1. INTRODUCTION

Environment is the entity that sustains human life through interaction of the processes that make up the ecosystem. The population of the world is on the increase and it demands the need to construct more buildings and other physical infrastructures where different activities take place through the provision of facilities therein [1, 2, 3]. Urbanization which led to the construction of buildings used for different purposes has been pivotal to solid waste generation in the municipalities based on materials used by its occupants [4, 5]. Throughout history, human advancement has been intrinsically linked to the management of solid waste due to its effect on both public and environmental health. Solid waste management (SWM) has a long and convoluted history [6]. In many regions and countries, national and international targets have been set for municipal solid waste management practices [7]. To develop and implement effective strategies to meet these targets require reliable information on the composition of all parts of waste stream.

UNEP [8] defined wastes as substances or objects, which are disposed of or are intended to be disposed of or are required to be disposed of by the provisions of national law. Waste also refers to "an item, material or substance an individual considers useless at a given time and place" [9]. Waste is a dynamic concept which can be defined in different ways [10]. In most cases, the definition of waste depends on the type or category of waste under consideration. Some of the

Corresponding Author: wahabak2002@yahoo.com (Akeem B. Wahab)
Received 14 June2018; Received in revised form 22 August 2018; Accepted 27 August 2018
Available Online 28 August 2018
Doi: ISSN: 2636-8498

dominant types of waste include; municipal waste, solid waste, hazardous waste and electronic waste amongst others.

Processes of solid waste management (SWM) have affected human history in many ways, just as they will continue to do so in the future. The modern waste management industry in the developed world has come far, and with recycling and other advances, it will continue to grow and change with the needs of the community [11]. However, countries in the developing world are yet to see many of these changes within the frame of their solid waste management systems (SWMS). Traditionally, municipalities have been in charge of providing SWM services in developing countries [12]. The municipal responsibility in this present world is to organize and manage public sanitation system, including provision of infrastructure for collection, transportation, treatment and disposal of wastes. However, with the ever-increasing population and economic growth, many municipalities in developing countries are struggling to keep SWMS working in a sustainable manner to address waste generated in different types of buildings occupied by people for different purposes. The municipals manage solid waste with the aim of providing good quality sanitation services in order to keep cities clean and to enhance public health and safety. Evaluation of resources for collection, transportation, processing and disposal of waste requires a correct assessment of the quantity of waste generated per capita per day from direct residential areas and the characteristics of waste generated [13].

A number of studies have been carried out on waste generation and management in Nigeria. Kadifa, Latifah, Abdullah and Sulaiman [14] carried out a study on the current status of municipal solid waste management practice in a city, in Nigeria. They were able to identify the challenges and areas requiring improvement, municipal solid waste generation, composition, storage, collection, and disposal systems. Ibrahim, Awomuti and Ajibade [15] examined storage and treatment system of solid waste as a strategy for sustainable environmental development in Ilorin metropolis. They considered the types and sources of waste generated, legislation on its storage and treatment. Afon [16] examined solid waste management practice in selected cities of Oyo State, Nigeria while [17] assessed waste management practices in selected hospital buildings in Ibadan Metropolis, Nigeria. By considering array of studies on waste management in Nigeria, through rapid urbanization, the quest for educational development has had influence on the need to increase construction of hostel facilities to ensure provision of accommodation for students that gain admission into higher institutions of learning. This would have attendant consequences on waste generation by the occupants of the hostel facilities. Most of the past studies did not focus on waste generation and its associated issues in hostel buildings. Hence, the aim of this study is to assess waste generated and adequacy of facilities used in managing streams of waste in privately owned hostel buildings in Ife Central Local Government Area, Nigeria with a view to providing information to enhancing its management practice.

2. RESEARCH METHODOLOGY

The study was carried out in Ife Central Local Government Area of Osun State, Nigeria. The sample frame consisted of the privately owned hostels in Ife Central Local Government Area. A preliminary survey was carried out to establish the types and numbers of hostel facilities that existed in the study area. A multi-stage sampling approach was employed during the course of the study. The first stage involved stratification of the hostels into occupancy form, either for male, female, mixed type and their typology or mode of construction. The second stage involved the use of systematic random sampling technique whereby the first hostel with respondents was randomly selected with further selection of every hostel that existed in the residential zones where the hostels were located. The survey obtained the total occupancy pattern in the selected hostels by selecting 18% of the occupants in the rooms of the hostels (Table 1). This indicated eight hundred and fifty-eight (858) occupants, and 18% of the total number of occupants was selected as sample size. Eleven (11) personnel involved in the management of the waste in the selected hostel buildings were randomly selected to get information on the current waste management practice. Such a limited sample was selected due to the available constraints [18]. A set of questionnaire was administered on the respondents that occupied the hostel buildings in order to depict information on the waste generated and effectiveness of the management practices on the methods of collection, sorting, transportation of waste etc. Waste audit was also carried out for five days to determine quantities of the sorted stream of waste in the hostels with the aid of a weighing scale and the mean weight of each stream determined (Fig 1). Data collected were analyzed with relevant descriptive and statistical methods such as frequency distribution, cross tabulation and mean score analysis based on a Likert scale of 1 to 5 and the results obtained were empirically compared with references in the literature.

Fig 1. Waste generated in the hostel building, sorted and weighed during the waste audit

Table 1. Selected hostels in the study area

Name of Existing Hostels	Number of rooms Per Block	Sample Frame		Total No of Occupants	Sample Size
		Number of Blocks	Number of Occupants		
Poplat	10	3	2	60	11
Rectas	20	4	2	160	29
Fine Touch	40	2	2	160	29
White House	23	2	2	92	16
Green House	13	1	2	26	5
Happy Land	11	2	2	44	8
Bims	28	1	2	56	10
Women Villa	12	2	2	48	9
CTCS	10	5	2	100	17
Mercy of God	16	1	2	32	6
Ebenezer	20	2	2	80	14
Total				858	154

3. RESULTS AND DISCUSSION

As shown in Table 2, based on the administration of questionnaire on the selected 18% (154) occupants out of a total of 858, 112 was returned and found useful for analysis. This indicated a return rate of 72.72% out of the total number of questionnaire administered on the occupants of the hostel buildings. According to [19], a response rate of 40% was adjudged adequate for studies in built environment related researches, and this implies, that the 72.72% return rate ought to be substantial to adequately reinforce findings of the study.

3.1. Profile of the occupants and the selected hostel buildings

This section presents background information on profile of the occupants and characteristics on typology of the selected hostel buildings. The results shows that about 55.36% of respondents sampled in the selected hostel buildings were female while 44.64% were male. This ought to have influence on the type and quantities of waste generated (Table 3). The length of stay is an important factor in determining respondents' knowledge on waste management practice. According to Jackson [20], the length of residency in an area is a function of respondents' experience of the environment. The study shows that a fairly large proportion, 31.25% of the respondents, had occupied the selected hostel buildings for 3 years and would have understanding of management practice of the waste generated. The profile of the study which informed the understanding of the respondents of the adopted waste management practice was also corroborated by the study of [21] that profile of respondents sampled on residential solid waste management in Sango-Ota, Ogun State, Nigeria was also useful in showing the management practice used.

Table 2. Percentage of questionnaire administered and retrieved

Number of Questionnaire Administered	Number of Questionnaire Retrieved	Percentage of Questionnaire Returned
154	112	72.72

It was also shown in the Table that the type of buildings used for hostel facilities in the selected buildings were flat apartment (41.96%) and followed by face-to-face storey building (37.50)%. Amongst the eleven (11) personnel sampled that were involved in the management of waste in the selected hostel buildings, 63.64% of them belonged to the 31-40 age group while 18.18% belonged to 21-30 and above 41 years age group respectively. This indicated that they were adults and would have reasonable knowledge on the job. It was also found that about 81.82% of the waste management personnel were on full-time mode of employment while 18.18% were on part-time mode.

3.2. Components and quantities of waste generated in the selected hostel uuildings

The study determined components and quantities of waste generated and collected in the hostel buildings sampled with the use of weighing instrument. Table 4 shows mean weight of the sorted streams of waste with seemingly variation in the quantities of the components. It was shown that component rubbish stream of waste was significantly most in quantities in male, female or mixed hostel buildings with 5.20, 5.71 and 4.13kg while paper stream had 4.11, 4.23 and 4.45Kg in male, female and mixed hostel types respectively.

Table 3. Profile of the respondents and the selected hostel buildings

Class of Gender of the Respondents in the Selected Buildings		
Gender	**Frequency**	**%**
Female	62	55.36
Male	50	44.64
Total	112	100.00
Length of Stay in the Hostel Buildings		
Period of Stay (Years)	**Frequency**	**%**
1	25	22.32
2	32	28.57
3	35	31.25
4	16	14.29
5	4	3.57
6	0	0.00
7	0	0.00
Total	112	100.00
Occupancy Type of the Hostel Buildings		
Type of Hostel Building (Typology)	**Frequency**	**%**
Face to Face (Bungalow)	15	49.70
Face to Face (Storey Building)	42	15.20
Flat	47	10.60
Duplex	8	8.60
Total	112	15.90

Table 4 also shows that gender characteristic of the hostel occupied by the respondents influenced the quantum of waste generated in female, male or mixed hostel building. This is evident in the variation in the quantities of stream of waste generated in the hostels occupied by the varying gender of the respondents. According to Alli and Eyasu [22], waste generation rate of domestic waste in Addis Ababa City is 0.45kg/capacity/day, while around 100,000 m^3 waste water is also produced per day from domestic activities alone, and waste collectors participate in the waste management at the approved service charges. Hence, the result carried out on the hostel buildings, in Ile-Ife also depicted that approved waste collectors were commissioned to dispose of quantities of waste generated per day by the occupants.

3.3. Perception of the respondents on the components of waste generated

The study assessed perception of respondents on the components of waste generated through the use of a likert scale of 1 to 5 in the mean score analysis method. Table 5 shows that garbage was rated as the most generated type of waste with a mean score of 3.89, rubbish (3.03) and ashes (2.24). The Table also indicated that dead animals had the lowest mean score of 1.75. The result of this Table also consolidates findings of the waste audit which showed that rubbish and garbage had the comparably highest amount of waste generated in the hostel buildings sampled.

3.4. Solid waste management facilities and its adequacy

The study established facilities used in the collection and management of waste generated in the hostel buildings sampled, factors that influenced choice of methods used and adequacy of the facilities used. Table 6 shows that nylon/polythene bags was mostly used by the respondents in collecting waste generated with a mean score of 3.50. Covered refuse bin and bucket without cover were also used with mean score of 2.89 and 2.78 respectively. The study also assessed availability of central waste storage facility used in the management of waste generated in the hostel buildings. Table 7 indicates that 79.50% of the

respondents indicated that there was availability of central waste management facility to collect waste collected in nylons, polythene bags and others in order to enhance effective waste management practice. Past studies of [23] also indicated that growing population in urban centers in Nigeria has led to great waste management problem in Nigeria, and many efforts at getting rid of them informed the provisions of waste collecting and disposal facilities by the Lagos and Abuja Environmental Protection Board respectively.

Table 4. Components and quantities of waste generated in the hostel buildings

Type of Waste	Component of Waste	Male Hostel (kg)	Female Hostel (kg)	Mixed Hostel (kg)
Garbage	Food	3.61	4.30	4.33
	Canning	1.34	0.55	0.73
	Freezing materials	1.71	1.95	0.35
Rubbish	Nylon	5.20	5.71	4.13
	Wood	0.49	0.89	0.68
	Paper	4.11	4.23	4.45
	Rubber/Plastic	1.54	1.58	1.63
	Leather/Fabrics	1.47	2.07	2.01
	Glass	0.70	1.00	2.00
	Metal	0.65	0.17	2.05
	Ceramics	-	0.99	0.54
	Stone/Sand/Soil	0.57	0.13	0.94
Ashes	Residue from combustion of	-	-	-
	Solid product after heating	-	-	-
Large Waste	Demolition waste	2.06	-	-
	Construction waste	-	-	-
	Furniture	1.33	0.58	2.06
	Automobile	-	-	-
	Home appliances	1.62	0.99	2.33
	Trees	-	-	-
	Fire driven waste	-	0.80	0.47
Dead Animals	Household pets	-	-	-
	Rodents	0.59	-	0.78
Sewage Waste	Sludge	-	-	-
	Screening waste	-	0.10	0.17
Industrial Waste	Chemicals	-	-	-
	Paints	-	-	-
	Explosives	-	-	-
Agricultural Waste	Farm animals	-	-	-
	Manure	-	-	-
	Weed	-	-	-
	Crop residues / Food peel	0.82	1.34	1.00

Table 8 indicates relative significance of the factors that influenced the choice of facilities used in the management of facilities used in the hostel buildings sampled. It was shown that infectious and hazardous nature of waste generated and collected, cultural and social basis and number of occupants per room most significantly determined facilities used with mean score of 3.75 respectively. The Table also shows that

logistics, financial capability, type and size of the hostel buildings, administrative process and waste characteristics also influenced choice of the facilities used with a mean score of 3.50. Equally, according to Wahab [17], different operating factors influenced the choice of facilities used in the management of medical waste generated in hospital buildings with financial capability with RII value of 4.05 in public owned hospitals and 3.76 in private owned hospitals respectively. The outlook of the results of this study on the level of facilities used can also be compared with [24] which found in their work that the Dhaka City Corporation is primarily responsible for collecting and managing waste and a significant amount of waste is not collected due to lack of infrastructure, funds and collecting vehicle, but however sought for future integration of waste management strategies in high density residential development areas.

3.5. Severity of environmental hazards associated with waste management facilities and practices used

The study examined respondents' alertness on the environmental conditions/hazards associated with the waste management facilities and practices used in the hostel buildings through the use of mean response analysis. Table 9 shows that respondents were mostly affected by the severity of the presence of cockroaches breeding with a mean score of 3.34, mosquito breeding and attraction to scavenging animals with mean score of 3.32 and 2.81 respectively. Other effects such as odour from collected waste and filthy drain are also determined by the environmental effects of the facilities and practices used in managing waste generated in the hostel buildings.

Table 5. Perception of the respondents on the components of waste generated

Type of Waste	5	4	3	2	1	Mean Score	Rating
Garbage (food, canning and freezing materials)	42	32	28	1	8	3.89	1
Rubbish (nylon, wood, paper, rubber, leather, glass, metal, ceramics, stone/sand/soil)	13	32	29	17	19	3.03	2
Ashes (Residues of combustion, solid products after heating)	8	10	25	22	43	2.24	3
Large wastes (Demolition and construction wastes, automobiles, furniture, and other home appliances, trees, fires etc.)	4	11	20	28	47	2.06	5
Dead animals: (Household pets, rodents)	4	5	15	22	64	1.75	7
Sewage waste (screening wastes, settled solids and sludge)	2	10	26	37	35	2.15	4
Industrial wastes (Chemicals, paints, sand and explosives)	4	8	6	24	68	1.69	8
Agricultural wastes (Farm animal manure, crop residues and others)	0	12	9	32	57	1.78	6

Table 6. Facilities used in the collection of waste generated in the hostel buildings

Facilities Used	Mean Score
Nylon/Polythene bags	3.50
Traditional basket	2.08
Bucket with cover	2.75
Bucket without cover	2.78
Covered refuse bin	2.89
Plastic drums with cover	2.72
Sack	2.53
Worn-out jerry can	1.89
Plastic drums without cover	2.33
Plastic bags	2.49
Card board boxes	2.00
Metal drums with covers	1.87
Metal drums without covers	2.03
Paper cartoon	2.00
Worn-out metal bucket	1.93

Table 7. Availability of central waste storage facility

Response	Frequency	%
Yes	89	79.50
No	23	20.50
Total	112	100.00

Table 8. Factors that influenced choice of facilities used in the management of waste generated in the hostel buildings

Factors	Mean Score
Infectious and Hazardous nature of waste	3.75
Cultural and social basis	3.75
Logistics	3.50
Financial capability	3.50
Type and size of hostel	3.50
Administrative process	3.50
Waste characteristics	3.50
Number of occupants per room	3.75
Organizational framework	3.25
Maintenance repair	3.25
Technical know-how of the manpower	3.13
Waste load time	2.75
Waste reduce time	2.75

Fig 2 shows sections of streams of waste collected in one of the hostel building selected that exposed the occupants sampled to associated environmental hazards/conditions analysed in Table 9. Comparably, past studies in the literature such as [25] showed that rapid urbanization, rural-urban migration, little or no town planning efforts coupled with attitudinal irresponsibility have created environmental challenge in Nigeria and the problems posed by the attendant waste management practice of the growing population has overwhelmed Nigerian government.

Fig 2. Streams of waste collected in one of the hostel buildings sampled

Table 9. Level of severity of environmental conditions of facilities used in managing waste generated

Severity of Environmental Conditions	Mean Score
Odour rom collected waste	2.42
Odour from filthy drain	2.59
Mosquito breeding	3.32
Rat breeding	2.72
Attraction to flies	2.45
Attraction to rats	2.57
Fly breeding	2.63
Cockroach breeding	3.34
Attraction to scavenging animals	2.81

4. CONCLUSIONS

The spate of increase in population has been observed to correspondingly affect intake of students in higher institutions of learning in Ile-Ife, Nigeria, which has paved way for the construction of more private hostel facilities for students' needs. This has had attendant effect on the generation of waste streams which would affect environmental sustainability of the hostel buildings based on the level of waste management practice adopted. In view of this, the study carried out waste audit to determine components cum quantities of waste and perception of respondents on the stream of waste generated in the selected hostel buildings, adequacy of the facilities used in the management of streams of waste generated, factors that influenced choice of the facilities used and the likely environmental conditions associated with the management practice.

The study found preliminarily that larger proportion of the respondents, 55.36% were female while 44.64% were male and a sizeable proportion of them have been occupying the hostel buildings for about 3 years, and this would give them appreciable understanding of the waste management practices adopted in the buildings occupied. The study established that component rubbish stream of waste

was significantly most generated in either male/female or mixed hostel buildings with 5.20, 5.71 and 4.13Kg respectively. Respondents also indicated with a mean score of 3.89 that garbage was most generated while 79.50% of the occupants had access to central waste storage facility to manage stream of waste generated in the hostel buildings and different operating factors influenced the choice of facilities used to collect the waste. In view of the effects and risks that hostel occupants can be exposed to based on the components and quantities of waste generated, waste audit should be taken as an integral part of waste management practice. Similarly, provision of adequate waste collecting, transporting and disposal facilities should be adhered to in order to prevent environmental hazards associated with waste generated in the hostel buildings.

REFERENCES

[1]. A.B. Wahab, "Erodibility of Built Environment Landmass in Egbeda Local Government Area. The Professional Builder," *The Nigerian Institute of Building Journal*, pp. 69-78, 2008.

[2]. N.B. Andrew, A.A. Simon, P. Chi-Sun, S. Li-Yin and W. Irene, "Reducing Waste in High-Rise Residential Buildings by Information Modelling at the Design Stage," *The Surveying and Built Environment*, Vol. 18, No.1, pp. 51-62, 2007.

[3]. M.T. Fubara. Guidelines and Standards for Environmental Pollution Control in Nigeria, Eguavoen Printers, Aba, Nigeria, 1999.

[4]. A.O. Afon, F.O. Abodunrin and T.C. Kolie, "Urban Solid Waste Management in Nigeria: Poverty Factor as a Constraint," in a National Conference on the City in Nigeria at the Conference Centre of the Obafemi Awolowo University, Ile-Ife, 2002.

[5]. UMP. Working Report; Micro and Small Enterprises Investment. In Municipal Solid Waste Management in Developing Countries. Urban Management Programme and Swiss Development Corporation (SDC). Collaborative Programme on Municipal Solid Waste in Low-Income Countries, 1996.

[6]. J. Nathanson, "Solid-waste management," Retrieved 10, 2015. Available: http://www.britannica.com/EBchecked/topic/553362/solid-waste-managementm, 2015 (accessed 10 February 2015).

[7]. A.A. Ali, "Characterization, Management and Improvement Strategies for Household Waste in Nairobi," Unpublished Ph.D. thesis, University of Nairobi, 2009.

[8]. United Nations Environment Programme (UNEP), "Solid Waste Management. United Nations Environment Programme," International Environmental Technology Center, 2005.

[9]. E. Mugambwa and J. Kizito, "What is Waste Management?," Available: http://www.nemaug.orgindex. phpoption=com_content&view=article&id=69:whatis-waste management&catid=1:latest-news&Itemid=59, 2009.

[10]. E. Pongrácz, "Through Waste Prevention towards Corporate Sustainability: Analysis of the Concept of Waste and a Review of Attitudes towards Waste Prevention," *Sustainable Development*, Vol. 17, pp. 92–101, 2009.

[11]. "Energy Recovery from Municipal Solid Waste," Available: http/urbanindia.nic.in/publicinfo/swm/chap15.pdf (accessed 12 September 2016)

[12]. I.A. Al-Khatib, H.A. Arafat, R. Daoud and H. Shwahneh, "Enhanced solid waste management by understanding the effects of gender, income, marital status, and religious convictions on attitudes and practices related to street littering in Nablus – Palestinian territory," *Waste Management*, Vol. 29 (1), pp. 449-455, 2009.

[13]. V. Gawaikar and V.P. Deshpande, "Source Specific Quantification and Characterisation of Municipal Solid Waste – a Review, Solid Waste Management Division," *National Environmental Engineering Research Institute (NEERI)*, Nagpur, India, Vol. 86, pp. 33-38, 2006.

[14]. A.Y. Kadafa, A.M. Latifah, H.S. Abdullah and W.N.A Sulaiman, "Current Status of Municipal Solid Waste Management Practise in FCT Abuja," *Research Journal of Environmental and Earth Sciences*, Vol. 5 (6), pp. 295-304, 2013.

[15]. S.T. Ibrahim, A.A. Awomuti and L.T. Ajibade, "Storage and Treatment of Solid Waste as a Strategy for Sustainable Environmental Development in Ilorin Metropolis, Nigeria," *Advances in Applied Science Research*, Vol. 3 (2), pp. 801-808, 2012.

[16]. A.O. Afon, "Solid Waste Management in Selected Cities of Oyo State, Nigeria," Ph.D thesis, Department of Urban and Regional Planning, Obafemi Awolowo University, Ile-Ife, Nigeria, pp. 289-306, 2005.

[17]. A.B. Wahab, "Medical Waste Management Practice in Selected Hospitals in Ibadan Metropolis, Nigeria," M.Sc. thesis, Department of Building, Obafemi Awolowo University, Ile-Ife, Nigeria, pp. 51-117, 2011.

[18]. L. Cohen, L. Manion and K. Morrison, "Research Methods in Education," London, Routledge, 2000.

[19]. E. Babies, "The Basics of Social Research," 3rd Edition, Belmont, C.A., USA, Thomson Wordsworth Learning, 2005.

[20]. J.B. Jackson, "The Stranger's Path, Land Scape," *Environmental and Earth Sciences*, Vol. 5 (6), pp. 295-304. 1957.

[21]. S.A. Oloyede, C.A. Ayedun, O.D. Durodola and J.N. Peter, "Residential Solid Waste Management in Sango-Ota, Ogun State: To Recycle or Not to Recycle," *Research on Humanities and Social Sciences*, Vol. 4 (26), pp. 189-194, 2014.

[22]. M. Alli and E. Eyasu, "Domestic Waste Management and its Environmental Impacts in Addis Ababa City," *African Journal of Environmental Waste Management*, Vol. 4 (3), pp. 206-216, 2017.

[23]. A.J. Gana and N. Dauda, "An Investigation of Waste Management Practices in Nigeria: A Case

Study of Lagos Environmental Protection Board and Abuja Environmental Protection Board," *West African Journal of Industrial and Academic Research*, Vol. 12 (1), pp. 112-126, 2014.

[24]. T. Ahsan and A.U. Zaman, "Household Waste Management in High-Rise Residential Buildings in Dhaka, Bangladesh: Users' Perspective," *International Journal of Waste Resources*, Vol. 4 (1), pp. 1-7, 2014.

[25]. B.A Oyeniyi, "Waste Management in Contemporary Nigeria: The Abuja Example," *International Journal of Politics and Good Governance*, Vol. 2 (2), pp. 1-18, 2011.

Environmental Research & Technology, Vol. 1(3), pp. 51-57, 2018

Environmental Research & Technology

http://dergipark.gov.tr/ert

RESEARCH ARTICLE

Cleaner production applications in various industries: metal industry

Arife Simsek[1,*], I. Damla Beytekin[1], Gulfem Bakan[1]

[1] Ondokuz Mayıs University, Department of Environmental Engineering, 55139 Samsun, TURKEY

ABSTRACT

In addition to many environmental issues, including climate change, the relationship between natural resource use and economic growth, and environmental impact and resource use must be reversed for the sustainable management of rapidly depleted natural resources. Cleaner production techniques enable a framework for identification, adaptation and harmonization for the best available technical (BAT) options in metal industry that aim at improving environmental discharges. Surface finishing, surface processing, surface covering, painting and similar processes are performed in the metal finishing industry. Although a wide variety of applications for the metal finishing industry covers cleaner production in Europe and in the world, these studies are limited in Turkey. In this study, it is aimed to evaluate the cooling liquid used in metal surface treatment and waste metal shavings, and to determine economical and ecological efficiency by determining the best available techniques and technologies. For this purpose, pH, conductivity NO^{-}_{2}-N, oil-grease analysis were carried out in SAMPA, a local metal processing company. According to the results of the analysis, the NO^{-}_{2}-N value increased until the end of the month over 10 mg L^{-1}, and the oil-grease and bacteria formation were also found to be quite high. All these analyzes and stages are determinants for the treatment and feed line to be established for the extension of the cooling liquid recovery and reuse and cleaner production practices will be determined.

Keywords: Best Available Techniques (BAT), cleaner production, metal industry

1. INTRODUCTION

Changes in our lifestyles and industrialization have led to an increase in the amount of waste in time and local environmental problems arising from these wastes have reached a global extent. Contrary to conventional pollution control approaches, cleaner production approaches aim to prevent / reduce pollution. Pollution control approaches adopt production and design phases as invariant factors and take pollution as an inevitable result of these steps and try to solve this problem once it emerges.

Approximately 99% of the enterprises in our country constitute Small and Medium Enterprises (SMEs) and their inability to complete their financial and technical infrastructure in general has always kept environmental investments backward. The solution to this problem is to enable industries to use more environmentally sensitive production techniques creating less waste, and at the same time increase their economic performance. Although cleaner production is based on "productivity" and brings permanent solutions to environmental problems, the difference between "pipe end treatment technologies" and cleaner production technologies is still not fully understood in our country. The number of countries adopting this approach is increasing day by day and cleaner production practices are started to be adopted and applied in every kind of production activities with the support of many institutions both at national and international scale [1].

The term "cleaner (sustainable) production" is defined by the United Nations Environment Program (UNEP) as a "holistic and preventive environmental strategy" the reduction of risks to people and the environment" [2]. The Integrated Pollution Prevention and Control Directive (IPPC-2008/1 / EC) issued by the European Union (EU) in 1996, covered legal regulations and supervisory authorities should allow industrial institutions within this general approach and administer environmental performance monitoring. In short, the IPPC directive provides an

Corresponding Author: arife.simsek@omu.edu.tr (Arife Simsek)
Received 29 May 2018; Received in revised form 27 July 2018; Accepted 13 August 2018
Available Online 15 August 2018
Doi: ISSN: 2636-8498

integrated approach to environmental air, water and soil conservation through the implementation of the "Best Available Techniques" (BAT), which is required to determine operating conditions and emission limit values for institutions to be granted.

1.1 Cleaner production and pollution prevention

Cleaner production relies on the principles of reducing the use of natural resources for unit production and reducing waste production by using high-yield production techniques. In other words, cleaner production should be understood not only to prevent environmental pollution, but also to increase productivity in economic terms. This approach consists of continuous and regular implementation of a preventive and integrated environmental strategy applied to production processes, products and services (Fig 1). As cleaner production is compatible with natural processes and the development of environmentally friendly new products, processes, systems and services, there is a close relationship with the concept of sustainability.

Fig 1. Cleaner production notion [3]

1.2 Tools and methods for cleaner production

Cleaner production practices are carried out in many stages of a product life cycle (raw material discovery, production, use and disposal after use). In this context, cleaner production practices require teamwork of many professions. Cleaner production tools include techniques regarding how cleaner production is to be implemented in the industry. These techniques can be explained in general under the following five headings.

- Waste Control
- Evaluation of Alternatives
- Chemical Evaluation
- Energy Assessment
- Environmentally Responsible Design

1.3 Benefits provided by cleaner production

Cleaner production can be applied to all small and large businesses, regardless of their level of material, energy and water consumption. Observations suggest that this approach offers an average resource reduction potential of 10-15% without making high cost investments. The possible benefits of integrating cleaner production approaches into production and management processes and resulting implementation are listed below [4].

- Integrated management strategy
- opportunity source
- harmonized strategy
- economic gains
- environmental benefits
- participation policy
- industry image and social benefits

1.4 Cleaner production practices in the World and Turkey

There are many studies in the literature about cleaner production especially in recent years. As can be seen from the studies listed below, the cleaner production approach is rapidly evolving to be new. Reduction in the use of raw materials and resources and in environmental impacts makes this approach important both for increasing the profitability of the companies and for ensuring the competitive advantage.

The studies on cleaner production work in the world and Turkey are given below.

Baral et al. [5] has achieved the result that chromium emissions can be reduced from 170 tons year^{-1} to 2 tons year^{-1} when fully compliant with EPA regulations, in a cleaner production operation electroplating industry in the United States.

Kupusovic et al. [6] in a cleaner production operation in a meat cutting plant in Bosnia, separate collection of animal blood, and spraying of the irrigation process; 32% reduction in BOD, 32% reduction in water use and 40% reduction in salt consumption, saving 669 Euros per year.

Fresner et al. [7] a study was carried out in a galvanizing plant in Austria to control the water and chemical inputs and outputs in production and to operate the factory with emission of "0". In this study, 50% reduction in water use and 40% reduction in acid consumption were achieved in the acid cleaning baths.

Environmental Program Support by Technology Development Foundation of Turkey (TDFT) in Turkey with environmental technologies (cleaner production/sustainable production) and their application projects undertaken by industry associations in the field of energy efficiency financing support is provided. In this context, practices that increase the environmental performance of the industrialist and reduce the production costs and thus increase the competitive power are supported. TDFT have done some studies in Turkey; Izmir Eco-efficiency (Cleaner Production) Program, UNIDO Eco-efficiency (Cleaner Production) Program, Industrial Symbiosis Project in Iskenderun Gulf, Bursa Eskişehir Bilecik Industrial Symbiosis Project, Trakya Industrial Symbiosis Project.

1.5 Best available technical (BAT) and documents

The Best Available Techniques (BAT) are defined as technologies that can be applied locally and economically, and the way they are applied, to provide the most effective protection of the environment as a whole. Reference documents (BREFs - Best Available Techniques Reference Document) have been created as part of the exchange of information under substance 13 of the Industrial Emissions Directive (IED, 2010/75/EU). The Existing Best Technicians (BAT) accepted under IPPC (2008/1/EC) and IED refer to the setting of permit conditions for facilities covered by the IED directives.

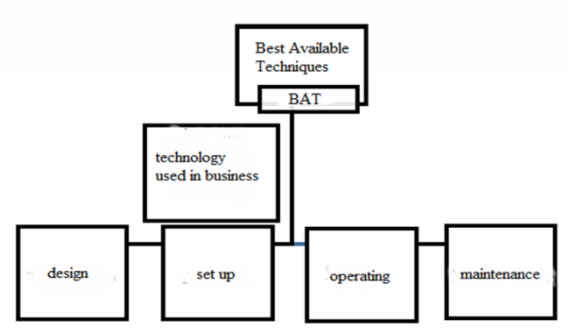


Fig 2. The Best Available Techniques (BAT) [8]

It should be emphasized that BATs do not only refer to the technology used within an enterprise, but also the way it is designed, installed, operated and maintained. (Fig 2). Some BATs are simple conclusions from common sense and do not require any investment. In practice, in order for a given technique to be considered as BAT, the following criteria must be considered:

1. If the technique is referred to as BAT in any BAT reference document (BREFs) then it is BAT.
2. If it is not referred to as a BAT in any BAT reference document (BREFs), it must be checked whether it is BAT, in accordance with the criteria contained in the Annex III list of the technical Integrated Environmental Requirements Directive (EC, 2006-a).

These criteria are:

- The use of technologies that cause low waste formation,
- Use of less hazardous materials,
- The necessity to prevent accidents and minimize the consequences for the environment,
- The general impact of the emissions on the environment and the need to prevent or minimize the risks,
- The time required to put the best available techniques into practice,
- The required period for the newly built or existing factory to run,
- Similar process, factory or business methods successfully tested on an industrial scale,
- The nature, effects and volume of the relevant emissions [8].

So, in this study, determination of pollution prevention and reduction activities in water and energy recovery, especially at metal industry, has been tried to be explained by determining the best methods for reducing and preventing the waste before it is generated by a continuous and preventive cleaner production approach.

2. MATERIALS AND METHODS

2.1 Study area- SAMPA industry

The company started to produce in Samsun in the 1950s, and in 1994, it was transformed into Sampa Automotive with its new structure. Sampa provides spare parts of heavy vehicles, tractors and trailers for the world automotive sector in Turkey, with its wide line of products ranging from motor for air suspension bellows to scissors, cabinet, stabilizer balance and bend arms, brakes, shafts, axles, V-arms.

With the use of precision metering, work is carried out by specialist molders in CNC Grinding Machines, multi CNC Cutting, CNC Turning, CNC Milling, vertical machining CNC Grinding Machines, all mold and machining metal parts requirement in 4000 square meters closed area mold and machining manufacturing unit (Fig 3).

Fig 3. SAMPA industrial machining unit with CNC workbenches

2.2 Method of production

In the Sampa industry, the cooling liquid used as input in the CNC machines for the metal surface treatment, and the waste metal shavings falling into the category of hazardous and toxic waste have been evaluated within the framework of the cleaner production approach and the best techniques and technologies that can be applied in this section have been determined and the economic and ecological efficiency has been studied.

In order to determine the characterization for recycling of the cooling liquid formed in this context, four CNC workbenches were applied to reflect the whole production. In addition, the technical and environmental performance of these chemicals has

been examined using the cooling fluid provided by two different industries as cooling liquid. Within the scope of this data, two different liquids in the industry were used to monitor water samples continuously for four months using four different benches. In Table 1, TRC-17 and TRC-18 lathe machines, in which Ecocool cooling oil has been used, were coded as N1 and N2, TRC-19 and TRC-20 turning machines with Eurolub cooling oil were coded as N3 and N4.

Table 1. Coding of the cooling fluid used in CNC looms in the determination of waste characterization

Cod	Bench	Cooling Fluid
N1	TRC-17	ECOCOOL SNK-GTG
N2	TRC-18	ECOCOOL SNK-GTG
N3	TRC-19	Eurolub TE 290
N4	TRC-20	Eurolub TE 290

2.3 Waste characterization of CNC workbenches

A total of 112 composite samples of two different liquids taken from four CNC workbenches in the Sampa manufacturing industry were placed in a 500-ml sample vessel at the end of each shift, resulting in approximately 1500 mL of composite samples of each day for each workbench. The life of the cooling fluid varies between 2 and 6 months and is used continuously in the system every day. This process lasted for 28 working days and all 112 samples taken from the four counters were measured at the specified parameters. The waste characterization was determined by measuring the concentration of refrigerant oil, the pH value, the NO^{-}_{2}-N concentration, the conductivity, the oil/grease concentration, the waste metal shale oil/grease concentration (Table 2).

2.4 Laboratory works for cleaner production options

Phase separation (sedimentation), filtration and centrifugation tests were carried out for the separation of metal powders, especially suspended solids (SS) (mixed in the cooling liquid), from the BAT options specified as the cleaner production option. The amount of oil / grease was determined for removing oil / grease formation and the methods of stripping were investigated. Parameters and measurement methods to be examined in this context are given in the table below (Table 3).

Table 2. Measurement parameters and measurement methods for waste cooling fluid (input and output)

Parameter	Measurement Method	Mark/Model
Coolant oil concentration	Refractometer	Hanna Instruments/HI 96801
pH value	pH meter	C5XX Series Multi-Parameter
NO^{-}_{2}-N concentration	Nitrite analysis	T70 UV/VIS Spectrometer - 14776
Conductivity	Conductivity meter	C5XX Series Multi-Parameter
Oil / Grease	Extraction	-
Oil / Grease (Metal Saw)	SM-5520 D Soxhlet Extraction	Procurement of services

Table 3. Experimental parameters and measurement methods for re-use of cooling fluid

Parameter	Measurement Method	Mark/Model
Suspended solids and phase separation	Sedimentation	IMHOFF Cone Separator
Suspended solid amount	Filtration	Whatman Filter Paper: CAT No: 1441-125
Phase separation	Centrifugal	SED Centrifuge

3. RESULTS AND DISCUSSION

3.1 pH analysis result evaluation

The pH value should be about 9 in the cooling liquid (according to the industry values) (Annex C) and the Water Industry Pollution Control Regulation must be between 6-9 according to the metal industry receiving environment discharge standards (Water Pollution Control Regulation, 2004). It may be possible for the pH value in the cooling fluid to decrease due to reasons such as the concentration change, the presence of too many bacteria, and the use of cooling liquid in the system for a very long time. The reduction in the amount of pH indicates that the cooling liquid is contaminated and is no longer available to the system. As a result of the analysis results, the minimum pH value for N1 machine was 8.53, the maximum was 9.82, the average was 8.94, the minimum value for N2 machine was 8.55, the maximum was 9.92, the average was 8.96, the minimum value for N3 machine was 8.58, maximum 9.65, For N4 machine it was determined that minimum 8.5, maximum 9.73, average 8.94, and the results were observed at the limit value range (Fig 4).

3.2 Evaluation of conductivity analysis results

Conductivity should be 0-6000 µS cm^{-1} in the cooling fluid. If the conductivity is > 6000 µS cm^{-1}, this is an indicator of the presence of harmful substances, such as dissolved heavy metals, and if necessary, a coolant oil change is required. Following the analysis results made, the minimum amount of conductivity for N1 machine was 1.95, maximum 4.11, average 2.76, minimum 2.08 for N2 machine, average 2.73, for N3 machine, maximum 4.04, average 3.54, minimum 3.14, for machine N4, maximum 3.92 , minimum 3.14 with

an average of 3.58. Fig 5 shows the change in conductivity values with respect to the dates.

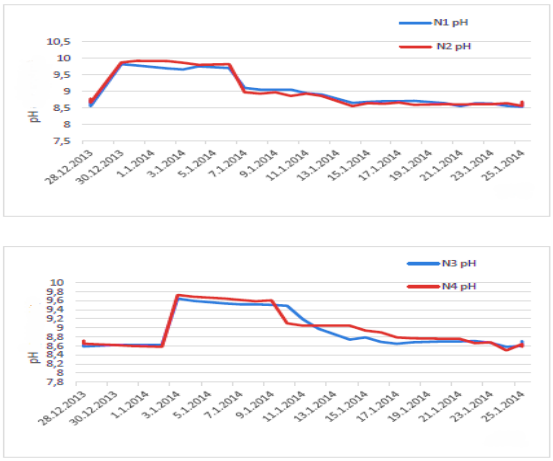


Fig 4. pH change for waste characterization

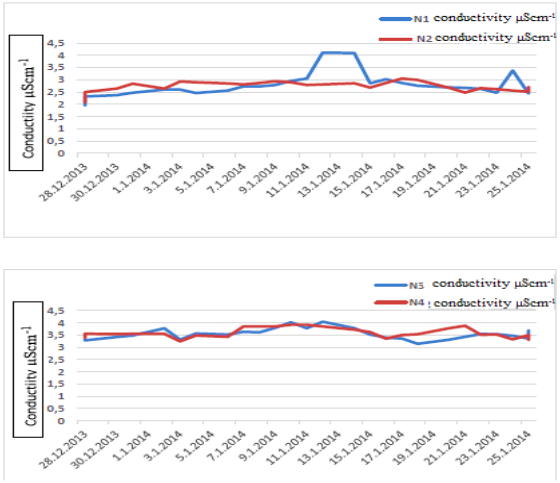


Fig 5. Conductivity change for waste characterization

3.3 Assessment of NO^{-}_{2}-N concentration results

The constant increase or increase in nitrite nitrogen concentration is indicative of bacterial growth with the formation of pollution in the cooling fluid. This result also shows that the quality of the cooling liquid deteriorates. At the end of the analysis results, the minimum NO^{-}_{2}-N concentration for the N1 machine was the minimum 3.83, the maximum was 9.33, the average was 5.46, the minimum for the N2 machine was 3.68, the maximum was 9.04, the average was 5.67, the minimum for the N3 machine was 3.17, the maximum was 10.4, the average was 5.94, the minimum for the N4 2.26, maximum 9.84, average 4.74. In order to be able to reuse the cooling fluid, nitrite nitrogen concentration should be within the range of 0-5 mg L^{-1} (Water Pollution Control Regulation, 2004), but this value is seen towards the end of one month and 10 mg L^{-1} for NO^{-}_{2}-N concentration (Fig 6). This reduces the service life of the cooling liquid.

Fig 6. Change of NO^{-}_{2}-N concentration change for waste characterization

3.4 Evaluation of oil/grease concentration results

Another important parameter is oil/grease. Results of the experiments show that cooling liquid is contaminated with oil/grease during metal working, which seem to be constantly increasing along with suspended solids with regard to the usage time of cooling liquid. Analysis results of oil/grease concentration were as follow; minimum 4.47, maximum 12.86, average 8.83 for N1 machine, minimum 3.01, maximum 15.34, average 9.43 for N2 machine, minimum 3.4, maximum 14.4, average 8.52 for N3 machine, minimum 2.78 , maximum 13.74, average 8.93 for N4 machine.

3.5 Evaluation of cooling concentration results

In order for the cooling fluid to be efficiently used in the system, the desired refrigerant concentration is in the range of 5-7%, which is a specific ratio for each operation. For the life, performance and more economical use of the cooling fluid, it is very important to measure the cooling oil concentration by certain periods. At the end of the analysis results, the minimum amount of refractometer for N1 machine was 3.74, maximum 6.46, average 5.38, minimum 4.93 for N2 machine, maximum 7.48, average 6.05 for N3 machine, maximum 6.37, average 5.51, for machine N4 minimum 4.16 , maximum 6.89 , with an average of 5.91, and the results were observed at the required range of values. As cooling oil and water were added to the system at certain intervals, there was no significant change in the refrigerant oil concentration.

Sedimentation, filtration and centrifugation experiments were carried out except for waste characterization in order to reduce the pollution load and reuse of two different cooling liquids (Eurolub and Castrol) used in metal surface treatment. For this study, the pH, conductivity, refractometer, NO2, oil / grease, suspended solids measurements were performed primarily to determine the waste

characterization before application for two different cooling liquids, which were used in different periods in the process (Table 4). Since two different cooling fluids were taken from the samples that reached the dirtiest point, the results were observed over the limit values. It was observed that the concentration of NO^{-}_{2}-N and the oil/grease concentration (Limit value: 10 mg L^{-1}) were higher than the limit values. The results for SS are quite high for the water pollution control regulation 50 mg L^{-1} which is the limit value in discharge standards.

Sampa industry uses Eurolub and Castrol cooling oils. The processing times of the cooling liquids processed for different periods of time for the cleaner production operation planned for the four milling looms (FRC-06, FRC-17, FRC-07, FRC-15) in the machining unit are given in Table 5.

Both samples were subjected to sedimentation and the amount of suspended solids determined by sedimentation was determined. After sedimentation, filtration and centrifugation were carried out to determine the amount of dissolved SS (Table 6). Solid matter yields of 63% (FRC06) and 50% (FRC17) were obtained by sedimentation and filtration and 10% (FRC06) and 29% (FRC17) after centrifugation and filtration. As a result of these processes, removal of suspended solid marked 67% for the first cooling fluid (FRC-06) and 64% for the second cooling fluid (FRC-17).

As a result of these applications, two different cooling fluids (Eurolub, FRC-06-Castrol, FRC-17) were evaluated and when the efficiency of suspended solids removal was evaluated, they both showed very close results. As a result, in practice, precipitation and filtration have been determined to be the BAT option that yields the highest score of SS removal.

Table 4. Initial analysis results for a cleaner production run in the laboratory

Sample	FRC-06	FRC-17	EUROLUB	CASTROL
View	Cloudy green	Light yellow	Green	Light yellow
pH	8.43	8.6	8.87	8.50
NO^{-}_{2}- N (mg L^{-1})	12.77	14.50	1.29	0.80
Conductivity µS cm^{-1}	14.50	14.1 0	4.90	4.10
Oil/Grease (mg L^{-1})	9.86	10.72	2.32	3.95
Suspended solid (mg L^{-1})	2322	1757	432	174

Table 5. Processing times of cooling liquids evaluated in Cleaner Production operation

Sample No	Explanation
FRC-06	5 month processed Eurolub refrigerated liquid
FRC-17	4 months processed Castrol cooling liquid
FRC-07	1 week processed Eurolub refrigerated liquid
FRC-15	10 day processed Castrol cooling liquid
EUROLUB	Unprocessed cooling fluid
CASTROL	Unprocessed cooling fluid

Table 6. Applied BAT options resultant SS (mg L^{-1}) analysis values

Sample	FRC-06			FRC-17		
Applied analysis	Pre-operation	sedimentation + filtration	Centrifuge + filtration	Pre-operation	sedimentation + filtration	Centrifuge + Filtration
SS (mg L^{-1})	2322	849	762	1757	870	615

4. CONCLUSION

Preventing environmental pollution is much cheaper and more effective than environmental restoration or reinstatement efforts. Today's developing technologies are solved by the end-of-pipe approaches, while solutions such as prevention and reduction of the waste are important. Cleaner production practice, however, provides sustainable benefits to businesses with optimal use of energy, natural resources and raw materials.

The purpose of this study is to determine pollution prevention and reduction practices in water and energy recovery by determining the best methods to reduce and prevent waste before it is generated by a continuous and preventive cleaner production approach. In this context, cleaner production application options of Sampa Company are evaluated, a comprehensive laboratory work is done, and with

this application, how these techniques can be applied to the industry has been determined.

As a result of the studies carried out and the information obtained from the industry, it has been determined that both cooling liquids reach a level that cannot be used again for a period of about 5 months. Within the framework of the cleaner production approach, the cooling liquids are fed back to the system and the recommended options for lengthening the lifespan with the treatment techniques have been identified. As a result of the cleaner production studies made, the stages determined under the cleaner production options to form the necessary feedback line for reusing the cooling liquid in the system are sedimentation, filtration, oil stripping, and membrane filtration. Suggested BAT options are based on the work and evaluations done in the Sampa, and it is specific to this company.

Cooling liquids are contaminated in a short time with particles worn from metal surfaces during the process, which leads to a loss in cooling fluid efficiency and metal surface quality. Expensive cutting tools are worn off soon and the cooling liquid needs to be replaced bringing undesirably high costs. Thus, filtration is essential. Due to its consistency, foreign oil pile up at the top of the cooling liquid, blocks the ventilation of lower parts and causes bacterial growth. This bacteria growth deranges the fragile cooling liquid balance and results in problems such as rust, contamination inside the machine, insufficient oiling (short cutting edge life and poor surface quality related to this) and foul odour. This leads to important economical loss for industries and environmental problems. Oil stripping is a simply effective solution to these problems. Oil is stripped and can also be used within the industry for other oiling processes. As a result of this implementation, an extension in the life of the cooling liquid and feedback to the system are achieved with the removal of suspended solids in cooling liquids, stripping off the oil and a decrease in bacteria level. Membrane filtration is also recommended as a BAT option to prevent bacteria growth. Membrane filtration may not be preferred because of flow rate problem. As there is a continuous feedback in the system, the amount of bacteria that will be in contact with air in the cooling liquid will reduce. Also, the reduction in the amount of the oil through stripping will help remove bacteria.

This stands to be a case study for similar industries in Turkey with its economic benefits and environmental performance indicator provided by good management practices and process changes that result in cleaner production in the relevant company. Rational changes that can be made on any industrial process increase the efficiency of the system, prevent rapid deterioration of the environmental quality and give the investor financial advantage and prestige.

ACKNOWLEDGEMENT

This study was prepared within the scope of the Project of Ondokuz Mayıs University Scientific Research Projects PYO.MUH.1903.14.001 "Determination of Recovery Opportunities and Reduction of Waste Volume in Sampa Company".

REFERENCES

[1]. G. Demirer, "Basic Principles of Pollution Prevention Approaches", *Environment and Engineer*, TMMOB, Vol. 25, pp. 13-20, 2003.

[2]. United Nations Environment Programme (UNEP), 1996. "Cleaner Production: A Training Resource Package", Paris: United Nations Publications.

[3]. https://www.slideshare.net/farhanahmad5249349/cleaner-production-techniques-32977890 (Visit date: 27 February 2018).

[4]. http://www.cprac.org/en/projects/sustainable-consumption-and-production (Visit date: 15 September 2013).

[5]. A. Baral and R.D. Engelken, "Choromium-based regulations and greening in metal finishing industries in the USA", *Environmental Science and Policy*, Vol. 5, pp. 121-133, 2002.

[6]. T. Kupusovic, S. Midzic, I. Silajdic, and J. Bjelevac, "Cleaner production measures in small-scale slaughter house ındustry a case study in Bosnia Herzegovina", *Journal of Cleaner Production*, Vol. 20, pp. 1-6, 2005.

[7]. J. Fresner, H. Schnitzer, G. Gwehenberger, M. Planasch, C. Brunner,K. Taferner, and J. Mair, "Practical experiences with the implementation of the consept of zero emissions in the suface treatment industry in Austria", *Journal of Cleaner Production*, Vol. 15, pp. 1228-1239, 2007.

[8]. European Commission, Joint Research Centre European IPPC Bureau (EIPPCB), 2006-a.

Environmental Research & Technology, Vol. 1(3), pp. 59-62, 2018

Environmental Research & Technology

http://dergipark.gov.tr/ert

SHORT COMMUNICATION

Assessment of noise pollution due to generators in Akure, Ondo State, Nigeria

Francis Olawale Abulude[1,4*], Samuel Dare Fagbayide[2], Smart A Olubayode[3], Ebenezer Alaba Adeoya[3]

[1] Science and Education Development Institute, Akure, NIGERIA.
[2] Agricultural and Bio-Environmental Engineering Department, Federal Polytechnic, Ilaro, NIGERIA.
[3] Engineering Materials Development Institute, Akure, NIGERIA.
[4] Department of Chemistry, Federal University of Technology, Minna, Niger State, NIGERIA.

ABSTRACT

World Health Organization declared noise in large cities as pollution (third after water and air). Most areas in the world have this menace. This menace has been on the increase due to population growth, increase in vehicular movements, high industrial activities and many others. This attendant problem has resulted in many sicknesses and even death. One of the causes of noise pollution is generators. Many developing countries rely on them for different activities. Nigeria is inclusive. This study was embarked upon to assess the level of noise from generators using a sound level meter. Four locations were identified: two residential, commercial, and industrial areas. A total of one hundred generators was monitored. The mean results in dBA (minimum and maximum respectively) are: Oke Eri Estate – (88.7 ± 10.3, 90.5 ± 15.2), Housing Estate (81.7 ± 9.2, 85.0 ± 9.5), Stadium Road (84.8 ± 10.0, 113.4 ± 17.5) and FUTA Road (81.9 ± 9.3, 90.0 ± 15.2). The study concluded that the areas are noise polluted because the levels obtained are above the permissible limits.

Keywords: Generator sets, pollution, permissible limits, loss of hearing, irregular frequency

1. INTRODUCTION

Generators (Fig 1) are meant to provide alternative sources of generating electricity. In developing countries, the use is rampant due to non-availability of electric current to perform daily activities. The equipment which supposed to be succor have turned to be a menace due to irregular frequency (noise) produced known as noise pollution.

Noise has no definite definition, the definition or explanation depends on an individual. According to American Speech-Language-Hearing Association (ASHA) (1), "One person's music is another person's noise. Sounds that are soothing for some are irritating to others" In explaining the sound, noise has waves with irregular vibrations and no definite pitch. An engineer will define noise as a sound signal that interferes with the quality of another sound signal, while others simply take it as an unwanted sound. Noise levels are measured in decibels (dBA). Table 1 summarizes sound effects as painful, extremely loud, very loud, moderate and faint. According to ASHA (1), sound levels up to 70 dBA or above are known to be hazardous to hearing over time (8 hours and above).

Fig 1. A Generator

Stansfeld and Mark (2) pointed out that continuous exposure to noise of 85–90 dBA in someone's lifetime in an industrial setting, could end up in loss of hearing.

Loss of hearing is a problem that occurs when the victim is continuously exposed to noise above 85 –

Corresponding Author: waleabul@outlook.com (Francis Olawale Abulude)
Received 21May 2018; Received in revised form 16 July 2018; Accepted 16 July 2018
Available Online 6 August 2018
Doi: ISSN: 2636-8498

140dBA over time. How harmful the noise is a function of the volume and the length of exposure to the sound. To sum it, the louder the noise, the less time required before hearing loss occurs (3).

Table 1. The noise chart average decibel levels for everyday sounds

Sound Effect		Decibel Levels
Painful	-	120 - 150 dB
Extremely Loud	-	90 - 110 dB
Very Loud	-	70 - 90 dB
Moderate	-	40 - 60 dB
Faint	-	30dB

Noise is encountered in our daily activities in the homes, offices, churches, mosques, schools, clubs and entertainment centers, movie theaters, quarries, industries, markets just to name a few. To be candid, living things is surrounded by noise. Continuous exposure to elevated levels causes high blood pressure, ear damage, reduced sleep, high anxiety, stress-related problem, annoyance and even difficult thinking (4) According to Mercola (5), $3.9 billion was projected to be the benefit or reducing noise from the environment. It was recommended that noise reduction (5 decibels) would reduce high blood pressure (by 1.4 %) and coronary heart disease (by 1.8 %) prevalence. An estimate from the US suggests that over 100 million Americans are prone to noise pollution (6). Evidence has shown that there are correlations between cardiovascular disease with noise (7, 8, 9).

The maximum safe noise level (MSNL) for human beings is 70 dB(A) for 24 h exposure without harmful effects (10).The U.S. Occupational Safety and Health Administration (11), pegged the noise level of an 8 h Time Weighted Average (TWA) to 85 dB(A). The U.S. Environmental Protection Agency (12) documented an 8 h level of 75 dB(A) as the safe level for occupational noise while 90 dB(A) is the limit for maximum 8-hr exposure. In India, the Bureau of Indian Standard has recommended acceptable noise levels to be 50dB, 55dB, 65dB and 75dB for silence zone, residential, commercial and industrial areas respectively (13).

In a presentation by Shabi (14), he classified the causes of noise pollution into industrial, traffic, religious, environmental, commercial, community and associated noise like street carnivals, socio-cultural activities, public events and others. Shabi (14) also provided a record of noise pollution in Lagos State for the year 2015 as:

1. No of noise pollution cases - 1527
2. Noise from medical concern - 57
3. Noise from religious activities - 51.08%
4. Noise from domestic generator - 84.50%
5. Noise from industrial activities - 33.33%
6. Noise from sanctions and closures - 80%

To control or reduce noise pollution, a legal framework was put in place in Nigeria, to this end National Environmental Standards and Regulations Enforcement Agency (NESREA) was established and enacted a noise standard and control in 2009 (section 35). The standard is provided in Table 2.

There is the awareness that Akure and its suburbs are faced with the challenges of noise from generators, but no efforts have been put in place to quantify the menace. The study, therefore, has been undertaken to solve this. Therefore the aim of the study was to assess the noise levels associated with generators from Akure, Ondo State, Nigeria.

Table 2. NESREA Standard of Noise Pollution Control

Facility		Maximum Permissible Noise Limits Db A (Leq)	
		Day (6:00am -10:00pm)	Night (10:00pm – 6:00am)
A.	Any building used as a hospital, convalescence home, home for the aged, sanatorium and institutes of higher learning, conference rooms, public library, environmental or recreational sites.	45	35
B.	Residential Buildings	50	35
C.	Mixed Residential (with some commercial and entertainment	55	45
D.	Residential + industry or small scale Production + commerce	60	50

2. MATERIALS AND METHOD

The study was carried out on generators using the Sound level meter (GB: 2266204) with specification: Measurement range 30dBA – 130dBA, accuracy (± 1.5dB), frequency range (31.5Hz – 8KHz) and power supply (3*1.5V AAA battery), made in China. The noise levels were taken at four selected locations, namely Oke Eri Estate, Housing Estate, Stadium Road and Federal University of Technology, Akure (FUTA) Road. One hundred generators were earmarked for the research with a minimum of twenty-five sets from each location. The time of measurements was during busy periods (night for Oke-Eri and Housing Estates and daytime for FUTA and Stadium Road) of the day. Noise sample readings were taken in dB (A) scale by pointing the meter close to the generator sets. The

generated values were determined using Minitab 16 Statistical Software.

3. RESULTS & DISCUSSION

Table 3 depicts the mean values of noise levels obtained at four different locations in Akure. From the results, it was observed that Stadium Road had the highest decibel levels followed by Oke Eri Estate. The reasons for the differences were: Stadium Road is an area where most publishing press companies are located. For the business to thrive well, generating sets were used as an alternative to the electric power supply. During the study, it was noticed that many generators used are 6.5 horsepower and above. Many of the sets are powered by diesel engines, which produce higher sound levels than sets that are powered by petrol engines. In addition, many generators in this location are old, many of them have no bolts and nuts, thereby making the disjointed parts to make noise which added to the noise of the engines. In fact, many of the generators have no silencer to reduce the noise. Housing Estate is a residential area. In this place, the number of houses is not many. During the daytime, most inhabitants are in the schools and offices. The highest results obtained were done in the night when most residents are back home. Most FUTA Road residents and industries use soundproof generators which produced less sound compared to other locations in this study.

The interesting thing noted in this study is that all the areas visited have decibel levels above the recommended limits set by WHO (10), NESREA, (15) and The U.S. Occupational Safety and Health Administration (11). The end result is a problem for the inhabitants of the selected places. According to a review on generators by jdowling (16), it was observed that the noise from the machines is mainly from engine mechanical, exhaust, cooling fan, alternator, induction (windings) and the structure of the generator. This observation collaborates what was observed in the study.

Table 3. Noise Levels at the different locations (Average)

Locations	Decibel Levels	
	Minimum	Maximum
Oke Eri Estate	88.7 ± 10.3	90.5± 15.2
Housing Estate	81.7 ± 9.2	85.0± 9.5
Stadium Road	84.8 ± 10.0	113.4± 17.5
FUTA Road	81.9 ± 9.3	90.0± 15.2

4. CONCLUSIONS

It is concluded that residents are chronically exposed to generator noise at the level between 81.7 dB(A) and 113 dB(A) which can cause negligible risk of hearing impairment. All locations evaluated in the study showed a noise level above the maximum permitted levels. The areas studied should receive constant guidance about the importance of acoustic adequacy and hearing aids. There is the need to measure and monitor noise levels in the environ regardless of any mitigation measures that have been put in place. Anti-vibrations should be mounted, the silencers should be perfect so that it can reduce the noise down to 40dB(A). Malik (17) is of the opinion that the oil and filter for generators should be changed after every 50 hours of use. He also recommended that canopies or rooms in the generator houses should be much bigger than the machine.

REFERENCES

[1]. American Speech-Language-Hearing Association (ASHA) *Noise. Audiology Information Series* (2017a).

[2]. Stansfeld S. A and Mark M. P "Noise pollution: non-auditory effects on health", British Medical Bulletin Vol. 68, 243–257, 2003.

[3]. The Noise Center (2017), "Common environmental noise levels", Center for Hearing and Communication. Retrieved on 17th May 2017.

[4]. American Speech-Language-Hearing Association (ASHA) (2017b). Home, Community, and Recreational Noise. Audiology Information Series, 2017.

[5]. Mercola J "Quieting Down Could Save Billions in Heart Disease Costs", The World's #1 Natural Health Website. Mercola.com, 2015

[6]. Swinburn T. K, Hammer M. S and Neitzel R. L "Valuing Quiet An Economic Assessment of U.S. Environmental Noise as a Cardiovascular Health Hazard", Am. J. Prev. Med.; 49 (3):345 – 353, 2015.

[7]. Basner M, Babisch W, Davis A, et al. "Auditory and non-auditory effects of noise on health", Lancet. 383:1325–1332.http://dx.doi.org/10.1016/S0140-6736 (13)61613-X, 2013.

[8]. Hansell AL, Blangiardo M, Fortunato L, et al. "Aircraft noise and cardiovascular disease near Heathrow airport in London: small area study", BMJ. 2013; 347:f5432. http://dx.doi.org/10.1136/bmj.f5432, 2013.

[9]. Babisch W. "Updated exposure-response relationship between road traffic noise and coronary heart diseases: a meta-analysis", Noise Health. 16:1–9. http://dx.doi.org/10.4103/1463-1741.127847, 2014.

[10]. WHO Guidelines for Community Noise, Geneva: World Health Organization 2000.

[11]. Li Q, Qiao F, Yu L "Risk Assessment of In-Vehicle Noise Pollution from Highways", Environ Pollut Climate Change 1: 107 2016.

[12]. Environmental Protection Agency "Information on levels of environmental noise requisite to Protect public health and welfare with an adequate margin of safety", EPA, Washington DC, 1974.

[13]. Anurag V. Tiwari, Prashant A. Kadu, Ashish R.Mishra "Study of Noise Pollution Due To Railway and Vehicular Traffic at Level Crossing and Its Remedial Measures", American J. Engineering Research. Vol. 2 (4), pp. 6-19, 2013.

[14]. Shabi A. "The regulation of noise pollution in a mega city. A paper presented at Noise Pollution Stakeholders; forum. Theme: Noise: A menace for urban development", Held on May 9, 2016, at LTV Blue Roof, Agidingbi, Ikeja, Lagos. Organized by Lagos State Government, Ministry of the Environment in collaboration with Ministry of Home Affairs 2016.

[15]. National Environmental (Noise Standards and Control) Regulations, S. I. No. 35. 2009.

[16]. jdowling "Noise reduction for Generators", Caribbean Northern Lights, 2015.

[17]. Malik S. "Power problems: Generators add to air and noise pollution", Published in The Express Tribune, May 22nd, Pakistan, Punjab. 2011.