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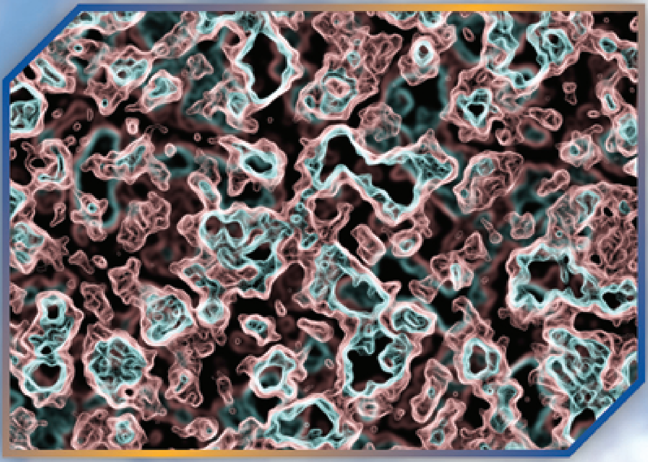

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CONTACT

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

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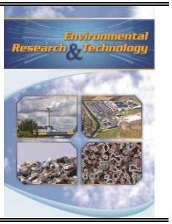

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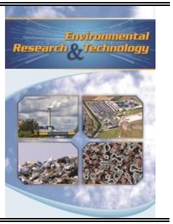

EDITORIAL ANNOUNCEMENT

Welcome to the first issue of the new journal – Environmental Research & Technology

Ahmet Demir[1], Mehmet Sinan Bilgili[1,*]

[1]Environmental Engineering Department, Yildiz Technical University, Istanbul, TURKIYE

ABSTRACT

We are very pleased to write an editorial announcement for the inaugural issue of the new journal, Environmental Research & Technology, as the Scientific Director and Editor in Chief. Environmental Research & Technology is a peer reviewed open access multidisciplinary journal dedicated to publish high quality articles in the field of environmental studies including but not limited to water, wastewater, solid waste, and air pollution topics. On behalf of the editorial board members, it is with great pleasure and honour that we welcome you to this first issue of Environmental Research & Technology, published by Environmental Engineering Department of Yildiz Technical University. We look forward to your submissions and to publish your manuscripts in all areas of environmental sciences.

Keywords: Environment, research, technology

1. INTRODUCTION

Environmental Research & Technology is a peer-reviewed open access interdisciplinary journal dedicated to publish high quality papers in almost all areas of environmental science and research. The journal will focus on the major environmental problems such as pollution, natural resource depletion, waste disposal, water pollution, public health issues, global warming, climate change, and loss of biodiversity [1, 2].

As we all know, environmental issues poses a major problem world-wide. Environmental problems have become globalized in recent decades in terms of their existence and impacts [3]. According to ecologists nature performs many services for human beings. Dunlap and Catton [4] categorized these services in three general functions. Firstly, the environment provides us resources necessary for life (air, water and food), and materials needed for the wide range of needs. Thus the environment is serving us as a “supply depot” with both renewable and non-renewable resources. When the resources consumed faster than the environment can supply them, shortages and scarcities may be created even if these resources are renewable [4].

Secondly, during the consumption of the resources, “waste” products produced. Thus, the environment provides us a “sink” for the produced wastes until these wastes are absorbed or recycled to useful or harmless substances. Highly populated societies generate more waste than that of the environment can process, resulting with various forms of pollution such as water, air, and soil. Finally, the environment provides us a living space, which is the third function of the environment [4].

The results of the overuse of the environment’s ability to fulfill these three functions are ``environmental problems’’ such as pollution and resource shortages [4]. Extensive research is being conducted in the field of environmental problems and their effects on human health and natural environment from researchers, practitioners and the general public.

Therefore, Environmental Research & Technology offers complete coverage of environmental issues with original contributions such as research articles, short communications, review papers, book reviews, editorial discussions, and conference papers.

Corresponding Author: mbilgili@yildiz.edu.tr (Mehmet Sinan Bilgili)

2. AIMS AND SCOPE

Environmental Engineering Department of Yildiz Technical University was founded in 1989 within the Faculty of Engineering. When the university became "Technical University" the department took its place under the Civil Engineering Faculty. Environmental engineers are being graduated from the department since 1993.

Since 2011, our department has been organizing an international symposium named EurAsia Waste Management Symposium. Therefore, the department has a great recognition in the international scientific platform in the environmental research area. The organizers of these well-known and prominent symposium, decided to launch a new journal that will focus on the research activities of environmental problems.

Environmental Research & Technology involve the environmental researches related with water, wastewater, solid waste and air pollution technologies. Topics include, but are not limited to;

Water: Water management, water quality, water pollution and prevention, and water treatment.

Wastewater: Wastewater management, municipal wastewater treatment, industrial wastewater treatment, wastewater reclamation and reuse.

Solid Waste: Waste (solid, hazardous, industrial, agricultural etc.) management, waste prevention, recycling and reuse, sludge treatment and disposal.

Air Pollution: Air quality management, indoor air quality, air pollution control, emission studies, and air pollution modeling.

Environmental Research & Technology has an interdisciplinary and multinational Editorial Board which reflects the composition of the research community the journal will serve. The open access format of the journal will provide the availability of all articles freely, and immediately upon publication.

As scientific director and editor in chief, we are delighted to be a part of this new journal which is the type of platform needed to highlight environmental research into widespread acceptance with the highest values of scientific integrity.

The success of Environmental Research & Technology will depend mainly on its team of editors and reviewers, who will be responsible for selecting high quality papers for publication and proceed through the peer review process in a timely manner. If you are interested in serving on the Editorial Board or as a reviewer, please contact us at ert@yildiz.edu.tr.

We welcome your submissions via the journal's submission and peer review website at http://dergipark.gov.tr/journal/1368/submission/start. Please visit the homepage at http://dergipark.gov.tr/ert to learn more about the journal.

3. JOURNAL HIGHLIGHTS

Some of the important highlights and advantages of publishing in Environmental Research & Technology are listed below:

1. The journal is open access, means that the articles are accessible to everyone, forever, and free of charge.
2. Papers can be submitted at any time, and all submissions are processed immediately with strict deadlines for reviewers, authors, and editors.
3. We start with four cycles per year, but hope to increase it in the near future.
4. The reviewing process is designed to take three months between the start of the reviewing and final decision.
5. The open access format will enables the public to become acquainted with the advance of environmental science and technology.
6. The knowledge access through the academia will be accelerated without any limitations.

4. CALL FOR PAPERS

As the Scientific Director and Editor in Chief, we are pleased to invite you to submit your valuable studies in Environmental Research & Technology. The journal is a multidisciplinary peer reviewed journal for publishing high quality research activities in the field of environmental sciences. Environmental Research & Technology offers complete coverage of environmental issues with original contributions including research articles, short communications, review papers, book reviews, editorial discussions, and conference papers.

The goal of this journal is to provide a platform for researchers and academicians in order to promote, discuss, and share new issues and developments in various areas of environmental research. The Editorial Board will consider papers for publication based on novelty, impact on environmental problems, and contribution to environmental research advancement.

Topics of interest are including but not limited to;

- Air Pollution
- Water Pollution
- Soil and Land Pollution
- Waste Treatment and Disposal
- Wastewater Treatment and Disposal
- Climate Change
- Global Warming
- Natural Resource Depletion
- Light and Noise Pollution
- Agricultural Pollution
- Public Health Issues
- Loss of Biodiversity
- Ozone Layer Depletion
- Nuclear Issues

If you are interested in contributing in the forthcoming issues of Environmental Research & Technology, please submit your manuscript to Online Manuscript Submission System.

The success of the journal will depend on the quality of submissions. At this point, we will work very hard to reach the high visibility of the published papers, and a high impact factor within a short time. We are also planning to aggressively promote the journal through social media and other creative methods.

5. FINAL REMARKS

We would like to thank to the Academic Advisory Board Members for their support and encouragement during the initial period of discussion about launching a new journal. From them, we would like to single out in particular Prof. Dr. Adem Baştürk, who was the founder of the Environmental Engineering Department. We would like to thank to our Co-Editors and Editorial Board Members for their work in helping to found the Environmental Research & Technology Journal.

Once more, on behalf of the editorial board members, we welcome you to this journal. We look forward to your submissions and to publish your manuscripts.

CONTACT DETAILS

Prof. Dr. Ahmet Demir
Scientific Director
E-mail: ahmetd@yildiz.edu.tr
Phone: +90 212 383 5370

Prof. Dr. Mehmet Sinan Bilgili
Editor in Chief
E-mail: mbilgili@yildiz.edu.tr
Phone: +90 212 383 5370

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

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RESEARCH ARTICLE

Fuzzy approach to predict methane production in full-scale bioreactor landfills

Martina Di Addario *,[1], Bernardo Ruggeri[1]

[1]DISAT, DEPT. of Applied Science and Technology, Politecnico di Torino, C.so Ducadegli Abruzzi 24, 10129 Torino, ITALY

ABSTRACT

Bioreactor landfills (BRLs) aim to increase moisture content of municipal solid waste to enhance the biodegradation kinetics of the organic fraction and biogas production. Prediction of biogas production is a key tool to design an appropriate energy recovery system from BRLs. In this paper, a fuzzy-based model to predict methane generation in full scale BRLs is proposed. Eleven deterministic inputs (pH, RedOx potential, chemical oxygen demand, volatile fatty acids, ammonium content, age of the waste, temperature, moisture content, organic fraction concentration, particle size and recirculation flow rate) were identified as antecedent variables. Two outputs, or consequents, were chosen: methane production rate and methane fraction in the biogas. Antecedents and consequents were transported in the fuzzy domain by a fuzzyfication procedure and then linked by 84 IF-THEN rules, which stated the effects of the input parameters in a linguistic form. The fuzzy model was built and tested on seven lab-scale studies, representing different operational conditions and waste qualities. The fuzzy model showed good performances in the prediction of methane generation, although lab-scale studies depicted ideal conditions that can be hardly reached in real BRLs. In order to deal with higher heterogeneities and lower data availability typical of full-scale landfills, new antecedents and rules were added to the proposed model. With few adjustments based on the available information, the fuzzy model could be applied to a retrofit BRLs located in Northern Italy. The results confirmed that fuzzy macro-approach can be a powerful and flexible tool able to model the complex processes taking place in BRLs.

Keywords: Bioreactor landfill, fuzzy logic, landfill gas, methane, modeling

1. INTRODUCTION

The concept of bioreactor landfill (BRL) has been introduced in the last few decades with the aim of a more rapid degradation of the organic fraction of municipal solid waste (MSW) [1]. BRLs have been suggested as a more sustainable alternative to conventional “dry tomb” landfills [2]. The main advantages of this technology can be achieved thanks to moisture increase of waste through leachate recirculation as the processes are strongly dependent on moisture content. The liquid injected into the landfill body stimulates microbial activity by promoting higher distribution of substrates, nutrients and From the pioneering work of Pohland [4], a number of studies have shown the positive effects of leachate recirculation on MSW degradation, either at laboratory scale [5]-[10] or on- site applications [11]-[16]. The main advantage of bioreactor landfills is the rapid stabilization of organic fraction, which can be reached in 5-10 years instead of 30-50 years of the conventional landfill [17]. Biogas production can be therefore increased with more volumes in less time, improving the efficiency of the energy recover. Moreover, long-term environmental impact and post-closure care costs can be reduced [11]. The major initial investments and costs related to the liquid injection system and operations can be offset by a number of economic benefits arising from the management of the BRL, including lower costs for treatment and disposal of leachate and the use of biogas for electric energy generation [18]. Although they represent a more sustainable alternative to conventional landfills, BRLs alone are not sufficient. In the perspective of sustainable landfilling, also the amount of biodegradable MSW destined to disposal should be reduced with appropriate pretreatments. The emission potential of waste can be reduced to large extent during pretreatments so that, compared to un-pretreated waste, significantly reduced emissions occur [19]. Mechanical-biological treatment

Corresponding Author: martina.diaddario@polito.it (Martina Di Addario)

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(MBT) represents a widespread option for the stabilization of the biodegradable fraction in the residual MSW. MBTs combine mechanical processes, such as shredding and sorting, with biodrying and biostabilization in order to obtain a more homogeneous and less biodegradable waste [20]-[22]. MBT waste still contains at least 5-20% of the organic biodegradable fraction, which can be finally treated in the landfill body. The combination of MBT and BRL technologies represent an emerging choice in those Italian districts without incineration facilities, aiming to reduce the amount of landfilled organic waste and to optimize energy recovery [23], [25]. In such emerging scenarios with lower organic content and different landfill configurations, where few and sometimes controversial data are available from previous studies [20], [23], [25] it becomes challenging to predict methane production without introducing high uncertainties. The prediction of biogas production in the landfill is commonly affected by uncertainties, due to the heterogeneity of the system, whose properties are changing both spatially and temporally during the landfill life. A landfill is a complex system in which different and interconnected processes take place. Biological processes play the main role in waste degradation, but they are strictly related to others of different nature such as physico-chemical, hydrological and geotechnical processes [26]. The description of all the processes involved become more challenging in case of BRLs, due to additional liquid injections and moisture distribution into the landfill body. Generally, biogas generation rates are estimated using mathematical models dependent upon poorly defined factors, thus introducing significant uncertainty in the modelling process and therefore in the its estimations [27]. In the literature, the most used model is the first-order [28]-[31], described by Equation (1):

$$Q = ML_0ke^{-(t-t_i)} \tag{1}$$

where Q is the methane production (m^3 yr^{-1}), M is the disposed waste (ton), L_0 is the biochemical methane potential (BMP) (m^3 ton^{-1}), t is the time after waste placement in the landfill (yr), t_i is the lag phase between the placement and the start of production, k is the first-order rate constant (yr^{-1}). Models like Equation (1) are intended for single batches or single years; every batch has to be integrated along the year the landfill was in service in order to build the whole gas generation curve, valid for the entire landfill. The first-order model is the most reliable model since the outcomes of the zero-order model present relatively high errors while higher order models have more complicated procedures in order to estimate the parameters, which are not justified by the increase in accuracy [27]. First-order model has two main adjustable parameters: the BMP (L_0), and the methane generation rate constant k. Both of them can be defined through lab-experimentations, pilot-scale cells or from ranges of the literature, in order to obtain a best-fit on field data and minimize the residual errors between the predicted and the experienced methane production [26]. In the pilot-scale study by Bilgili [30], BMP test was used to determine initial and remaining L_0 during the landfilling operations. However, it is often challenging to obtain accurate field-scale data in order to calculate and validate the model parameters [27], [29], [32], [33]. In attempt to solve the limitations of deterministic approaches, artificial intelligence based models, such as fuzzy logic, have recently been conducted in the modeling of complex systems, thanks to their predictive capabilities by handling a large number of parameters of non-linear nature [34]-[36]. As reported in the pioneering work of Ruggeri and Sassi on fuzzy modeling of bioreactors [37], if the complexity of a system increases, its quantitative information become more and more incomplete. The use of macro-approach based on qualitative knowledge about BRLs behavior can offer an easier alternative in CH_4 production modeling. Fuzzy approach is a macro-approach that is able to consider numerous aspects affecting a specific process, without the necessity to handle differential equation models with high computational efforts. In its knowledge-based structure different sources of information can be combined, not only experimental data but also literature, theoretical findings and expertise. As reported by Turkdogan-Aydinol and Yetilmezsoy [34], in the prediction of biogas and methane production rates of a pilot-scale anaerobic digester treating molasses wastewater, the applicability of fuzzy logic is very simple and there is no need to define the complex reactions and their mathematical description or accurate biochemical pathways. To date, few studies have proposed the application of fuzzy logic in the estimation of methane production from BRLs. Garg [33] proposed a multilevel fuzzy composite programming method to combine various parameters affecting landfill gas extraction into a biogas potential index. In addition, a fuzzy logic controller was developed to identify the operational phase of a BRL [36]. Another artificial intelligence based model, that is artificial neural networks, was used to predict methane fraction in biogas by considering leachate components from a BRL [38].In this paper, we propose the use of a fuzzy-logic- based model to estimate methane generation from BRLs at different operating conditions and waste qualities [3], [7]-[9], [24]. Methane production rate and methane concentration in the biogas were predicted from 11 input parameters describing (*i*) leachate quality, such as pH, RedOx potential (*ORP*), chemical oxygen demand (*COD*), volatile fatty acids (*VFA*), ammonium content; (*ii*) waste quality, such as age, moisture content (*MC*), organic fraction concentration, particle size; (*iii*) operational conditions, such as temperature and leachate recirculation flow rate. In a first step, the fuzzy model was developed using experimental data from seven lab-scale studies simulating BRLs. The seven studies were selected because they were representative of BRLs with different properties and operating conditions. In this way it was possible to develop a model that could be applied in a wide range of scenarios. The second step consisted in modeling the full-scale case study of Cerro Tanaro (CT) landfill, a retrofit BRLs for MBT waste located in Northern Italy. Using the previously developed model as a basis, new inputs and rules were added in order to adjust the model for the prediction of CH_4 generation from a single gas extraction well. Finally, the modeling was extended to the entire volume of CT landfill and an estimation of its heterogeneity could be made by comparing the model results to the actual landfill data. The main aims of this study were to confirm the potential use of fuzzy macro-approach for complex processes taking place in BRLs and to offer a valid basis of a biogas prediction tool for BRLs, which can be easily adapted to various site-specific conditions.

2. MATERIALS AND METHODS

2.1. Fuzzy-Logic-Based Model from Lab-Scale Studies Input and Output Parameters

Eleven input parameters were selected among the main factors influencing methane production in BRLs (Table 1). Methane production rate and methane concentration in biogas were the two desired outputs (Table 1). The input parameters describing the leachate quality were chosen because they provide information about waste decomposition phase and waste stabilization [36], [38]: anaerobic digestion is stable for pH in the range 6.5-7.5; ORP shows if a reducing environment is present to support methanogenesis; COD is and indirect measurement of the total oxydable organic content; VFAs is an indication of how the acidogenic and methanogenic microorganisms interactions are well balanced, in fact if acidogenic phase prevails high amount of VFAs causes a decrease of pH with the inhibition of CH_4 production; accumulation of NH_4^+ due to recirculation can lead the concentrations of NH_4^+ in the inhibition range [7]. Waste quality parameters such as waste age and percentage of organic fraction are indexes of how much biodegradable matter can be converted into methane. In the most of laboratory experimental works, the waste was previously shredded, because lower particle size increases the available surface for microorganisms and nutrients distribution, hence decreasing mass transfer phenomena always present in such systems. Due to the difficulties in taking into account this kind of phenomena by a deterministic approach, mean particle size of waste was selected as macro parameter able to give indication of the amplitude of the mass transfer phenomena. Optimized moisture content provides an aqueous environment containing the necessary nutrients and microbes able to improve micro/macro convective phenomena in the waste [39]. Regarding the operational conditions, most of the landfills operate in the mesophilic field, in the range 30-35 °C, depending on climate conditions. A proper flow rate for leachate recirculation should increase MC and liquid distribution, without causing flushing of organic matter and methanogens bacteria [26]. Methane generation can be estimated through the two outputs methane production rate and methane concentration in the biogas. The fuzzy logic based model thus offers a tool to predict an efficient energy recovery strategy of BRLs. The cumulative methane production was calculated from the methane production rate with Equation (2):

$$Q_{CH_4} = \sum_{i=0}^{n} R_i \Delta t_i \tag{2}$$

where Q_{CH4} is the cumulative CH_4 production (L kg^{-1}), R_i is the CH_4 production rate at day i (L kg^{-1} day^{-1}), Δt is the time interval with rate R_i (days), n is the total time of operation (days).

Table 1. Input and output parameters of the fuzzy-logic-based model for laboratory BRL

	Parameters
	INPUTS
Leachate quality	pH ORP (mV) COD (mg O_2 L^{-1}) VFA (g CH_3COOH L^{-1}) NH_4^+ (mg L^{-1})
Waste quality	Age (yr) Moisture content (% *w/w*) Organic Fraction (% *w/w*) Particle size (cm)
Operational conditions	Temperature (°C) Recirculation flow rate (% V water/V waste day^{-1})
	OUTPUTS
Methane generation	CH_4 production rate (L kg^{-1} day^{-1}) CH_4 concentration in biogas (% *v/v*)

2.2. Fuzzy Model Development of Lab-Scale BRLs

The fuzzy logic based model of BRLs was developed using data from different literature sources, all at lab-scale, working in different operating conditions and different initial waste compositions. The implementation of the model was carried out by using the Fuzzy Logic Toolbox present in MATLAB (MATLAB® V8.3). Here only a brief introduction on fuzzy logic is reported, major details can be found in [40], its application in bioreactor engineering is presented in [41] while a model for biogas estimation in anaerobic digestion in described in [34]. A general fuzzy model has basically four steps: (*i*) fuzzification which permits to move from the deterministic to the fuzzy dominion, (*ii*) fuzzy rules definition in order to describe the reality to be modeled, (*iii*) fuzzy inference engine which handle fuzzy variable inputs to obtain fuzzy outputs, and (*iv*) defuzzification procedure to convert the fuzzy output back to the deterministic dominion.

In the first step, the numerical values of inputs and outputs from [3], [7]-[9], [24] were converted into linguistic terms, fuzzy sets, thus defining the antecedents and consequents of the system. The degree of truth of a fuzzy set A (verbal variables such as low, medium, high etc.) is defined by a value of membership function (MF), μ_A, in the interval [0 1], differently from conventional deterministic numerical sets where an element either belongs or does not belong to a particular set (μ_A= 0 or μ_A=1). Abdallah [36] reported that this distinctive feature is advantageous in case of controlling a landfill where the change in input variables does not cause the controlled process to shift abruptly from one state to another. MFs can be represented in different shapes such as triangular, trapezoidal, Gaussian or Sigmoid, depending on the system under study. Among them, triangular and trapezoidal are the most used, due to their simple handling and implementation [35]. In our case, all the MFs for both antecedents and consequents presented trapezoidal shape, as shown in Equation (3):

$$A(x) = \begin{cases} 0, & x \le a \\ \frac{x-a}{b-a}, & a \le x \le b \\ 1, & b \le x \le c \\ \frac{a-x}{a-c}, & c \le x \le d \\ 0, & x \ge d \end{cases} \tag{3}$$

where μA is the MF of a vector x, and *a, b, c, d* are four scalar parameters. As example, the MFs of two of the eleven antecedents inputs are showed in Fig. 1 with their shape and linguistic labels: very low (VL), low (L), medium low (ML), medium (M), medium high (MH), high (H) and very high (VH); the same linguistics variable were adopted for the two consequents. The second step, concerning the definition of fuzzy relations between antecedents and consequents, resulted in 84 rules in the form of IF-THEN statements, which were established through the experience and the experimental data sets. Approximately 70% of the available crisp data were used to train the model and build the corresponding fuzzy rules with the Fuzzy IF-THEN Rule Editor on the MATLAB® environment. An example of one of the IF-THEN rules is presented below:

IF ‘PH’ is ‘M’ & ‘ORP’ is ‘M’ & ‘COD’ is ‘VL’ & ‘VFA’ is ‘VL’ & ‘NH_4’ is ‘VL’ &

‘MC’ is ‘L’ & ‘T’ is ‘M’ & ‘ORG’ is ‘M’ & ‘SIZE’ is ‘M’ & ‘FLOWRATE’ is ‘VL’

THEN ‘CH_4 RATE’ is ‘VL’ & ‘CH_4%’ is ‘VL’.

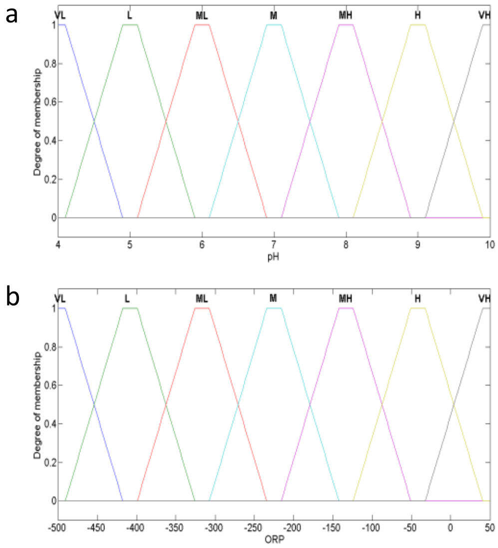

Fig 1. Membership functions of the fuzzyfied inputs: a) “pH” and b) “ORP” (mV).

Once the MFs and the rules had been built, it was possible to enter the fuzzy model with a set of inputs and obtain the corresponding outputs. The experimental data of laboratory tests of different Authors under different operational conditions were used as inputs, Table 2 reports the main characteristics of experimental tests. The model was tested on the total number of available inputs from the chosen lab-scale studies. The fuzzy outputs were calculated through the fuzzy inference engine that processes the fuzzy inputs based on their relevant fuzzy rules. Mamdani-type fuzzy inference method was chosen, as it is the most commonly applied fuzzy methodology [34]. The last step is the defuzzification procedure, which incorporates different fuzzy sets to give a single crisp value in the deterministic domain for the two outputs. The defuzzification method here used was the centroid or center of gravity method which is the most popular among different defuzzification methods [42],[43]:

$$(yi)d = \frac{\sum_i \mu(yi)yi}{\sum_i^r \mu(yi)} \tag{4}$$

Where $(yi)_d$ is the defuzzified output, *r* is the number of fired rules for the specific situation, y_i is the output value in the *i* subset and μ_i is the MF value of y_i.

Table 2. Summary of the different characteristics of the seven lab-scale studies used.

Ref. Study	Main characteristic
[7]	29% organic content; low initial MC; constant low leachate recirculation rate
[7]	8 years old waste; 29% organic content; low initial MC; constant low leachate recirculation rate
[3]	tropical climate; 55% organic content; recirculation rate of leachate + water increasing with time
[3]	tropical climate; 55% organic content; recirculation rate of only leachate increasing with time
[9]	aerobically pretreated waste; 40% organic content; constant low leachate recirculation rate
[8]	synthetic waste; 45% organic content; constant leachate recirculation rate
[24]	MBT waste, low biodegradable waste, leachate recirculation rate decreasing with time

2.3. Extension of Fuzzy Model to CT Landfill Case Study

The case study of CT landfill depicts a scenario typical of small/medium Italian waste management facilities without incineration plants. CT landfill had been originally built as a conventional landfill for non-hazardous pretreated wastes. After source segregation, the residual MSW was pretreated in a MBT plant in order to reduce considerably the amount of organic waste destined to landfilling, according to the EU Landfill Directive (Directive 1999/31/EC). Low water content and lack of rapidly degradable matter implied slow biogas production and long post-management period. With the Bio.Lea.R. Project [47] financed by EU Life+ Program, part of CT landfill was equipped with a leachate recirculation system, in order to optimize the moisture content and the energy recovery with a retrofit BRL technology. The landfilled MSW was hence characterized by a low organic content, which had been pretreated by means of aerobic MBT and partially bio-decomposed in the conventional landfill operations. The peculiarity of this case study made it difficult to predict biogas production with conventional deterministic biogas models, due to the lack of information regarding the kinetics of methane generation from that specific low biodegradable waste. Moreover, the amount of moisture increase into the landfill body under leachate recirculation could not be quantified. Although experimental tests were conducted at lab-scale and pilot-scale to investigate the behavior of CT landfill [24], they represented an ideal scenario with very little spatial heterogeneities, which is very difficult to obtain at full scale. The up-scaling of the laboratory results to the full-scale BRLs is not an easy task due to the different scale of heterogeneity of the mass of waste and the spatial/temporal changes of the leachate properties that cannot be controlled. These were the main reasons why the use of fuzzy logic seemed to be a proper choice to model methane generation from CT landfill. However, the fuzzy-logic-based model developed on lab-scale studies had to be adjusted to obtain a better fitting of the different conditions and the lower data availability encountered in the full scale plant of CT. The extension of the fuzzy-model based on the laboratory results to full scale landfill was reached by two steps: first a cylindrical volume, around a single biogas extraction well, was modeled introducing additional antecedents able to depict the heterogeneities of the well behavior calibrated on the quality and the quantity of biogas experimentally evaluated, and then the extension to the entire volume of the landfill by considering the total experimentally evaluated biogas produced, as described in the following sections.

2.4. *Fuzzy-Logic-Based Model for a Single Well of CT Landfill*

The leachate recirculation system of CT landfill mainly consists of 8 sub-irrigation rings of 20 m diameter, located at the top of 8 gas extraction wells, under the final waste capping, as shown in Fig 2. Leachate recirculation was initially conducted on three injection rings, chosen because their relative wells gave the worse performances in term of methane generation. At the beginning of the experimentation, the injection was performed on one ring at a time, in order to monitor if some liquid leakage could occur, with a flow rate in the range 5-2.5 m^3 h^{-1}, 8 hours per day. In particular, the gas extraction well named CTB110 (Fig 2.) had the longest injection time and its data on methane production were used for the fuzzy-logic modeling. In order to apply the fuzzy model on CT landfill, a cylindrical volume around one biogas extraction well was chosen as control volume. Taking into consideration that a depression at the head of the well of around 15-20 cm H_20 generates a depression which propagates till around 10 m in the landfill body of usual compaction (0.5-0.7 ton m^3) [48], the dimensions of the control volume were assumed to be cylindrical with 10 m radius and 13 m height, that is the actual height of CT landfill. The control volume consisted in approximately 3,500 ton of pretreated waste. 20 sets of crisp experimental data from the monitoring of leachate and biogas quality, along 1.5 years (January 2014 to July 2015), were used to develop the fuzzy model. The first problem encountered dealt with the data of monitoring of leachate, since they were representative of the leachate of the entire landfill and did not depict the specific conditions of the control volume alone. Moreover, in contrast to what happened in lab-scale, where temperature was maintained constant, at full-scale local changes of the leachate temperature occurred depending on the seasonal variation (10 – 30 °C). Although temperature inside the CT landfill body could not be monitored, by analyzing the available data, it was noticed that during the summer an increase of methane generation was registered from CTB110 under leachate recirculation.

In order to fuzzy model the biogas production from the well two new antecedents were added to the lab fuzzy based model. The first originated by the observation of behaviors under seasonal temperature variation above reported; antecedent called "*season*" was used. Another important parameter is the moisture content of the landfill body that could not be monitored at the full-scale plant.

Considering that the moisture is dependent on the quantity of recirculated leachate, another antecedent was added "*Vrec*", which is the volume of leachate re-added in the landfill; this is considered an index able to give information of the moisture present in the landfill.

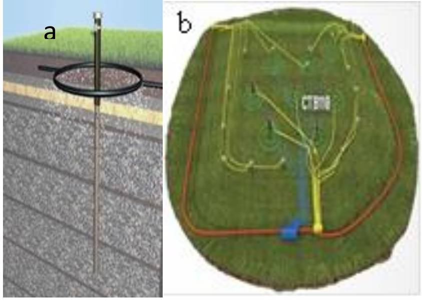

Fig 2. Illustrations of the sub-irrigation system in CT landfill: a) detail of a sub-irrigation ring around one gas extraction well; b) landfill surface showing, gas extraction system (yellow lines), and leachate injection system (blue lines) with the 8 sub-irrigation rings [47].

The final adjustment made on the lab fuzzy-logic-based model regarded the addition of a membership function named very very low, "VVL", in the output variable of CH_4 production rate. This was necessary in order to capture the changes in methane production at the very lower rates recorded on the full-scale, compared to the ranges obtained at lab-scales.Thanks to the above described adjustments, whose MFs are reported in Fig 3, on the model developed from lab-scale studies, it was possible to build 20 new IF-THEN rules, able to simulate the behavior of CTB110. In order to avoid overfitting, the fuzzy model was then tested on other 10 sets of data, in addition to the 20 sets used to develop the model.

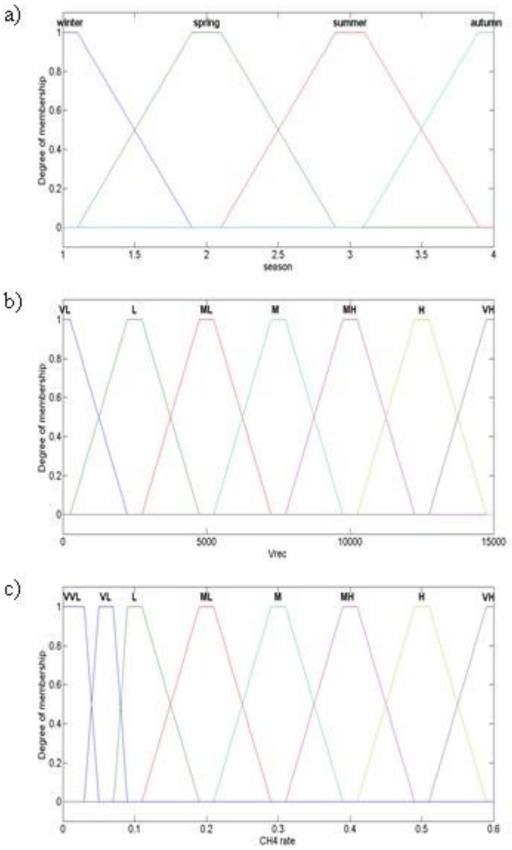

Fig 3. Extension of fuzzy model to biogas capture well: MFs of the new antecedents a) "season" and b) cumulative volume of leachate recirculated "*Vrec*" (m^3) and the modified label of output c) "CH_4 rate" (L kg^{-1} day^{-1}).

2.5. Extension of the Fuzzy-Logic-Based Model on the Entire CT Landfill Volume

The fuzzy-logic-based model of a single gas extraction was used to simulate the entire volume of CT landfill. It was assumed that each of the 26 vertical wells behaved following the IF-THEN rules developed for the well CTB110, as if the waste properties were homogeneously distributed on the entire volume. By comparing the fuzzy model results on biogas production with the actual biogas data of all the 26 wells, it was possible to evaluate the spatial heterogeneity via a Heterogeneity Index (*HI*), expressed as discrepancy between the predicted and the observed data of the total biogas production rate from CT landfill:

$$HI = \left| 1 - \frac{\sum_{i=1}^{n} {}^{P_{RATE\ i}}/_{P_{\%\ i}}}{\sum_{i=1}^{n} {}^{Q_{RATE\ i}}/_{Q_{\%\ i}}} \right| \qquad (5)$$

where P and O are the predicted and the observed values, respectively, of methane production rate (RATE) and methane fraction (%) of the i_{th} well.

3. RESULTS AND DISCUSSION

3.1. Lab-Scale BRL Fuzzy Model

The outputs of the fuzzy-logic-based model were compared with the experimental data from [3], [7]-[9], [24]. The proposed model could fit reasonably well the experimental data from 7 lab-scale studies simulating BRLs working at different conditions and with different MSW qualities (Table 2). Fig 4 and Fig 5 show a good agreement between observed and predicted data from two of the selected lab-scale study, while Fig 6 illustrates the goodness of fit with the performance indicators R2 for all the laboratory data. The fuzzy model fitted the experimental methane production data reasonably well, with small deviations and coefficient of determination of 0.96 and 0.95 for cumulative and fraction of CH_4, respectively. The results suggested that the approach chosen, although applied on lab-scale studies, could be a valid basis to predict landfill gas production from BRLs with a wide range of operational conditions and it paved the way for the application of fuzzy modeling on the full-scale.

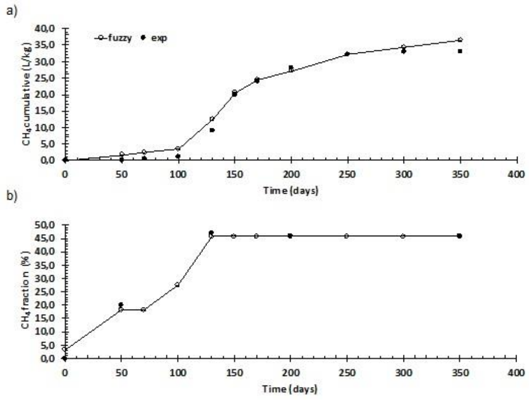

Fig 4. Comparison of experimental data and fuzzy modelling results of a) cumulative methane production and b) methane fraction from [7].

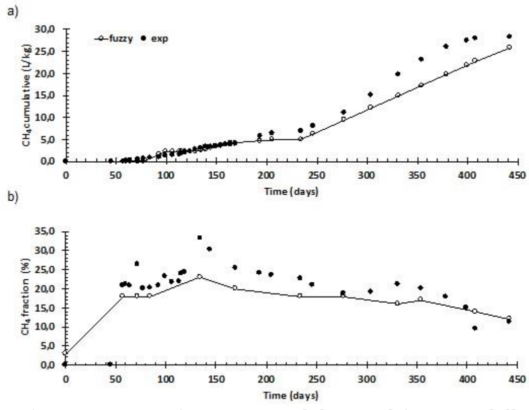

Fig 5. Comparison of experimental data and fuzzy modelling results of a) cumulative methane production and b) methane fraction from [24]

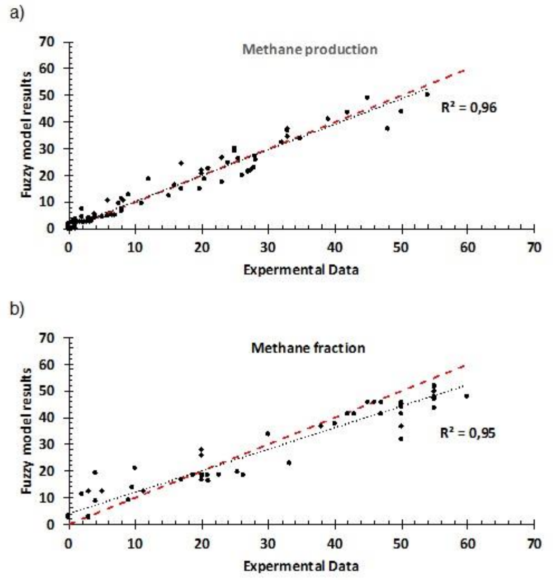

Fig 6. Linear regression between the fuzzy model outputs and the corresponding lab experimental data with the resulting R2 for a) cumulative methane production and b) methane fraction in the biogas.

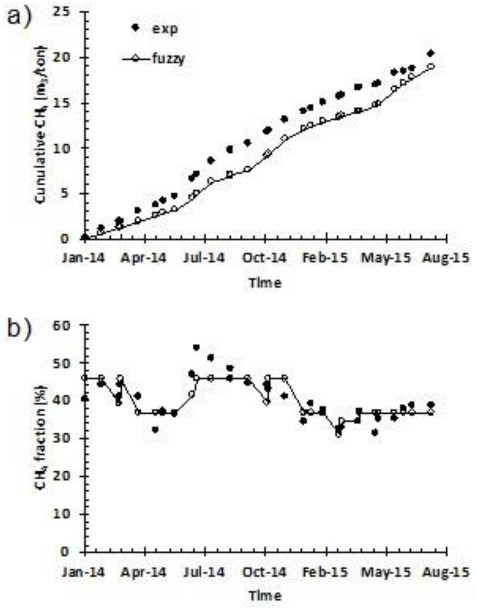

Fig 7. Comparison of one well of Cerro Tanaro full plant experimental data and prediction from modified fuzzy-logic-based model for a) cumulative methane production and b) methane fraction from one gas extraction of CT landfill.

3.2. *Full-Scale BRL Fuzzy Model*

On the basis of the data available on the full-scale plant of CT landfill, the proposed lab fuzzy-logic-model was adjusted in order to predict methane and biogas production from pretreated MSW under leachate recirculation. Although this case study was characterized by lack of information from the previous literature, fuzzy modelling represented a valid tool which could be easily adapted to the specific system under study. The prediction of methane generation from well CTB110 gave good results. Fig 7 shows the comparison of predicted and detected results. The performance indicator R2 of 0.99 and 0.66 for cumulative methane production and methane percentage, respectively confirmed a good agreement between the predicted and the actual data, especially for the first output.

In order to extend the model on the entire volume of BRL, the modified fuzzy model developed on the single well CTB110 was applied to all the 26 wells present in CT landfill. By comparing the total biogas generation rate observed and predicted on one day, it was possible to quantify approximately the spatial heterogeneity of the system with the calculation of the index HI through Equation (8), which resulted of 9.7%. It means that approximately 90.3% of the total volume of CT landfill behaved as the modelled control volume around well CTB110 in terms of biogas production rate, expressed as fraction between the two outputs CH_4 rate and CH_4 fraction. The HI index is a corrective index of the fuzzy model output in the simulation of other full scale BRL landfill with similar quality of refuses and under similar environmental condition of CT landfill. For different situations the above procedure permits to evaluate analogous HI index.

The results obtained by applying the fuzzy-logic-based model on the full-scale confirmed the flexibility of fuzzy modelling, thanks to its learning structure able to represent complex systems with any kind of available information. Without formulating complicated mathematical equations, it was possible to adapt the model to the specific scenario represented by CT landfill. This approach can be further applied on a number of different BRL technologies, with no need of detailed data, which are often difficult to collect and manage in the case of full-scale facilities.

4. CONCLUSION

A fuzzy-logic-based model was developed for the evaluation of methane production rate and methane fraction in landfills under leachate recirculation, using experimental data of literature of lab-scale studies simulating BRLs. In new generation landfills, aiming at more sustainable waste management, biogas generation estimation is a key tool to run an efficient energy recover and to evaluate energetic and environmental sustainability. In complex and heterogeneous system, such as a BRL, the existing models are often affected by high uncertainties due to the difficulty in identifying all the interconnected processes and in collecting all the necessary data. The fuzzy-logic-based model proposed can be a simpler alternative to the deterministic approaches, which need complex and tedious mathematical formulations with difficult tuning parameters. The fuzzy model showed good performances in the prediction of methane generation for different lab-scale BRLs. The results showed good agreement between the observed and the predicted data, suggesting that the approach chosen, although applied on lab-scale studies, could be a valid basis to predict landfill gas production from BRLs with a wide range of operational conditions.

The proposed fuzzy model was then applied on the full-scale case study of CT landfill, a retrofit BRL treating MBT waste. Although this case study was characterized by lack of information from the previous literature, fuzzy modeling represented a valid tool which could be easily adapted to the specific system under study. Few adjustments were made on the model in order to better fit the data of methane generation, based on the available inputs. Additionally, by applying the model on a smaller control volume of landfill and extending the results on the entire landfill volume, it was possible to quantify approximately a mean value of the spatial heterogeneity of CT landfill. It resulted that the proposed fuzzy model was able to predict 90.3% of the total biogas production rate, suggesting that 9.7% of the waste volume had a different behavior of the selected control volume of landfill due to its heterogeneities.

Finally, the results obtained both on lab-scale and the extension to full-scale confirmed that fuzzy approach is a powerful and flexible tool that, thanks to its learning structure, is able to model the complex processes taking place in BRLs, with no need of sophisticated mathematical modeling and accurate value of parameters, but simply the necessity of accurate as much as possible, of the site-specific information.

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RESEARCH ARTICLE

Sub optimal e-waste management and the lost opportunity

Rakesh Tyagi [1], Priyanka Kaushal[2,*]

[1] Kampak Energy Solutions, 4515 Varsity Drive (NW), Calgary, Alberta T3A0Z8, CANADA
[2] Department of Energy and Environment, TERI University, 10, Institutional Area, Vasant Kunj, New Delhi 110070, INDIA

ABSTRACT

Electronic waste or e-waste is the waste generated from discarded and end of life electronic items. In recent times with change in lifestyle and improved purchasing capacity of people has accelerated the demand of new and improved electronic items, quick technology obsolescence,as a consequence the generation of e-waste has seen a huge rise. In year 2016, globally 93.5 tons of e-waste was generated, India, one of the leading producers of e-waste, produced 1.65 Milliontones of e-waste. Apart from domestic generation, a huge chunk of global e-waste was also dumped in India. 90 % of the e-waste is handled and managed by the unorganized sector. Hence there is a dire need to develop a mechanism to handle the enormous flux of e-waste in India.In this paper the e-waste sector has been reviewed. Also a detailed analysis of the material flow in the e-waste sector has been done. Results reveal that if mismanaged, e-waste can impose huge environmental penalty, however if it is regulated and handled scientifically it can become an asset for resource recovery whose carbon footprint is 70-80 % lower than its primary production.

Keywords: E-waste generation, stakeholders, policies, emission reduction

1. INTRODUCTION

With the arrival of new technology, growing income and change in lifestyle the rate of generation of e-waste has seen a steep rise, and this is a global phenomenon now. In year 2014 the world produced 41.8 Million tons of e-waste [1]. And it is expected to reach 130 million tons in 2018 from 93.5 million tons in 2016 [2].It is one of the fastest growing sectors in the world. India is the seventh-largest country and its population stands at 1.25 billion and is experiencing an annual growth rate of 1.2 per cent. In 2015, India's GDP was valued more than 2 trillion USD [3]. The demand for electronic products and systems in the country is estimated to reach US$ 400 billion by 2020 [4]. The estimated production will reach USD 104 billion by the year 2020, creating a gap of USD 296 billion in demand and production. This creates a unique market opportunity for businesses to look at India to cater to the domestic demand as well as act as an export-hub. As the demand for electronic products goes up, so will the generation of electronic waste. Electronic waste or e-waste or Waste Electrical and Electronic Equipment (WEEE) is the term used to describe old, end-of-life or discarded appliances using electricity as shown in Fig 1, it includes computers, mobile phones, television, refrigerator, air conditioner, medical equipment, printer, scanners etc. [5]. There are more than 1000 toxic substances [6] associated with e-waste, the more commonly reported substances are categorized in Table 1.

Table 1. E-waste material classification

Category	Material	Potential Environmental Impact
Hazardous	Cd, Cr, Pb, Hg CFCs, PAHs, PBDEs, PCDD/Fs	Negative
Non-hazardous	Cu, Se, Zn, Ag, Au, and Pt	Negative

India is witnessing a rapidly growth in the consumption of electrical and electronic products. This, accompanied with high obsolescence rates, has led to higher rates of e-waste generation. The Indian manufacturing segment alone contributed 110 million mobile devices during FY 2015-16, from 60 million in FY 2014-15, i.e. an increase of more than 80 % in a

Corresponding Author: priyanka.kaushal@teriuniversity.ac.in (Priyanka Kaushal)
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year time [7]. Studies suggest that as much as 80% of the e-waste generated in developed countries sneaks into the grey market of developing countries like India, Bangladesh etc. [8]. In year 2014, e-waste produced, domestically, in India was 1.641 Mt [9] e-waste handling is a problem of increasing proportion, especially when crude methods are adopted for recovery of useful components from it. Literature suggests that the contamination due to the recycling of electronic waste in China and India is 80% higher than the rest of the world [10].

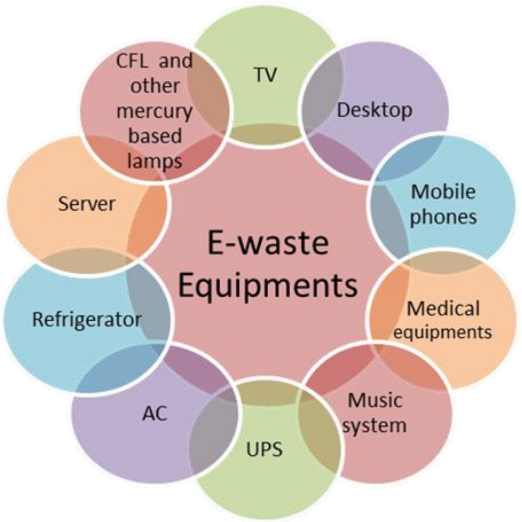


Fig 1. E-waste equipment in India

The impact of mismanagement of e-waste in India is reported in detail in the literature [11]. Fig 2 and Fig 3 show the sectorial contribution and the projection for e-waste generation in India.

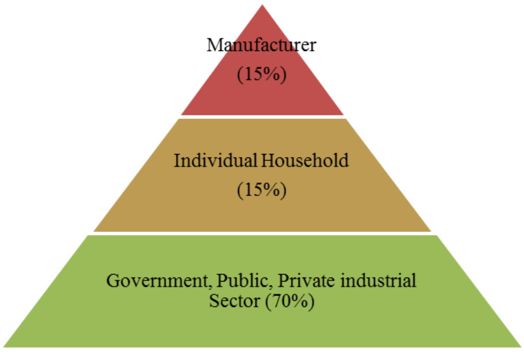


Fig 2. Pyramid form showing sector's share in e-waste in India

With government of India migrating towards e-initiatives, where in the idea is to digitize the services the rate of volume of e-waste in this sector has gone up considerably.

2. E-WASTE IN INDIA

India's approach to manage waste is based on the following principles: (a) precaution i.e. economic develop but no damage to environmental (b) Penalty i.e. polluter must bear the costs for the environmental damages. The journey and major milestones India has achieved in order to manage waste is as follows.

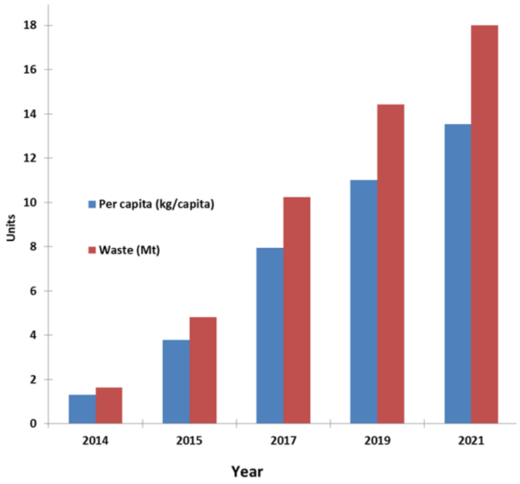


Fig 3. E-waste generation in India

2.1. Policy & Regulation

In 1986, The Environment (Protection) Act 1986 was passed by an Act of the Parliament of India. The purpose of the Act was to implement the decisions of the United Nations Conference on the Human Environments [12]. In 2006 came, The National Environment Policy. This policy was more comprehensive; it encompassed Legal Liabilities, Legislative Reforms, and Environment Impact Assessment. It also talked about the threats due to genetically modified organisms, challenges of Coastal regions and environmentally sensitive area. In 1989, came The Hazardous Wastes (Management and Handling) Rules. This was a document that laid down the foundation to deal with the hazardous wastes. It identified the various central and state players like MOEF, CPCB, PCC etc. and their corresponding duties and responsibilities. The rules are notified to ensure safe handling, processing, treatment, package, storage, transportation, use, reprocessing, collection, conversion, destruction and disposal of Hazardous Waste. These Rules have been amended later in the years 2000, 2003 and 2008 [13]. This was followed by E-waste (management and handling rules), 2011; and E-waste (management) rules, 2016 [14] These policy and regulation encouraged reuse and recycling, established system for assortment and recycling of materials to recover resources, produce guidelines for Environmentally safe disposal of residues, put e-waste under hazardous waste, regulation for trans-boundary movement. Despite the regulations, e-waste is handled in pseudoscientific means that contaminates soil air and water [15]. Policy makers are proactive and routinely revise and update the rules and regulations. To this end, GoI, under E-waste (Management) Rules, 2016, has, additionally brought under its horizon the management of the waste generated from disposal of different mercury containing lamps. Though the responsibility to implement these rules lies with the state governments, new economic instruments such as `exchange' and `deposit refund' can act as incentives for consumers to adopt the waste management strategies.

Waste management policy formulation and regulation is a work in progress and is evolving. Though the new rules have laid down the responsibilities of various stakeholders in clear terms it has not included the informal sector, a sector that handles more than 95 per cent of e-waste generated in the country. It is essential that any long-term policy on e-waste integrates the informal sector by including them under the stakeholder-umbrella and then slowly faze them out by integrating them into the mainstream.

2.2. *E-Waste Handling*

The main stakeholders in e-waste management are the manufacturers, distributors, importers, consumers, collectors, recyclers, policy makers and policy implementers.

The informal sector, also known as unorganized sector, is part of a very well-organized hierarchy and structure, as elaborated in various studies and reports [16]. It is interesting to view this structure and understand the waste flows. The waste collectors locally known as "kabadiwalas" are the most important link in this waste flow and are responsible for the collection of waste from all consumers and manufacturers [17]. There is another set of operators, waste traders with better financial capacity, who bid for larger volumes of waste being discarded by companies and organization through auctions. The waste then flows down to scrap dealers, who recovers the functional component and then pass on the remaining waste to the dismantlers. It is here that the waste is further separated and then broken down to individual components and materials. The waste then finally reaches the recycler by materials as glass, plastics, metal and circuit boards for material recovery. The recyclers in a particular cluster are generally engaged in a specific set of activities and operations. For other equipment like refrigerators, washing machines or air conditioners, the segregation is more material-based and plastic and metal parts are separated and treated in specific streams. Some useful components such as power supplies or motors are taken out for further use if possible. Since most electronic and electrical products have a value at the end of their useful life, the informal sector is able to pay the consumer to acquire this waste. The formal sector, because of its larger infrastructure and operational costs, finds it hard to compete with the informal sector.

In case of large companies and PSUs, the flow is a little different. As the quantity is large and auctioned through tenders to highest bidders, only waste dealers with large financial capacities can participate in this trade. At times the dealers jointly bid for the scrap and share the total waste among them for further processing. Most dismantling and recycling units are owned by individuals who make good profit, but the workers employed in these facilities earn less than minimum wages.

2.3. *Informal Sector*

The processing of e-waste in India is largely carried out in an informal backyard setup, which is unregulated and does not follow the prescribed environmental norms for handling hazardous substances [11]. Some of the processes and activities practiced by the informal sector have serious environment and social impacts (use of toxic chemicals, poor working conditions, child labor, etc.). The recycling chain of e-waste consists of two sets of processes, as shown in Fig 4, one being dismantling and segregation of components and the other being material recovery.

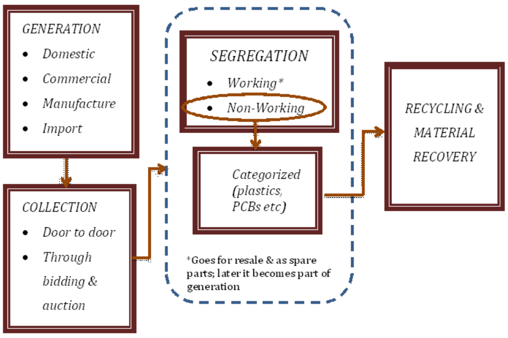


Fig 4. Waste flow chain in India

The first stage of waste processing involves cannibalization of serviceable parts and refurbishment of components and products. All unserviceable components and products are then shifted to dismantlers. Individual products such as monitors, keyboards or CPUs are then dismantled and broken down to individual components using bare hands and basic tools such as hammers and screwdrivers. Blowtorches and heaters are used to loosen solders to remove the components attached to the circuit boards. Printed circuit boards are placed directly above the heaters, allowing the solder to melt and drop. The process of dismantling is carried out in unventilated rooms without any semblance of housekeeping or concern for occupational health. These segregated components are sorted by their material composition and then shifted for material recovery. 95% of e-waste is handled by informal sector. And this is alarming. The informal sector uses primitive [18]. All these processes cause environmental degradation and sickness to the poorly paid employees. With the alarmed rate of rise of e-waste in India, correct formal handling and registered recyclers have become the highest priority for the country. In India most of the e-waste utilization facilities are registered with Central Pollution Control Board (CPCB). As on 2015, 149 recycling units were registered with CPCB, their cumulative capacities as shown in Fig 5 and Fig 6, is around 410,000 MTA.

3. E-WASTE & RESOURCE RECOVERY

Industries are growing at a rapid pace and so are the emissions related to it. Mining industry-extracting metals from their ores and processing it, is energy-intensive and generate significant direct greenhouse emission (GHG) emissions, together with carbon dioxide. Environmental impacts will be impaired because it becomes tougher to extract metals and minerals. Also rising fuel prices, water constraints, and environmental regulation can place downward pressure on profit margins in this trade. Mining metals like iron and copper is energy-intensive, requiring six fold additional energy to supply every ton of metal in comparison to mining industrial materials like phosphate, stone, sand, and gravel [19, 20].

Fig 5. States with registered recycler under CPCB in year 2015

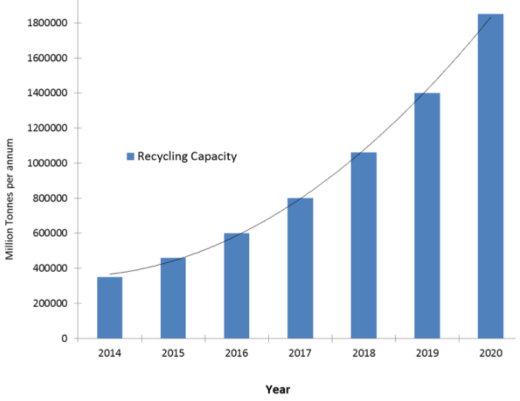


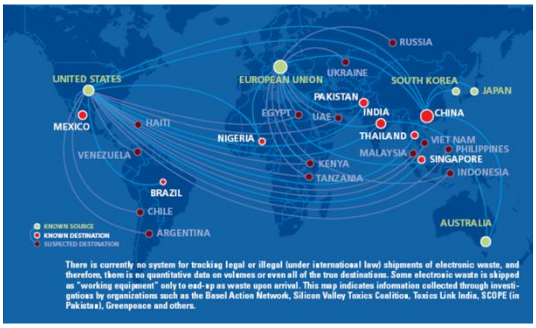
Fig 6. Recycling capacity of registered recyclers in India

Electronic waste products mainly contain a thin deposit of a metal on a substrate [21]. As a whole, electronic waste consists of:

1. Plastics: (C-H-O polymers like polyesters, polyethylene, polycarbonates),
2. Metals: classified further as base metals and precious metals. Copper, Iron, Zinc, Aluminum, Tin, Lead, Nickel are the base metals. The precious metals are Gold, Silver and Palladium.
3. Refractory oxides: silica, alumina, alkaline and alkaline earth oxides.

Market penetration, replacement market and high obsolescence rate makes e-waste one of the fastest growing waste streams globally [13]. This new kind of waste is posing a serious challenge in its disposal and recycling. The dumping of e-waste, particularly computer waste, into India from developed countries, primarily because of economic benefits, has further complicated the problems with waste management in India [22].

Studies so far reveal that the e-waste generation in India in 2015 is approximately 1.67 million tones .The projected growth for e-waste generation for India is about 34% per annum [23]. Besides the domestic e-waste generated, an additional 50,000 MT a year is illegally imported into the country [24]. Fig 7 has mapped the global source and dump sites for e-waste.



There is currently no system for tracking legal or illegal (under international law) shipments of electronic waste, and therefore, there is no quantitative data on volumes or even all of the true destinations. Some electronic waste is shipped as "working equipment" only to end-up as waste upon arrival. This map indicates information collected through investigations by organizations such as the Basel Action Network, Silicon Valley Toxics Coalition, Toxics Link India, SCOPE (in Pakistan), Greenpeace and others.

Fig 7. Known and suspected route for e-waste dumping
Source: BASEL ACTION NETWORK; UNEP

3.1. Emission Reduction Potentials from e-waste

As a consequence of continuous modifications of function and design of EEE, WEEE is a highly heterogeneous mix of materials. The precious metals are mainly found in printed circuit boards (PCBs). The concentration of precious metals in PCBs is usually much higher than their ores. Mined ores for the extraction of gold and palladium contain less than 10 g t^{-1} of precious metals where as in PCB it is 250 g t^{-1} & 110 g t^{-1} for gold and palladium respectively [25]. Hence the temptation to recover precious and expensive metals from electronic waste becomes obvious. Also mining by its very virtue is complex (it involves land acquisition, resettlement etc.) and has upfront negative environmental impacts. The environmental impacts of the secondary production in state-of-the-art operations are much lower than primary production [26]. Besides environmental protection and legislative pressure, recycling also serves the economic interests. Precious metals contribute to more than 80% of the materials' market value of obsolete personal computers, despite their small quantity [27]. Secondly, the limited availability of precious metals reserves provides additional impetus to improve the recovery of precious metals from WEEE [28].

4. MATERIALS AND METHOD

Waste, especially e-waste is a new form of waste. As reported earlier, 95% of e-waste (includes both domestic production and international dumps) in India are handled by informal sector and as of now, no information, particularly on e-waste is captured in any of the national surveys. However to generate data and to understand the system, the research team has visited and interviewed the owner (proprietor) and the workforce in the e-waste handling clusters in Delhi only. The informal sector is very well aware of the fact that the work carried out in their backyard is not legal they were reluctant for any interaction let alone information, However after repeated visit and networking some confidence was established before they shared information with us. The information, is called primary data in the study, was not complete for analysis purposes. To bridge the missing information secondary sources of data like newspaper articles, journal articles, open source data, were extracted. With this an attempt has been made to formulate an inventory of metals and plastic content in consumer electronic waste i.e. for television, mobile phone and personal computer. These items are the fastest growing sector in India as shown in Fig 8.

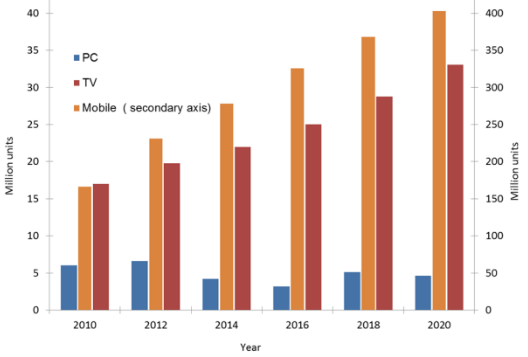


Fig 8. Growth of consumer electronic in India [29]

In India market penetration rate for TV is, 3 times of refrigerator, and an order of magnitude higher than other consumer electronics like AC or washing machine. As on 2016, India had 1250 million populations and it had around 330 million mobile phones. In the consumer electronic category, mobile phones, TV and PC together hold more than 85 % sales [29]. They also hold the highest rate of discard probability [1]. Therefore this study is limited to these three product category only.

Emission reduction calculation is done as per the general guidelines for the selected small scale (SSC) clean development mechanism (CDM) methodologies given by UNFCCC. Fig 9 is the schematic of the methodology.

4.1. UNFCCC methodology

Emission reduction was estimated by calculating the difference between

(i) the energy used for production of metals and plastics from virgin materials (i.e. baseline emission)
(ii) the production of the same metals and plastics from e-waste recycling(i.e. Project activity emission)

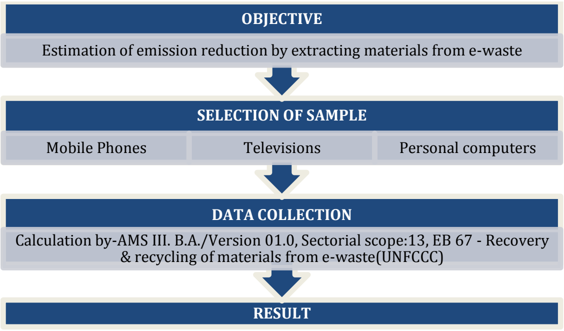


Fig 9. Methodology for Emission reduction calculation [30]

The baseline emissions were calculated using following equations;

$$BE_y = BE_{m,y} + BE_{p,y} \tag{1}$$

$$BE_{m,y} = \sum_i \left(Q_{i,y} * B_i * SE_i\right) \tag{2}$$

$$BE_{p,y} = \sum_i \big(Q_{i,y} * L_{p,i} * B_i * (SEC_{Bl,i} * EF_{el,y} + SFC_{Bl,i} * EF_{FF,CO2}\big) \tag{3}$$

The project activity emissions were calculated using following equations;

$$PE_y = PE_{r,y} + PE_{p,y} \tag{4}$$

$$PE_{r,y} = \sum_i \left(EC_{i,y} * EF_{el,y} + FC_{i,y} * NCV_{rec,ff,y} * EF_{rec,ff,CO2,y}\right) \tag{5}$$

$$EC_{i,y} = EC_y * \frac{Q_{i,y} * \$_{i,y}}{\sum_r Q_{r,y} * \$_{r,y}} \tag{6}$$

$$FC_{i,y} = FC_y * \frac{Q_{i,y} * \$_{i,y}}{\sum_r Q_{r,y} * \$_{r,y}} \tag{7}$$

$$PE_{p,y} = \sum_i \left(Q_{i,y} * EFP_i * EF_{el,y}\right) \tag{8}$$

$$ER_y = BE_y - PE_y - LE_y \tag{9}$$

It was also assumed that there was no leakage due to the project activity. The details of the methodology are given elsewhere [31].

5. RESULTS & DISCUSSION

Suboptimal management: For efficient management of e-waste the whole trade chain must be acutely monitored and the responsibilities should be distributed among all the stakeholders, as illustrated in Fig 10.

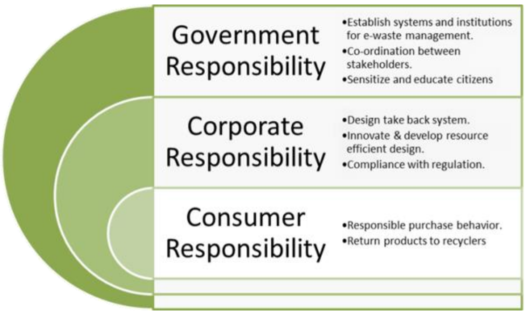


Fig 10. Stakeholder participation in e-waste management

Lack of infrastructure capacity: Even though the recycling rate of the CPCB registered recyclers are growing but it can be clearly projected that by the year 2020, the percentage of recycled e-waste is very negligible (Fig 11). This also highlight that the government policy and initiatives are not in sync with the realities. India would face rising environmental damage and health problems if e-waste recycling is left to the vagaries of the informal sector. The lack is in the infrastructural facility only; there is no dearth of experienced human resource. This is also an opportunity to mainstream the workforce, who is currently engaged in the illegal informal sector. They have the experience and skillset to take up. With little training they will integrate seamlessly in to the formal sector of e-waste recycling.

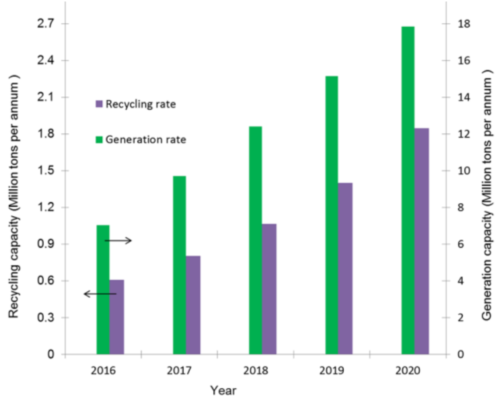


Fig 11. Generation and recycling rate of recyclers in India

Emission reduction: As shown in Fig 12, if India had managed (or is willing to manage), its e-waste efficiently and extracted metals from top three contributor of e-waste (i.e. mobile phones, desktop and television) in FY year 2015/16 then the emission reduced would have been 1.1 million tons of CO_2 equivalent. As shown in the Figure, the emission reduction potentials are also increasing at a CAGR of 14-15 %.

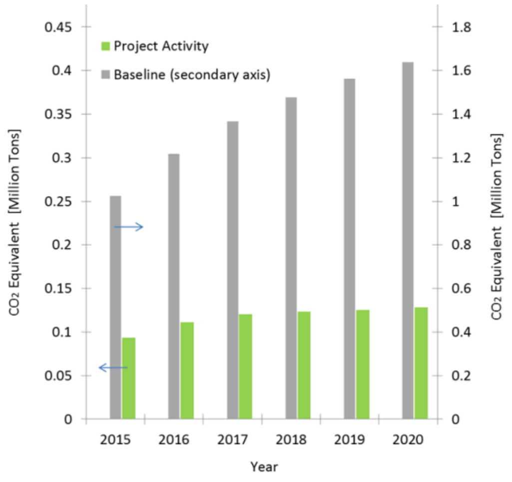


Fig 12. Emission reduction potentials by extracting materials from e-waste in India

5.1. Challenges

In India, few immediate challenges and concern in the e-waste sector are as follows:

Fast growing stream: A UN-report predicted that by 2020, e-waste from old computers only would jump by 500 per cent on 2007 levels in India and e-waste from discarded mobile phones would be about 18 times higher than 2007 levels [18]. Hence, there is an urgent need for strategic planning for handing and management of e-waste in India. Also, the rules, regulations and laws, that govern the e-waste sector, that are very well documented need to be practiced.

Hazardous materials: If not handled safely the hazardous e-waste will leak into the eco-system; they have very high carcinogenic potency. For example, mercury from electronics has been cited as a leading source of mercury in municipal waste [32]. Similarly, brominated flame retardants that are commonly added to plastics used in electronics, if not handled safely, they release toxic fumes during incineration; and post combustion if the ash is dumped either at landfill site or otherwise it contaminates the ground water.

Data Security: It is also very important that agencies engaged in the e-waste management do not have facilities to access the data (if any) in the e-waste. Data storage devices and media contain critical personal, financial, legal, technical, operational, and classified information. Though it is the prime responsibility of the consumer to sanitize the goods before discarding, however, it is rational to have second level of data security too.

Feedback mechanism: On the national or state level, the government currently has no mechanism or information management system to determine the number or volume of equipment put into the market. Similarly, there is no data or information about the e-waste. For planning purposes all data is generated on normative basis. Currently e-waste is dealt by the informal sector. In the absence of any information management system for the informal sector, the e-waste flow goes unreported. There is no legitimate source of primary data available on the quantity collected, re-used, refurbished and recycled in the informal sector. There is a critical requirement to develop an information management system to track e-waste flows along the value chain for its sound management. The problem of imported e-waste is another threat.

5.2. Way forward:

Merger of formal and informal sectors: The informal and formals sector needs to be integrated. The collection and the physical sorting of e-waste can be done by the informal sector and post segregation the e-waste should be passed on to the formal facility for recycling and resource recovery (Fig 13). It is also important to monitor and ensure the performance of the unit adheres to the resource recycling and recovery guidelines.

Some ways by which e-waste management can be improvised are:

Improved efficiencies: On a holistic level one way to reduce waste is to “generate less waste”. Therefore Indian industries engaged in manufacturing should move to ‘precautionary principle’ by employing waste minimization techniques and by a sustainable product and service design. Globally this concept is receiving lots of attention of late [33, 34].

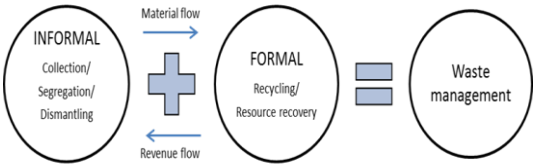


Fig 13. Proposed e-waste management model

Awareness and sensitization: The current awareness regarding the existence and dangers of e-waste are extremely low, partly because the e-waste being generated is not as large as MSW and hence public as a whole do not perceive it as a menace. Secondly, the consumer has no information about the recycling and resource recovery potential in the electronic goods they possess. They are equally unaware of the impacts it might bring to environment if the electronic waste is not disposed of scientifically. Urgent measures are required to address this issue. To this end it is important that the agencies involved in waste management should plan sensitization activities.

6. CONCLUSIONS

Despite positive outcomes, the reins of e-waste handling and management, in India, is in the hands of informal sectors and it is limited to (1) insufficient collection (2) nonscientific resource recovery (3) passive participation from implementation agencies and (4) illegal import of e-waste from the developed economies. All together they pose serious health risks to human and environment. India needs urgent approach to manage e-waste by technical and policy-level interventions and implementation. Data analysis also showed that India should build infrastructural capacities to handle high flux of e-waste in near future. Secondly, the country is committed to scale down its emissions intensity per unit GDP by 33% to 35 % below 2005 by 2030. With the tons of emission reduction by extracting materials from e-waste, it will contribute constructively to achieve the emission reduction target.

ACKNOWLEDGEMENT

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LIST OF ABBREVIATIONS

AC	Air Conditioner
CAGR	Compounded Annual Growth Rate
CDM	Clean Development Mechanism
CFCs	Chloro Fluoro Carbons
CPCB	Central Pollution Control Board
CPU	Central Processing Unit
EEE	Electrical and Electronic Equipment
FY	Financial Year
GDP	Gross Domestic Product
GHG	Green House Gas
GoI	Government of India
MTA	Metric Tons Annually
MOEF	Ministry of Environment and Forestry
PAH	Poly Aromatic Hydrocarbon
PBDE	Poly Brominated Diphenyl Ethers
PC	Personal Computer
PCBs	Printed circuit Board
PCC	Pollution Control Committee
PCDD	Poly Chlorinated Dibenzo Dioxins
PSUs	Public Sector Undertakings
SSC	Selected Small Scale
TV	Television
UN	United Nations
UNFCCC	United Nations Framework Convention on Climate Change
USD	US Dollar
WEEE	Waste Electrical and Electronic Equipment

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RESEARCH ARTICLE

Adsorption of 2,4-dichlorophenoxyacetic acid on peanut shells: effect of initial concentration

Elcin Demirhan *,1, Elif Culhaoglu1

1Yildiz Technical University, Chemical Engineering Department, 34220 Esenler, Istanbul, TURKIYE

ABSTRACT

Pesticides are an integral part of modern agriculture in most countries as a tool for controlling pests. In the last few decades, increasing use of pesticides is polluting environment and water resources day by day. Adsorption is one of the most used method for removal of these pollutions due to the simple ease of processing, low cost and effective even in very low concentrations. Active carbon is very efficient adsorbent for removing pesticides from aqueous solutions thanks to its high surface area and porosity. However, the high cost of active carbon can be sometimes restricted for several purposes.

In recent years, research on the production of low cost adsorbents alternative to commercially available activated carbon has increased. Therefore, in this work, peanut shells were used as an adsorbent for removing 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous solutions. The adsorption performance was studied depending on initial concentrations of 2,4-D solutions.

Keywords: Pesticide, adsorption, peanut shell, low-cost adsorbent

1. INTRODUCTION

Water pollution by chemical pollutants has become a primary public concern in the recent years. Among these pollutants, increasing use of pesticides in agriculture, forestry, and domestic activities for controlling pests is the major organic compound caused the water pollution. They are carcinogenic in nature and toxicity of pesticides and their degradation products is making these chemical substances a potential hazard by contaminating our environment [1, 2]. 2,4-Dichlorophenoxyacetic acid, more commonly referred to as 2,4-D, is member of the phenoxy family of pesticides. This pesticide is commonly used in the world to control broad-leaved weeds and pests in farm because of its low-cost and good selectivity. The maximum concentration of 2,4-D must be 20 mg L^{-1} in drinking water based on the World Health Organization regulation [3]. Therefore, different processes have been used for the removal of these pesticides, such as enhanced electrochemical oxidation [4], photo degradation [5], oxidation by ozone [6] and adsorption [7-11].

Adsorption process is the most widespread treatment used due to the high removal efficiency and activated carbons are usually favored adsorbents based on their adsorption performance. However, the high cost of activated carbon had led to interest in utilizing low cost materials as adsorbents for pollutants. Therefore, in the present study, peanut shells were used as low-cost adsorbent for removal of 2,4-D from aqueous solutions. The equilibrium and kinetics of the adsorption process were studied to understand the adsorption mechanism of this pesticide onto the peanut shells.

2. MATERIALS AND METHODS

2.1. *Adsorbent and Pesticide*

Peanut shells were used as low-cost adsorbent for removal of pesticide 2,4-D from aqueous solutions. Peanut shells are consisted of lignin, cellulose, and hemicellulose. The percentages of these components are determined as approximately 31% lignin, 36% cellulose and 19% hemicellulose [12]. Peanut shells

Corresponding Author: demirhan@yildiz.edu.tr (Elcin Demirhan)

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were obtained from a local supplier in İstanbul. For experimental studies, the peanut shells were rinsed with tap water, then washed with distilled water dried at 80 °C in a hot air oven for 24 h, ground and then sieved to sizes of −50 and + 100 mesh. The powder was preserved in airtight bottles for experimental use.

2,4-D was purchased from Sigma Aldrich. The chemical formula of 2,4-D is $C_8H_6Cl_2O_3$ and its chemical structure was shown in Fig 1.

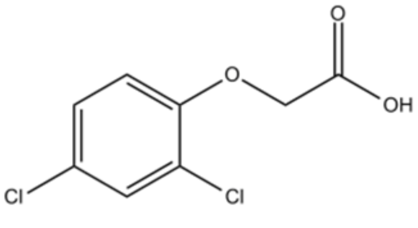

Fig 1. Chemical structure of 2,4-D

2.2. Equilibrium Experiments

The equilibrium adsorption experiments were performed to evaluate the efficiency of peanut shells for the removal of 2,4-D from aqueous solution. The experiments were carried out by adding 1 g of adsorbent into a set of 100 mL of different initial concentrations (10–50 mg L^{-1}) of 2,4-D solution. The samples were kept at constant temperature in an incubator shaker at 170 rpm and 25 °C for 3 h. The solutions were then centrifuged and the filtrate was analyzed using UV/vis spectrophotometer at 282 nm.

The equilibrium amount of 2,4-D adsorbed per unit mass of adsorbent, q_e (mg g^{-1}), was calculated by:

$$q_e = \frac{(C_0 - C_e).V}{m} \tag{1}$$

where, C_0 and C_e are the initial and equilibrium concentrations of 2,4-D (mg L^{-1}), respectively. V is the volume of the solutions (L) and m is the weight of adsorbent (g).

2.3. Kinetic Experiments

For kinetic studies, 1 g of peanut shell was contacted with a set of 100 ml of 2,4-D solutions with constant concentration. At a given time intervals, solutions were centrifuged and analyzed by UV/vis spectrophotometers for the residual concentration of 2,4-D. The amount of 2,4-D adsorbed at any time, q_t (mg g^{-1}), was computed by:

$$q_t = \frac{(C_0 - C_t).V}{m} \tag{2}$$

where C_t is the concentration of 2,4-D at any time (mg L^{-1}).

2.4. Adsorption Isotherm Models

Langmuir, Freundlich and Temkin isotherm models were used to evaluate the data obtained from the 2,4-D adsorption experiments:

Langmuir model:

$$\frac{1}{q_e} = \frac{1}{Q * b * C_e} + \frac{1}{Q} \tag{3}$$

where q_e is the equilibrium adsorbed concentration (mg g^{-1}), C_e is the equilibrium concentration (mg L^{-1}), Q is the maximum sorption capacity (mg g^{-1}) and b is the adsorption equilibrium constant.

Freundlich model:

$$lnq_e = lnK_f + \frac{1}{n} lnC_e \tag{4}$$

where K_f is the Freundlich affinity coefficient, n is the Freundlich exponential coefficient.

Temkin model:

$$q_e = \frac{RT}{b_T} lnA_T + \frac{RT}{b_T} lnC_e \tag{5}$$

where A_T and b_T are the Temkin coefficients.

2.5. Adsorption Kinetics

Several methods are available to study the adsorption mechanism. In this study, in order to determine the adsorption kinetics, the data obtained from the 2,4-D adsorption process were analyzed with the pseudo first order, pseudo second order, Elovich and intra particle diffusion models.

Pseudo first order model:

$$ln(q_e - q_t) = k_1 t + ln(q_e) \tag{6}$$

where; q_e is the adsorbed amount at equilibrium (mg g^{-1}), q_t is the adsorbed amount at time t (mg g^{-1}), and k_1 is the rate constant (min^{-1}).

Pseudo second order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

where, k_2 is the pseudo second order adsorption kinetic parameter (g mg^{-1} min^{-1}).

Elovich model:

The Elovich equation is valid for chemisorptions kinetics and systems in which the surface is heterogeneous.

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{8}$$

where; α is the initial adsorption rate (mg g^{-1} min^{-1}), β is the constant related to extent of surface coverage and activation energy consumption (g mg^{-1}).

Intra particle diffusion model:

$$q_t = k_i t^{0.5} + C_i \tag{9}$$

where; k_i is the intra particle diffusion kinetic parameter (mg g^{-1} min^{-2}), and C_i is the constant related to layer thickness (mg g^{-1}).

3. RESULTS AND DISCUSSION

3.1. Effect of Initial Concentration

In order to determine the effect of initial concentration of 2,4-D, the adsorption of this pesticide on peanut shell adsorbent at constant pH and temperature value was studied as a function of different initial concentrations and the results were shown in Fig 2.

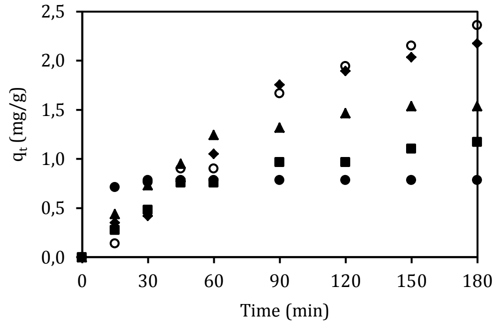

Fig 2. Effect of initial concentration on the adsorption of 2,4-D on peanut shells (● 10 mg L^{-1}; ■ 20 mg L^{-1}; ▲ 30 mg L^{-1}; ♦ 40 mg L^{-1}; ○ 50 mg L^{-1})

3.2. Adsorption Isotherms

Three classic adsorption models (Langmuir, Freundlich and Temkin isotherm models) were used to describe the equilibrium adsorption data of the 2,4-D onto peanut shell samples.

The % removal value decreased from 78.6 to 47.2 as the initial concentration was increased from 10 to 50 mg L^{-1}; indicating the effect of loading of pesticides molecules on adsorption. However, the total amount of 2,4-D adsorbed on the adsorbent increases with increase in 2,4-D concentration in the initial solution. It is clear that the rate of adsorption of both the pesticides depends on the initial concentration of pesticides.

Among these isotherm models, Freundlich isotherm model was determined as the most appropriate one for the pesticide adsorption data with the high values of correlation coefficient (R^2) and low values of standard error (δ). The statistical parameters of these models were presented in Table 1. K_f and n were Freundlich coefficients which show the capacity of adsorption and adsorption intensity, respectively. The adsorption intensity, n, represents the degree of non-linearity between solution concentration and adsorption. If n<1 then adsorption is chemical adsorption; if n>1 then adsorption process is physical [13]. From Table 1, the K_f and n were found as 0.5231 and 2.40, respectively. This n value (2.40) indicates the physical adsorption of pesticide onto peanut shell. The situation n>1 is most common and may be due to a distribution of surface sites or any factor that causes a decrease in adsorbent-adsorbate interaction with increasing surface density [13]. This result (n>1) was in agreement with the results obtained from literature for adsorption of Tartrazine using hen feathers [14], adsorption of zinc ions using coal fly ash [15].

3.3. Adsorption Kinetic Modelling

Evaluation of the adsorption kinetic as well as adsorption equilibrium is very important to plan and control the adsorption process. In order to describe the adsorption kinetic, the pseudo first order, the pseudo second order, Elovich and the intra particle diffusion models were used for the evaluation of kinetic data obtained from the adsorption experiments. As can be seen from Table 2, among these models, pseudo first order kinetic model was observed as the most appropriate one for all the experimental data with the high values for the coefficient of determination and low the standard error values. According to Table 2, the rate constant, k_1, was found as 0.0143 min^{-1} for adsorption of 2,4-D pesticide onto peanut shell. Similar kinetic model was found from literature for adsorption of acid dyes onto chitosan [16], adsorption of N719 dye on TiO_2 surface [17] and adsorption of Cr(VI) onto hazelnut shell activated carbon [18].

Table 1. The estimated parameters and statistical values of isotherm models for 2,4-D adsorption onto peanut shell samples

Adsorption Isotherm	**Isotherm Equations**	**R^2**	**δ**
Langmuir	C_e/q_e= 0.3143C_e + 3.6618	0.8194	1.4231
Freundlich	ln(q_e)=0.416ln(C_e)–0.6479	0.9347	0.1368
Temkin	q_e = 0.6269ln(C_e) – 0.0624	0.8160	0.2999

Table 2. The estimated parameters and statistical values of kinetic models for 2,4-D adsorption onto peanut shell samples

Kinetic Model	**Model Equations**	**R^2**	**δ**
Pseudo First Order	$ln(q_e$-$q_t)$ = 0.0143t + 0.907	0.9902	0.1061
Pseudo Second Order	q_t/t = 0.2416t + 33.087	0.9701	2.7162
Elovich	q_t = 0.8063ln$t$ -1.9364	0.9672	0.6542
Intra Particle Diffusion	lnq_t = 0.6851ln$t$ – 2.6362	0.9895	0.7819

4. CONCLUSION

Adsorption experiments were carried out using adsorption equilibrium and kinetics to investigate the adsorption ability of the peanut shell samples. The amount of 2,4-D adsorbed increased with increasing 2,4-D concentration in the initial solution. The isotherm data for 2,4-D adsorption on peanut shell fitted well to the Freundlich isotherm model. Furthermore, kinetic data were fitted to the pseudo-first-order kinetic model. As a result, it can be concluded that peanut shell samples can be employed as effective adsorbents for adsorption of pesticides.

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RESEARCH ARTICLE

Method for synthesis and control of biofuel supply chains integrated with the relevant systems for utilization of production-generated waste by-products

Yunzile R. Dzhelil*[,1], E. Ivanov Ganev[1], B. Bonev Ivanov[1], D. Gospodinov Dobrudzhaliev[1]

[1]Bulgarian Academy of Sciences, Institute of Chemical Engineering, 1113 Sofia, BULGARIA

ABSTRACT

Last decade has seen reduction of amount of fossil raw materials for production of conventional fuels that in turn has been accompanied by deepening of the environmental problems. There is a trend of biofuel production rise accompanied by increase of the amount of waste produced. The waste is classified as productive (i.e. technological) one and operational one (for utilization of biofuels and their value). The study is focused on the creation of tools for supply chains (SC) by description/formulation of optimal management of production and operational waste. Tools are developed for production and use of biofuels that include a mathematical model and its optimization. The procedures are based on the following criteria/conditions: known production technology, spatial distribution logistics and production units and environmental pollution by waste fuel gases containing prevailingly CO_2. The SC building also aims to provide the necessary fuel quantities for heating and transport systems as well as to foresee their optimization in terms of the environmentally-friendly aspect.

Keywords: Biofuels, synthesis and management, supply chain, greenhouse gas, solid waste

1. INTRODUCTION

Production and use of biofuels are promoted worldwide. Their use could potentially reduce emissions of greenhouse gases and the need for fossil fuels [1]. Accordingly, the European Union imposes a mandatory target of 10% biofuels by 2020 [2]. These fuels are produced from biomass. Their use for energy purposes has the potential to provide important benefits. Burning them releases such amount of CO_2 as was absorbed by the biomass in its formation [3]. Another advantage of biomass is its availability in the world due to its variety of sources (energy and oilseeds, algae, wood, agricultural, municipal, industrial and animal waste). Despite the advantages of biomass with increasing quantities of biofuels to achieve the objectives of the European Union, this is accompanied by growing quantities of waste products. These wastes are related to the lifecycle of biofuels from crop cultivation, transportation, production to distribution and use. The main liquid biofuels are bioethanol and biodiesel. Depending on the raw material used, production is considered in three generations.

The first generation used as feedstock crops containing sugar and starch (corn, wheat, sugarcane, etc.) to produce bioethanol, and oilseed crops (sunflower, canola, soybean oil, etc.) to produce biodiesel [4]. In the production of biodiesel, the advantage of these materials is that they can be grown on contaminated and saline soils, as the process does not affect the fuel production. The drawback is that they raise issues related to their competitiveness in the food sector. These materials also have a negative impact in terms of the quantity of water consumed. This is related to their cultivation that requires significant amounts of water resources. Excessive use of fertilizers, pesticides and chemicals to grow them also leads to accumulation of pollutants in groundwater that can penetrate into water courses and thus degrade water quality.

According to the second generation, bioethanol is produced by using as raw material waste biomass (agricultural and forest waste) [5], i.e. lignocellulose which is transformed into a valuable resource as bioethanol. In this case, biodiesel can be produced by using as energy crops raw material obtained from

Corresponding Author: unzile_20@abv.bg (Yunzile R. Dzhelil)

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kitchen, animal, organic industrial waste and sewage. Many European countries have a problem with overproduction of organic wastes from industry and households. Biofuel production second generation is an excellent way to deal with increasingly restrictive national and European regulations in this area and the use of organic waste for energy production and fertilizer as a byproduct. Logistics and use of these materials can be challenging due to the fact that they are usually dispersed. Another disadvantage from an environmental perspective is the need for further purification and processing.

The third generation comprises production from microalgae which occur as promising feedstock for biofuel production. The advantage of this biomass is that it is a year-round production and does not compete with the food industry [6].

The main technologies for production of bioethanol are fermentation, distillation and dehydration. In the preparation of biodiesel using the transesterification method, as a result of these technologies receives the fuel and waste. The wastes of biofuels are divided into production and performance. The technological waste is produced mainly in the creation of products that occur as waste production. The management of these wastes is related to their reduction, recovery and disposal. These guidelines are united in the idea of acquiring more sophisticated production processes. Efforts are focused on the use of new sources of raw materials, new processes, and new ways of realization of the side products. The use of by-products as raw materials for other production closes cycle in the supply chain, reducing the price of obtaining fuel. Operational waste associated with gases and emissions released during operation and the burning of biofuels.

2. PROBLEM STATEMENT

The present study deals with the issue of designing optimal integrated Supply Chains (SC) for waste management in the process of biofuel production and usage. Tools have been developed for formulation of a mathematical model for description of the parameter, the restrictions and the goal function.

The problem addressed in this work can be formally stated as follows. Given are a set of biofuel crops that can be converted to biofuel. These include agricultural feedstock's e.g. sunflower, energy crops, etc. A planning horizon of one year for government regulations including manufacturing, construction and carbon tax is considered. A Biofuel Supply Chain (BSC) network superstructure including a set of harvesting sites and a set of demand zones, as well as the potential locations of a number of collection facilities and bio refineries are set. Data for biofuel crops production and harvesting are also given. For each demand zone, the biofuel demand is given, and the environmental burden associated with biofuel distribution in the local region is known. For each transportation link, the transportation capacity, available transportation modes, distance, and emissions of each transportation type are known.

2.1. General Formulation of the Problem

The overall problem can be summarized, as follows:

- Potential locations of fuel demand centers and their biofuel demand,
- Demand for petroleum fuel for each of the demand centers for fuel,
- The minimum required ratio between petroleum fuel and biofuel for blending,
- Biomass feedstock types and their geographical availability,
- Specific Green House Gas (GHG) emission factors of the biofuel life cycle stages,
- Potential areas where systems for utilization of solid waste from production can be installed.

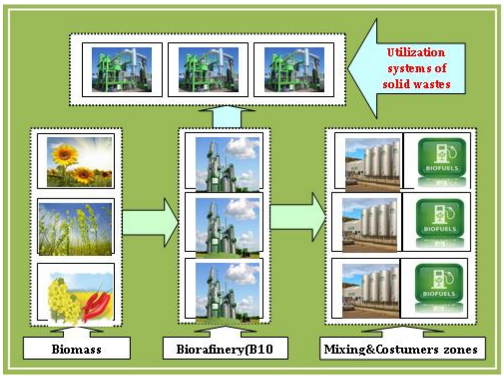

Fig 1. Superstructure integrated biofuel supply chain

The objectives are to maximize the environmental performances of the BSC by optimizing the following decision variables:

- Supply chain network structure,
- Locations and scales of biofuel production facilities and biomass cultivation sites,
- Flows of each biomass type and biofuel between regions,
- Modes of transport for delivery for biomass and biofuel (B100),
- The GHG emissions for each stage in the life cycle,
- Supply strategy for biomass to be delivered to production facilities,
- Distribution processes for biofuel to be sent to demand zones.

2.2. Mixed Integer Linear Programming (MILP) Model Formulation

The role of the optimization model is to identify what combination of options is the most efficient approach to supply the facility. The problem for the optimal location of biofuel (B100) production plants and the efficient use of the available land is formulated as a MILP model with the following notation:

The input sets, input parameters and the decision variables are given in Table 1, Table 2 and Table 3, respectively.

Table 1. Input sets used in the model

Sets/Indices	Index
Set of biomass types	I
Set of transport modes for biomass	L
Set of transport modes for solid wastes	M
Set of transport modes for biofuel and petroleum fuel	B
Set of life cycle stages of a BSC	ST
Set of plant size intervals	P
Set of utilization plant size intervals	S
Set of regions of the territorial division	GF
Set of candidate regions for biomass production, which is a subset of GF	G
Set of candidate regions for biofuel plant established, which is a subset of GF	F
Set of biofuel customer zones, which is a subset of GF	C
Set of utilization waste zones, which is a subset of GF	W

Table 2. Input parameters for the problem

Symbol	Description	Units
$EFBP_i$	Emission factor for biofuel (B100) production from biomass type $i \in I$	$\frac{kg\ CO_2 - eq}{ton\ biofuel}$
$EFBC_{ig}$	Emission factor for cultivation of biomass type $i \in I$ in region $g \in G$	$\frac{kg\ CO_2 - eq}{ton\ biomass}$
$EFTRA_{il}$	Emission factor for transport of biomass per unit of type $i \in I$ with transport type $l \in L$	$\frac{kg\ CO_2 - eq}{ton\ km}$
$EFTRB_b$	Emission factor for transport of biofuel (B100) with transport $b \in B$	$\frac{kg\ CO_2 - eq}{ton\ km}$
$EFTRW_m$	Emission factor for transport of solid waste with transport $m \in M$	$\frac{kg\ CO_2 - eq}{ton\ km}$
$EFTM_l$	Emission factor of transportation for mode $l \in L$	$\frac{kg\ CO_2 - eq}{ton\ km}$
ESW	Emission factor of pollution caused by one tone of solid waste if not used	$\frac{kg\ CO_2 - eq}{ton\ solid\ waste}$
ECB	Emissions emitted during the combustion of **CO_2** unit biofuel (B100)	$\frac{kg\ CO_2 - eq}{ton\ biofuel}$
ECG	Emissions emitted during the combustion of **CO_2** unit petroleum fuel	$\frac{kg\ CO_2 - eq}{ton\ biofuel}$
$GHGB$	GHG emission from biofuel supply chain	$\frac{kg\ CO_2 - eq}{ton\ km}$
ADD_{gfl}	Actual delivery distance between regions producing biomass and regions producing biofuel (B100) via model $l \in L$	km
ADF_{fcb}	Actual delivery distance between regions producing biofuel (B100) and demand regions $c \in C$ via model $b \in B$	km
ADW_{fwm}	Actual delivery distance between regions producing biofuel(B100) and utilization systems of solid wastes $w \in W$ via mod $m \in M$	km
γ_i	Biomass to biofuel (B100) conversion factor for biomass type $i \in I$ to biofuel (B100)	$\frac{ton\ biofuel}{ton\ biomass}$
YO_c	Years demands of petroleum fuel in the customer zones $c \in C$	$ton/year$
ENO	Energy equivalent unit of petroleum fuel	GJ/ton
ENB	Energy equivalent unit of biofuel (B100) from biomass	GJ/ton
PB_p^{MAX}	Maximum annual capacity of the plant of size $p \in P$	$ton/year$
PB_p^{MIN}	Minimum annual capacity of the plant of size $p \in P$	$ton/year$
PW_s^{MIN}	Minimum annual capacity of the utilization systems of solid wastes size $s \in S$	$ton/year$
PW_s^{MAX}	Maximum annual capacity of the utilization systems of solid wastes size $s \in S$	$ton/year$
QI_{ig}^{MAX}	Maximum flow rate of biomass $i \in I$ from region $g \in G$	$ton/year$
QB_f^{MAX}	Maximum flow rate of biofuel (B100) from region $f \in F$	$ton/year$
PBI_{ig}^{MAX}	Maximum biomass of $i \in I$ produced in the region $g \in G$ per year	$ton/year$
PBI_{ig}^{MIN}	Minimum biomass of $i \in I$ produced in the region $g \in G$ per year	$ton/year$
α_f	Operating period for the region $g \in G$ in a year	$ton/year$
αf_f	Operating period for plants in region $f \in F$in a year	$ton/year$
αc_c	Operating period for the region $c \in C$ in a year	$day/year$
αw_w	Operating period for region $w \in W$ within a year	$day/year$
A_g^S	Set-aside area available in region $g \in G$	ha
A_g^{Food}	Set-aside area available in region for food $g \in G$	ha
$TEIF^{MAX}$	Max. permissible values for the environmental impact of biofuel network of supply chain and fossil fuel in the regions	$kg\ CO_2 - eq\ /\ day$
B_{ig}	The yield per hectare of type $i \in I$ biomass in the region $g \in G$	ton/ha
QB_i^{Food}	The total amount of bio-resources of type $i \in I$ which must be provided for all regions $g \in G$ for food security	ton
$QT_l^{\ MIN}$	Optimal capacity of transport $l \in L$ for transportation of biomass	ton
$QTB_b^{\ MIN}$	Optimal capacity of transport $b \in B$ for transportation biofuel	ton
K_c^{MIX}	Proportion of biofuel (B100) and petroleum fuel subject of mixing for each of the customer zones $c \in C$	Dimensionless
SW	The total amount of solid waste generated for production of 1 ton biofuel	$\frac{ton\ solid\ waste}{ton\ biofuel}$

Table 3. Decision variables for the problem

Symbol	Description	Units	Type
PBB_{ig}	Production rate of biomass $i \in I$ in region $g \in G$	*ton/day*	*Continuous*
QI_{igfl}	Flow rate of biomass $i \in I$ via mode $l \in L$ from region $g \in G$ to $f \in F$	*ton/day*	*Continuous*
QB_{fcb}	Flow rate of biofuel via mode b from region $f \in F$ to $c \in C$	*ton/day*	*Continuous*
QW_{fwm}	Flow rate of solid waste via mode $m \in M$ from region $f \in F$ to $w \in W$	*ton/day*	*Continuous*
QEO_c	Quantity of petroleum fuel to be supplied to meet the energy needs of the region $c \in C$	*ton/year*	*Continuous*
QEB_c	Quantity of biofuel (B100) to be supplied to meet the energy needs of the region $c \in C$	*ton/year*	*Continuous*
QW_{fwm}	Flow rate of solid waste via mode m from region $f \in F$ to $w \in W$	*ton/day*	*Continuous*
A_{ig}	Land occupied by crop $i \in I$ in region $g \in G$	*ha*	*Continuous*
A_{ig}^F	Land occupied by crops $i \in I$ needed for food security	*ha*	*Continuous*
X_{igfl}	0-1 variable, equal to 1 if a biomass type $i \in I$ is transported from region $g \in G$ to $f \in F$ using transport $l \in L$ and 0 otherwise	*0 or 1*	*Binary*
Y_{fcb}	0-1 variable, equal to 1 if a biofuel is transported from region $f \in F$ to $c \in C$ using transport $b \in B$ and 0 otherwise	0 or 1	*Binary*
Z_{pf}	0-1 variable, equal to 1 if a plant size $p \in P$ is installed in $f \in F$ and 0 otherwise	0 or 1	*Binary*
W_{fwm}	0-1 variable, equal to 1 if a solid waste is transported from region $f \in F$ to $w \in W$ using transport $m \in M$ and 0 otherwise	0 or 1	*Binary*
ZW_{sw}	0-1 variable, equal to 1 if a utilization plant size $s \in S$ is installed in region $w \in W$ and 0 otherwise	0 or 1	*Binary*

2.3. Basic Relationships

As noted above, the assessment of BSC production and distribution of biofuel (B100) will be made by environmental criteria.

The environmental impact of the BSC is measured in terms of total GHG emissions (*kg CO_2-eq*) stemming from supply chain activities and the total emissions are converted to carbon credits by multiplying them with the carbon price (per *g CO_2-eq*) in the market.

The environmental objective is to minimize the total annual GHG emission resulting from the operations of the BSC. The formulation of this objective is based on the field-to wheel life cycle analysis, which takes into account the following life cycle stages of biomass-based liquid transportation fuels:

- biomass cultivation, growth, and acquisition,
- biomass transportation from source locations to processing facilities,
- transportation of biofuel (B100) facilities to the demand zones,
- local distribution of liquid transportation fuels in demand zones,
- emissions from biofuel (B100) usage in vehicle operations.

The ecological assessment criteria is the total environmental impact at work on BSC, estimated through the resulting greenhouse gas emissions as proposed in Akgul, O. et al. [7]. These emissions are equal to the sum of the impact of each stage of the life cycle:

$$TEI = EL_{BC} + EL_{BP} + EL_{TR} + EB_{CAR} + EW_{SW} \tag{1}$$

where;

TEI is total environmental impact on BSC (*kg CO_2 eq d^{-1}*);

$\left\{ \begin{matrix} EL_{BC} \\ EL_{BP} \\ EL_{TR} \end{matrix} \right\}$ are GHG impact of life cycle stages (*kg CO_2 eq d^{-1}*)

EB_{CAR} is emissions from biofuel (B100) usage in vehicle operations (*kg CO_2 eq d^{-1}*),

EW_{SW} is emissions from solid waste that are not processed in any of the utilization systems (*kg CO_2 eq d^{-1}*)

The evaluation of the environmental impact at every stage *st* ∈ *ST* of the life cycle estimates:

- growing biomass;
- production of biofuel (B100);
- transportation resources (biomass and biofuel (B100));
- utilization of solid waste.

The greenhouse gases to grow biomass EL_{BC} *are;*

$$EL_{BC} = \sum_{i \in I} \sum_{g \in G} (EFBC_{ig}\ PBB_{ig}) \tag{2}$$

where, EL_{BC} denotes the total environmental impact (*kg CO_2 eq d^{-1}*) of biomass cultivation, which in general represents the production rate of resource $i \in I$ in region $g \in G$, in this equation it refers to the cultivation rate of biomass $i \in I$ in that region.

The total emissions from biofuel (B100) production EL_{BR} are determined by the equation:

$$EL_{BP} = \sum_{g \in G} \sum_{i \in I} \sum_{f \in F} \sum_{l \in L} (EFBP_i \gamma_i\ QI_{igfl}) \tag{3}$$

where EL_{BP} is total environmental impact of biofuel (B100) production (*kg CO_2 eq d^{-1}*).

The environmental impact of transportation EL_{TR} is calculated by:

$$EL_{TR} = EL_{TR}^{Biomass} + EL_{TR}^{Biofuel} + EL_{TR}^{Waste} \tag{4}$$

where;

$$EL_{TR}^{Biomass} = \sum_{i \in I} \sum_{g \in G} \sum_{f \in F} \sum_{l \in L} (EFTRA_{il} ADD_{gfl} QI_{igfl})$$

$$EL_{TR}^{Biofuel} = \sum_{f \in F} \sum_{c \in C} \sum_{b \in B} (EFTRB_b\ ADF_{fcb}\ QB_{fcb})$$

$$EL_{TR}^{Waste} = \sum_{f\in F}\sum_{w\in W}\sum_{m\in M}\left(EFTRW_m\ ADW_{fwn}\ QW_{fwm}\right)$$

where $EL_{TR}{}^{Waste}$ is environmental impact of transportation of resources and solid waste (*kg* CO_2 *eq* d^{-1})

Emissions from biofuel (B100) usage in vehicle operations EB_{CAR}:

$$EB_{CAR} = \sum_{f\in F}\sum_{c\in C}\sum_{c\in B}\left(ECB\ QB_{fcb}\right) \qquad (5)$$

where EB_{CAR} is emissions from biofuel (B100) usage in vehicle operations (*kg* CO_2 *eq* d^{-1})

Emissions from solid waste not treated in any of the waste recovery systems installed:

$$EW_{SW} = ESW\left(SW\sum_{f\in F}\sum_{c\in C}\sum_{b\in B}QB_{fcb} - \sum_{f\in F}\sum_{w\in W}\sum_{m\in M}QW_{fwm}\right) \qquad (6)$$

2.4. Total Environmental Impact of the Used Fuels to Provide the Energy Balance of the Region

The environmental goal is to reduce the annual equivalent of GHG emission, resulting from the operations of SC of biofuel and petroleum fuel to meet the energy needs of the regions.

The annual equivalent of greenhouse gases by the used fuels is determined by the equation:

$$TEIF = TEI + EG_{CAR} \qquad (7)$$

where *TEIF* is the total environmental impact of the used fuels (biofuel (B100) and petroleum fuel) to provide the energy balance of the region; *TEI* is the total environmental impact at work on BSC; and EG_{CAR} is the emissions from petroleum fuels usage in vehicle operations.

Emissions from fuel EG_{CAR} vehicles used, to supplement the energy balance:

$$EG_{CAR} = \sum_{c\in C}\left(\frac{ECG\ QEO_c}{\alpha c_c}\right) \qquad (8)$$

2.5. Restrictions

Plants capacity limited by upper and lower constrains:

Plants capacity is limited by upper and lower bounds, where the minimal production level in each region is obtained by:

$$\sum_{p\in P}\left(PB_p^{MIN}\ Z_{pf}\right) \le \alpha f_f\sum_{c\in C}\sum_{b\in B}QB_{fcb} \le \sum_{p\in P}\left(PB_p^{max}Z_{pf}\right), \forall f\in F \qquad (9)$$

Constraints balance of biofuel (b100) to be produced from biomass available in the regions:

$$\sum_{c\in C}QEB_c \le \sum_{i\in I}\sum_{g\in G}\left(\gamma_i\ \beta_{ig}\ A_g^S\right) \qquad (10)$$

A condition that ensures that the total amount of solid waste generated by all bio-refineries can be processed in the plants built for this purpose:

$$\sum_{w\in W}\sum_{m\in M}QW_{fwm} \le SW\sum_{c\in C}\sum_{b\in B}QB_{fcb}, \forall f\in F \qquad (11)$$

A restriction that ensures that the amount of solid waste processed at the plant is within its production capacity:

$$\sum_{s\in S}P_S^{MIN}\ ZW_{sw} \le \alpha w_w\sum_{f\in F}\sum_{m\in M}QW_{fwm} \le \sum_{s\in S}P_S^{MAX}\ ZW_{sw}, \forall w\in W \qquad (12)$$

Restriction guarantees that a given region g ∈ G installed power plant with p ∈ P for biofuel (B100) production. Constraints (13) and (14) state that can be chosen only one size for each facility and for utilization systems of solid wastes, respectively.

$$\sum_{p\in P}Z_{pf} \le 1, \forall f\in F \qquad (13)$$

$$\sum_{s\in S}ZW_{sw} \le 1, \forall w\in W \qquad (14)$$

Limitation ensure the availability of at least one connection to a region of bioresources and region for biofuel:

$$\sum_{g\in G}\sum_{l\in L}X_{igfl} \ge \sum_{c\in C}\sum_{b\in B}Y_{fcb} \ge \sum_{p\in P}Z_{pf}, \forall i\in I, \forall f \qquad (15)$$

Limit which guarantees that each region will provide only one plant with a biomass type i∈ I:

$$\sum_{f\in F}\sum_{l\in L}X_{igfl} \le 1, \forall i\in I, \forall g\in G \qquad (16)$$

Limitation of assurance that at least one region $g\in G$ *producing biomass is connected to a plant located in a region* $f\in F$:

$$\sum_{b\in B}Y_{fcb} \le 1,\ \forall f\in F,\ \forall c\in C \qquad (17)$$

Limitation of assurance that at least one region $f\in F$ *producing biofuel is connected to a plant located in region* $w\in W$:

$$\sum_{m\in M}W_{fwm} \le 1,\ \forall f\in F,\ \forall w\in W \qquad (18)$$

Condition ensuring that the solid waste produced from a given bio-refinery will be processed in only one of the plants for use:

$$\sum_{m\in M}\sum_{w\in W}W_{fwm} = \sum_{p\in P}Z_{pf},\ \forall f\in F \qquad (19)$$

Condition ensuring that a plant used in a given region will be connected to at least one plant in which solid waste is generated:

$$\sum_{m\in M}\sum_{w\in W}W_{fwm} \ge \sum_{s\in S}ZW_{sw},\ \forall w\in W \qquad (20)$$

Restriction on transportation of biomass is;

$$PBI_{ig}^{MIN}\sum_{l\in L}X_{igfl}\le\alpha_g\sum_{l\in L}QI_{igfl}\le PBI_{ig}^{MAX}\sum_{l\in L}X_{igfl},\forall i\in I,\forall g\in G,\forall f\in F \qquad (21)$$

Restriction for total environmental impact of all regions:

$$TEIF\ \le TTEIF^{MAX} \qquad (22)$$

where *$TEIF^{MAX}$* are the maximum permissible values for the total environmental impact of the biofuel (B100) network of supply chain and fossil fuel in the regions (*$kg\ CO_2\ eq\ d^{-1}$*).

Mass balances between biofuel (b100) plants and biomass regions:

The connections between biofuel (B100) plants and biomass regions are given by:

$$\sum_{l\in L}\sum_{g\in G}\sum_{i\in I}\left(\gamma_i QI_{igfl}\right)\le\sum_{p\in P}\left(PB_p^{MAX}Z_{pf}\right),\ \ \forall f\in F \qquad (23)$$

Mass balances between biofuel (b100) plants and biofuel customer zones:

$$\sum_{b\in B}\sum_{f\in F}\left(\alpha f_f QB_{fcb}\right)=\ QEB_c\ ,\ \ \forall c\in C \qquad (24)$$

Limitation guaranteeing crop rotation:

The crop rotation allows ensuring control of pests, improving soil fertility, maintenance of the long-term productivity of the land, and consequently increasing the yields and profitability of the rotation [8], [9]. The combination of crop rotation and fallowing is a common practice that is gaining momentum again due to environmental benefits and promoted reduction in the dependence on external inputs.

Crop rotation implemented in a region $g\in G$ means that the growing area of energy crops are rotated so that the next time the same area is used by other crops grown under are optimal scheme of crop rotation. This can be achieved if for land A_{ig} and A_{ig}^F inequalities are implemented:

$$\left(A_{ig}+\ A_{ig}^F\right)2.0\ \le\ \left(A_g^S+A_g^{Food}\right),\forall i\in I\ ,\forall g\in G \qquad (25)$$

Energy restriction:

Limitation ensuring that the overall energy balance in the region is provided by:

$$ENO\sum_{c\in C}QEO_c+ENB\sum_{c\in C}QEB_c=ENO\sum_{c\in C}YO_c \qquad (26)$$

Limitation ensuring that each region will be provided in the desired proportions with fuels;

$$ENBQEB_c=\ K_c^{mix}ENOYO_c\ , \qquad \forall c\in C \qquad (27)$$

2.6. Optimization Problem Formulation

The problem for the optimal design of a BSC is formulated as a MILP model for the objective function of Minimizing GHG emissions. As discussed above the environmental objective is to minimize the total annual CO2 -equivalent greenhouse gas emissions resulting from the operations of the biofuel supply chain and oil, used to provide the energy balance of the regions. The formulation of this objective is based on total the GHG emissions in the supply chain and other fuels are estimated, throw Life Cycle Assessment (LCA) approach, where emissions are added for every life stage.

The task of determining the optimal location of facilities in the regions and their parameters is formulated as follows:

$$\left\{\begin{matrix} Find: X[Decision\ variables]^T \\ MINIMIZE\ \{TEIF(X)\}\rightarrow(Eq.7) \\ s.t.: \{Eq.8-Eq.27\} \end{matrix}\right\} \qquad (28)$$

The problem is an ordinary MILP and can thus be solved using standard MILP techniques. The present model was developed in the commercial software General Algebraic Modeling System(GAMS) [10] using the solver CPLEX. The model chooses the less costly pathways from one set of biomass supply points to a specific plant and further to a set of biofuel (B100) demand points. The final result of the optimisation problem would then be a set of plants together with their corresponding biomass and biofuel (B100) demand points.

3. DISCUSSION AND CONCLUSIONS

This paper studies the interactions among biofuel supply chain design, agricultural land use and local food market equilibrium. The study has been focused on the eco comparable behavior of the stakeholders in the biofuel supply chain incorporating them into the supply chain design model. The model includes the problem of crop rotation and solid waste utilization. The model is believed to be important for practical application and can be used for design and management of similar supply chains.

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RESEARCH ARTICLE

CO_2 capture analysis of tobacco biochar-$AlCl_3$ composite

Nejmi Soyler[*,1], Selim Ceylan[1], Yildiray Topcu[1]

[1]Ondokuz Mayis University, Department of Chemical Engineering, 55139, Samsun, TURKIYE

ABSTRACT

In this study, the performance of tobacco biochar-$AlCl_3$ composite for CO_2 capture was investigated. Biochar-$AlCl_3$ composites were prepared at different blend ratios (10:0.4; 10:2; 10:4, wt./wt.) and used for CO_2 capture experiments to determine the optimal Al metal content at which CO_2 adsorption was highest. Biochar composites were produced through slow pyrolysis under inert nitrogen atmosphere in a fixed bed reactor at 600°C for 3h. Properties of biochar-metal composites and raw biochar samples were characterized with SEM-EDS, XRD and FTIR analysis. CO_2 experiments were conducted in TGA under N_2 atmosphere with a flow rate of 50 ml/min at 25°C. The maximum CO_2 adsorption was observed as 59.97 mg g^{-1} for biochar: $AlCl_3$ composite at a ratio of 10:2. Finally, results of study showed that biochar-$AlCl_3$ composites have great potential as a CO_2 capture material due to its low-cost, sustainability and CO_2 capture capacity.

Keywords: Biochar, composite, CO_2 capture, $AlCl_3$

1. INTRODUCTION

Industrialization and increase in population has resulted in excess usage of fossil fuels (coal, natural gas, petroleum). There is increasing worldwide concern in relation between the use of fossil fuels and the fossil fuel derived emissions of greenhouse gases. The global warming is a serious environmental problem and attributed primarily to the increase of the greenhouse gases [1] which is threatening the life. Carbon dioxide (CO_2) is the major component of greenhouse gases and mainly produced from fossil fuel consumption [2]. In recent years, amount of CO_2 liberated by the utilization of fossil fuels has been over 30 gigatonnes [3]. Therefore, a great deal of researchers has intensively studied on CO_2 capture [4]. There are currently available CO_2 capture materials which are usually applied in power plants, cement manufacturing factories where CO_2 release. However, cost of current CO_2 capture adsorbents are still high, making process economically unfavourable. Furthermore, these systems use amine and other alkaline solvents to chemically bind CO_2, but they have negative effects on environment, such as high energy requirements and corrosion of process equipment. Thus, developing highly efficient and cost-effective adsorbents are urgently needed to capture and store CO_2. It is reported that carbon materials have potential to be used in CO_2 capture with high stability, high regeneration ability, and lower energy consumption than conventional chemical systems [5].

Biomass is a clean, renewable source which can be found in high amounts widely. Biochar is a pyrogenic carbon produced by pyrolysis of biomass under inert atmosphere conditions [6]. It has received much attention recently because of its application potential [7]. Biochar is a low-cost carbon material and it can be also used for soil improvement and carbon sequestration. Also, recent studies showed that biochar has the ability to capture CO_2 at levels comparable to well-known adsorbents. Biochar can also be regenerated easily using low level energy due to its physical adsorption behavior.

The CO_2 adsorption performance of biochar is strongly influenced by the modification of surface chemistry [8]. In a previous study, Creamer et al., (2016) used metal oxyhydroxide–biochar composites of cotton wood biochar and reported that CO_2 can be adsorbed at high amounts using metal oxyhydroxide–biochar composites. Tobacco is an important agricultural and industrial product for Turkey.

Corresponding Author: nejmisoyler@gmail.com (Nejmi Soyler)

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According to the data given by Turkey Statistical Institute, the annual production of tobacco was approximately 75 thousand tons at 2014. A great amount of waste tobacco biomass occurs after processing and causes an environmental problem. Therefore, in this study, waste biomass residues from tobacco industry were used to produce biochar and its composites with $AlCl_3$ through one-step slow pyrolysis at 600 ^oC. The tobacco biochar and its composites with various blend ratios of $AlCl_3$ were investigated to determine the potential and efficiency for CO_2 capture process.

2. MATERIALS AND METHODS

2.1. Materials

For this study, tobacco waste (TW) residues provided by a local company were used as a low-cost CO_2 capture material. TW was thus dried in oven at 70°C for 4 h. Dried residues were grounded with a kitchen type blender. Grounded samples were sieved and a particle size below 250 μm was used in experiments to prevent mass and heat transfer limitations. Aluminium chloride was purchased from Sigma-Aldrich Chemistry.

2.2. Preparation of Biochar/Metal Oxyhydroxide Composite

The biochar and its composite with different ratios of $AlCl_3$ were prepared according to procedure of a previous work by Creamer et al. (2015). Three different $AlCl_3$ amounts (0.2, 1 and 2 g) were solved in 60 mL of deionized (DI) water. 5 grams of tobacco waste was added into the solution and mixture was stirred. Raw biomass and its composites with $AlCl_3$ were placed in a tubular furnace (Magmatherm MT) and pyrolysed under inert N_2 atmosphere at 600 ^oC for 3 h. At the end of pyrolysis, samples were taken and washed with DI water several times to remove excess metal and impurities. Then, the product composite samples were dried at 60 °C in a vacuum oven and stored in sealed containers in desiccator until usage. The four biochar samples are labeled as TW0, TW02, TW1 and TW2 based on added $AlCl_3$ amount.

2.3. Characterization of Samples

The main characteristics of raw biochar and composites are given in Table 1. Composite samples and raw biochar were characterized for their metal content and crystal structure. Energy dispersive X-Ray spectroscopy (EDS) at 1000x magnification was used and Al content of biochars were determined. The elemental compositions of samples are shown in Table 1. Scanning electron microscope (SEM) imaging analysis of samples was conducted at 5000x and 8000x magnification to investigate distribution of Al on surface of composites. To detect and verify the existence of surface functional groups, FT-IR spectra of the biochar samples were taken with a Perkin Elmer-2000FTIR spectrometer. The spectra were recorded from 4000 to 650 cm^{-1} at a resolution of 1 cm^{-1}.

2.4. Carbon Dioxide Capture in TGA

CO_2 mass measurements were carried out using a Simultaneous DTA-TG Analyser (Shimadzu, Japan). For each experiment, about 20 mg sample was used. At first, temperature was ramped from room temperature to 120 ^oC with a heating rate of 20 °C min^{-1} under inert nitrogen gas and held for 20 min at this temperature to remove moisture and potential volatile components. Then sample was cooled to 25 ^oC with 10 °C min^{-1}. The inert gas flow rate was 50 mL min^{-1} for both heating and cooling. When the thermal equilibrium established, the CO_2 gas was fed at a rate of flow rate of 50 mL min^{-1} for 3 h.

2.5. Regeneration in TGA

TW1 biochar sample was selected to evaluate the efficiency of regeneration, since it showed the best CO_2 gas adsorption capacity in TGA experiments. Regeneration experiment study was conducted using a Simultaneous DTA-TG Analyzer (Shimadzu, Japan). After the CO_2 passed at 25^{o}C for 3 h, the gas switched to N_2 and the temperature was ramped to 120^{o}C again for 2 h with a heating rate of 20°C min^{-1}.

3. RESULTS AND DISCUSSION

3.1. Characteristics of Biochar

In order to determine elemental content of samples, EDS analysis was conducted at 1000x magnification. Fig 1 shows images obtained by SEM and results of EDS analysis. Location of elements on the surface of samples can be seen from images. EDS data analysis confirmed the presence of Al metal for each sample. As presented in Fig 1a-d, content of Al was gradually raised related with the biochar-metal ratios. The Al metal on the surface of the biochar samples can be identified with clear peak.

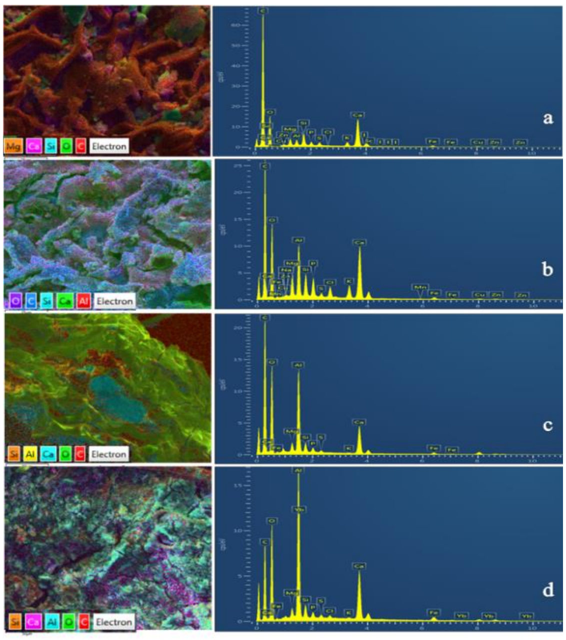

Fig 1. SEM-EDS analysis of representative biochar samples: (a) TW0 (b) TW02, (c) TW1, (d) TW2

Table 1. Elemental analysis of various biochar- $AlCl_3$ composites and raw biochar sample

Sample	***C***	***O***	***Mg***	***Al***	***Si***	***P***	***S***	***Cl***	***K***	***Ca***	***Sc***	***Fe***	***Cu***	***Zn***
TW0	64.85	24.88	0.82	**0.55**	1.15	0.37	0.34	0.03	0.62	4.98	0.1	0.47	0.32	0.33
TW02	53.08	30.73	1.53	**3.23**	1.33	1.23	0.26	0.76	1.13	5.48	-	0.56	0.25	0.29
TW1	53.1	35.84	0.68	**5.63**	0.61	0.33	0.14	-	0.03	3.14	-	0.49	-	-
TW2	41.95	37.93	0.77	**10.49**	0.97	0.45	0.24	0.22	0.11	5.71	1.16	-	-	-

- below detection limit

Elemental compositions of samples obtained by EDS analysis are tabulated and shown in Table 1. As can be seen from the table, various amount of Al metal successfully loaded into the biochar. Al metal content increased from 0.55 wt% for TW0 to 10.49 wt% for TW2.

XRD analysis was used to observe the crystallinity and type of metal oxyhydroxides present in samples. Fig 2 shows the wide angle XRD patterns of various $AlCl_3$-biochar samples. Apparently these samples had similar diffraction peaks, which could be indexed as the diffraction pattern of AlOOH. The XRD results confirmed that the metal oxyhydroxide particles in all the samples were highly crystalline.

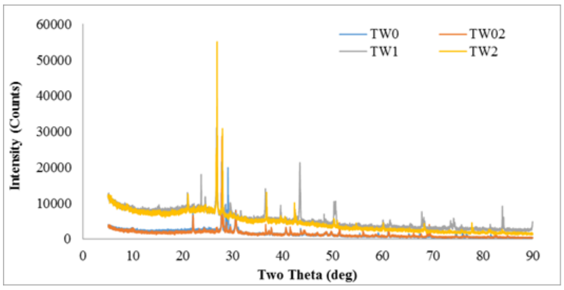

Fig 2. Wide angle XRD patterns of various biochar- $AlCl_3$ composite and raw biochar samples

In order to compare the nature of the functional groups present on the surface of the samples, FTIR analysis was performed. Fig 3 shows the results of FTIR measurements taken for tobacco biochar-$AlCl_3$ composite samples (TW0, TW02, TW1 and TW2). In spectrum of raw biochar (TW0), several peaks were observed at 3312, 1784, 1554, 1411 and 1316 cm^{-1} which can be attributed to O-H stretching vibration (alcohol), C=O group moieties, C=C aromatic groups [9, 10].

Biochar composites with metal optimization caused some changes in the spectra of samples (TW02, TW1 and TW2). At least six different peaks are found between 1519 and 1270 cm^{-1}. Karge (1992) [11] stated that $Al_xO_y^{n+}$ gives rise to a typical band at about 1450 cm^{-1}. FTIR results confirmed the presence of the Al metal in biochar composites.

3.2. Measurements of CO_2 Adsorption

A performance test of the CO2 adsorbing for each composite sample was carried out under the same conditions and results are shown in Fig 4.

As seen in Fig 4 a weight loss between 40-85 min for each sample was observed. This loss can be attributed to evaporation of moisture content. Adsorption capacities became gradually higher as the content of Al metal concentration was raised. Thereafter, the adsorption was constantly maintained until 10:2 blend ratio and then substantially decreased at 10:4 blend ratio. Based on these results, TW2 reacted with CO_2 from the starting point at room temperature and the maximum adsorption was observed as 59.74 mg g^{-1} at 165 min. Amounts of adsorbed CO_2 according to raw biomass and blend ratios at 10:0.4; 10:2; 10:4 was determined to be 40.10 mg g^{-1}, 59.02 mg g^{-1}, 59.97 mg g^{-1}, and 44.38 mg g^{-1}, respectively.

These adsorption capacities of different samples were referenced to explain the effect of metal content in tobacco biochar composites.

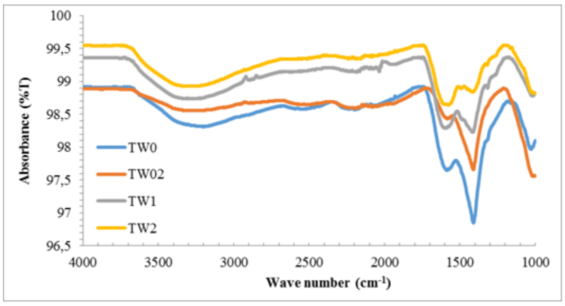

Fig 3. Representative FT-IR spectra of biochar- $AlCl_3$ composite and raw biochar samples

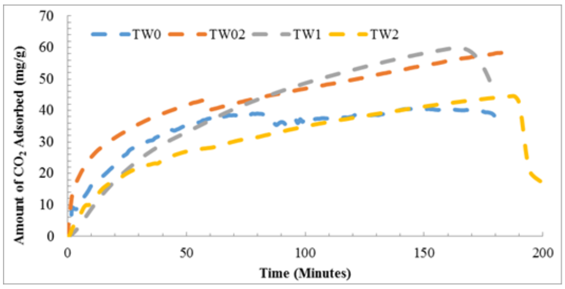

Fig 4. CO_2 adsorption capacities of biochar- $AlCl_3$ composite and raw biochar samples

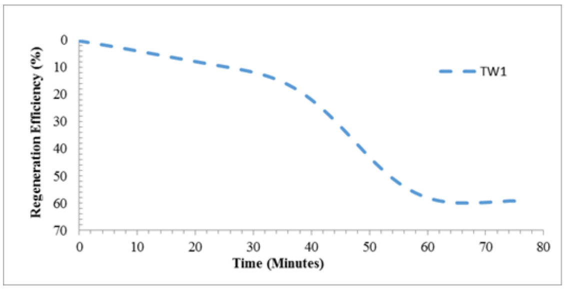

Fig 5. Regeneration efficiency curve of selected biochar sample (TW1) according to temperature under pure N_2 feeding condition

Bhagiyalakshmi et al. (2011) [12] stated that adsorbents for CO^2 capture suffer a high regeneration temperature around 400 to 800 ^oC. As seen in Fig 5, the desorption occurred between 0-60 min at 120 ^oC. Results confirmed that CO^2 is substantially removed from biochar composite and TW1 can be easily regenerated by simple desorption at low temperature.

4. CONCLUSION

In this study, the effect Al metal content on CO_2 capture performance of biochar composites was investigated. In summary, it was found that adsorption capacity of CO_2 can be increased with the increase in Al content up to 10:4 blend ratio. Then a decrease in adsorbed CO_2 amount was absorbed. The Aluminium–biochar composite at 10:2 blend ratio (TW1) has shown the best adsorption capacity as 59.97 mg g^{-1}. The results were comparable with the results given in literature. Therefore, it is concluded that tobacco biochar-$AlCl_3$ composites have a potential for CO_2 capture and can be proposed as a low-cost and high-efficient adsorbent with high adsorption capacity. Furthermore, it can be regenerated at lower temperatures which mean reduced energy needs for re-usage.

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RESEARCH ARTICLE

Copper removal from ammoniacal spent etchant by using magnetic nanoparticles

Oumer Ali Yassin*,[1], Zehra Semra Can[1], Gul Gulenay Haciosmanoglu[1], Ebru Toksoy Oner[2], Seval Genc[3]

[1]Marmara University, Environmental Engineering Department, 34722 Goztepe, Kadikoy, Istanbul, TURKIYE
[2]Marmara University, Bioengineering Department, 34722 Goztepe, Kadikoy, Istanbul, TURKIYE
[3]Marmara University, Metallurgical and Materials Engineering Department, 34722 Goztepe, Kadikoy, Istanbul, TURKIYE

ABSTRACT

Using magnetic nanoparticles (MNPs) is becoming popular method to remove heavy metal ions from different waste streams because it is simple, low-cost and effective. In this study, the bare and polymer coated Magnetite Iron Oxide (Fe_3O_4) MNPs were assessed for their adsorption capability in removing cupric (Cu^{2+}) ions from ammoniacal spent etchant solution, which is originated from the production of Printed Circuit boards (PCBs). The polymers used to coat the MNP in this study were chitosan, levan and oleic acid. The batch adsorption experiments were conducted at a temperature of 20^{o}C and the pH of the solution was between 9.0 and 9.5. Experimental results showed that adsorption was achieved within 2 hours, and the maximum amount of Cu^{2+} ions adsorbed by unit weight of MNP was observed by chitosan coated MNP with an adsorption capacity of 125 mg g^{-1}. In addition, Zeta potential measurements showed that all MNPs used in adsorption tests had negative surface charges at around pH 9.0. The more negatively surface charge MNPs the more copper ions they can adsorb. From this experiment it can be concluded that chitosan coated magnetic nanoparticle can be widely used for the removal of copper ions from water and wastewaters.

Keywords: Copper adsorption, magnetic nanoparticles, printed circuit boards, spent etchant

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1. INTRODUCTION

Heavy metals released into the environment from industries like plating plants, mining, metal finishing, welding and alloy manufacturing pose a significant threat to the environment and public health [1]. Unlike some organic pollutants, heavy metals cannot be degraded into lower-toxic substances and, therefore, they can accumulate in soil and water reservoirs, leading to harmful effects on living species via the biological accumulation of food chain [2]. The metals that cause serious pollution and toxicity problems include chromium (Cr), mercury (Hg), copper (Cu), nickel (Ni), zinc (Zn) and cadmium (Cd) [3].

Copper, which is a common harmful heavy metal ion in industrial wastewaters, is one of the essential elements that are required to maintain the normal structure and function of cells. However, excessive amount of copper can cause abnormal metabolism [4]. The consumption of water that contains copper at concentrations more than the permissible level of 2 mg L^{-1} could cause stomach and intestinal distress, anaemia, liver and kidney damage [5]. In addition, if copper is ingested excessively in human diet, it may result in vomit, cramps, convulsion, and even death [6]. According to the United States Environmental Protection Agency (USEPA) and the World Health Organization (WHO), the permissible levels for copper in drinking water are 1.3 and 2 mg L^{-1}, respectively [7].

One of the industrial wastewaters that contain high amount of copper in their effluents is Spent Etchant. The spent etchant solution, which is the waste product of etching operation from printed circuit board (PCB) industries, is a high concentration hazardous waste [8]. PCBs are important components of modern electronic products, which have generated 40 billion of US dollars globally in 2009 [9]. The PCB processes result in the production of around 0.7 million m^3 of the waste yearly if keeping using the conventional way of maintaining constant etching rate, known as chemical regeneration [10]. PCBs use

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Corresponding Author: nuralah.seid2002@gmail.com (Oumer Ali Yassin)

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around 28% of metal content, 10–20% of which is copper, 1–5% is lead and 1–3% is nickel [11].

The manufacture of PCBs involves several technical processes, and etching is one of the most important steps. According to the design of PCB, the unmasked copper is chemically dissolved into the etchant and the desired circuit pattern is produced. Numerous etching solutions have been used including ferric chloride, chromic acid, sulfuric acid, hydrogen peroxide, acidic copper chloride and ammoniacal (alkali) etchant solutions. Among these, the ammoniacal etchant solution presents advantages of fast etching, stability and high efficiency, so it is widely used in PCB process [12].

Spent ammoniacal etchant solution is a hazardous solution produced when copper is etched with ammoniacal etchant. This waste solution is alkaline solution at a pH of 8.5-9.5, having a typical copper concentration of 130-160 g L^{-1}, a chloride concentration of 175-190 g L^{-1}, ammonia concentration of 170-201 g L^{-1} and a molar ratio of ammonia to copper 4:1. Usually the solution contains also trace quantities of organic and/or inorganic chemical additives required for the etching process [13].

The presence of ammonia and other heavy metals in the solution make it hazardous and cause health and environmental problems. The most difficult problem of the solution is caused by due to the complex formed between copper and ammonia. Tetraamminecopper (II) ion $[Cu(NH_3)_4^{2+}]$ is the major complex specie formed in spent ammoniacal etchant. The complex is very difficult to break and prevents the precipitation of metal [14]. If this waste solution is discharged in to the environment without treating, it can cause a complicated environmental and health problems. Thus, the rapid and effective removal of Cu^{2+} from wastewater is among the most important issues in wastewater treatments.

Nowadays, adsorption of Cu^{2+} ions on magnetic nanoparticles is becoming popular to remove copper from different waste streams because it is simple, low-cost and effective. Therefore, the aim of this study is to assess bare and polymer coated Fe_3O_4 MNP for their adsorption efficiencies of Cu^{2+} ions from ammoniacal spent etchant wastewater. The polymers used to coat the MNP in this study were chitosan, levan and oleic acid. In this work, the synthetic ammoniacal spent etchant (copper stock solution), MNP and levan were produced in Marmara University Environmental, Metallurgical and Materials, and Bioengineering departments respectively.

2. MATERIALS AND METHODS

In this work, hydrated copper chloride ($CuCl_2.2H_2O$) and ammonia (NH_3) were used for the synthesis of copper stock solution to simulate the waste effluent generated from the etching stage of PCB. Whereas, Iron (II) chloride (0.5 Molar), iron (III) chloride (0.5M), ammonium hydroxide (NH_4OH) (4M) and ethanol were used for the preparation of MNP. Levan polymer was produced from *Halomonas smyrnensis* $AAD6^T$, which is a Gram-negative, aerobic, exopolysaccharide-producing, and moderately halophilic bacterium.

The detailed description for the synthesis of copper stock solution was as follows: 16.1142 grams of $CuCl_2.2H_2O$ and 28.2 mL of NH_3 (25%) solutions were mixed in 2L of ultra pure water. The mixture was stirred by magnetic stirrer for 20-30 minutes at room temperature. Finally the mixture turned to blue color, which is the true color of spent ammoniacal etchant.

The synthesis of Fe_3O_4 MNP was clearly described in the following procedures: 20.3 g of 0.5 M ferric chloride ($FeCl_3$) and 9.94 g of 0.5 M ferrous chloride ($FeCl_2$) were added in to two different beakers containing 150 and 100 mL of distilled water respectively and stirred with magnetic stirrer at 250 revolutions per minute (rpm) for 5 minutes. Then, the two solutions were combined in another beaker and stirred again at 550 rpm for 5 minutes. After that 100 mL of 4 M NH_4OH was added until the pH was 9. Then the mixture was mixed with mechanical stirrer for 30 minutes. The solution was heated for 20 minutes till 70 ^oC and then cooled to room temperature. After cooling, the MNP was separated by using magnetic separation. The separated MNP was washed by distilled water and ethanol to remove all other contaminants. Finally the MNP was dried in furnace for 24 hours at 100 ^oC. Similar procedures were followed to prepare levan, oleic acid and chitosan coated MNPs in such away that the coating organic compounds were added and stirred at 550 rpm for 5 minutes before adding NH_4OH [15]. The structures of magnetite iron oxide, levan, chitosan and oleic acid are shown in Fig 1.

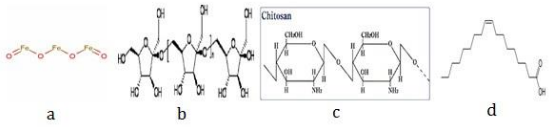

Fig 1. Structures of Fe_3O_4 (a), levan (b), chitosan (c) oleic acid (d)

2.1. Batch Adsorption Experiment

Batch adsorption experiments were carried out at 20 ^oC in aqueous solutions containing copper (II) ions. For this purpose, 50mL of stock solutions were added in to flasks containing 0.1, 0.2, 0.3, and 0.4 grams of MNPs. Blank samples were also prepared without the addition of MNP. All flasks were sonicated in ultrasound bath for 15 minutes. Batch adsorption experiments were conducted by using IKA KS 4000ic control shaker for two hours at 200 rpm and 20 ^oC. The initial and final pH was measured after sonication and shaking respectively and found to be between 9.0-9.5. After equilibrium was reached, the MNPs were separated from the solutions by magnetic separation technique and the supernatant was collected and filtered with syringes. 2% nitric acid was added to the supernatant to remove any black precipitation. 100 µL of supernatant was taken and diluted to 500 for the determination of the remaining copper ion concentration in the solution that was measured by Atomic Absorption Spectrometer (AAS). The amount of copper ions adsorbed by unit weight of MNP was calculated by using equation 1.

$$q_{(t)} = \frac{(C_0 - C_t)}{m} \times V \qquad (1)$$

where $q_{(t)}$ (mg g^{-1}) is the amount of copper ions adsorbed by unit weight of MNP; C_o and C_t (mg L^{-1}) are the initial and final Cu^{2+} ion concentrations respectively; $V$is the solution volume (L), and m (g) is weight of MNP.

3. RESULTS AND DISCUSSION

3.1. Adsorption Studies Results

Batch adsorption studies were conducted according to the procedures described above. The MNPs used in the adsorption studies were uncoated iron oxide, iron oxide coated with levan, oleic acid and chitosan. According to equation 1, the copper ions adsorbed by unit weight of the above mentioned MNPs were 69 mg g^{-1}, 46 mg g^{-1}, 66 mg g^{-1} and 125 mg g^{-1} respectively. The adsorbed copper ions (q_e, mg g^{-1}) versus equilibrium copper ion concentration in solution (C_e, mg L^{-1}) is given in Fig 2.

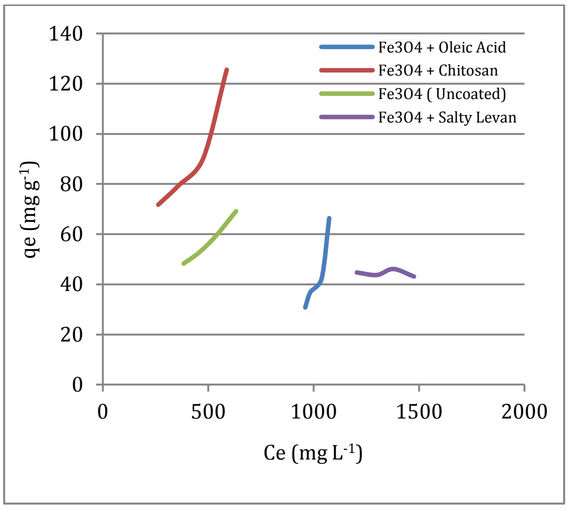

Fig 2. C_e vs q_e graph

From Fig 2, it was observed that the adsorption capacity increases with decreasing the mass of MNPs except for the MNP coated with levan which had almost constant adsorption value for all MNP masses. This indicates that levan coated MNP showed Langmuir adsorption that reached to maximum adsorption (q_{max}) which is a parameter in Langmuir adsorption isotherm. However, the MNP coated with oleic acid showed less adsorption behavior than even the uncoated MNP. The maximum amount of copper ions adsorbed by unit weight of MNP was observed by chitosan coated MNP with an adsorption capacity of 125 mg g^{-1}. This is due to the fact that the strong attraction between the negatively charged amine groups found on the surface of chitosan and the positively charged copper ions in the aqueous enable more copper ions be adsorbed on the surface of chitosan [16]. The values of the adsorption capacities found in this work is higher than many reported results also using amino-functionalized MNPs (~27 mg g^{-1} [17]), (~30 mg g^{-1} [18]) and (~46 mg g^{-1} [19]). However, high adsorption capacity of copper (maximum 625 mg g^{-1}) was also reported using glycine-functionalized maghemite (γ-Fe_2O_3) MNP [20].

3.2. Zeta Potential

Zeta potential is the electrostatic potential at the shear surface. It is usually related to the stability of a colloidal suspension. A colloidal suspension is stable if the particles remain in suspension and do not coagulate. The colloidal stability depends on the relative magnitude of the forces of attraction and the forces of repulsion [21]. Zeta potentials were performed using titration method to check the binding of polymers onto Fe_3O_4. For this purpose, 0.03 g MNPs were dispersed in 600 mL deionized water and titrated to pH 2-10 using 0.1 M HCl or NaOH solution. The pH versus Zeta potential for the MNPs is shown in Fig 3.

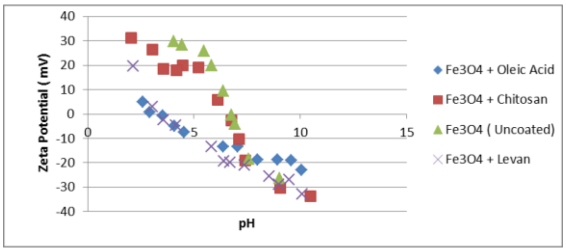

Fig 3. *pH* versus *zeta potential*

From the results of Fig 3, it is observed that zeta potential of the magnetic nanoparticles decreases as pH increases because of the release of H^+ ions [22]. As a result, higher pH values can be preferred for adsorption of Cu^{2+} ions on the surface of the MNPs. The results also showed that all MNPs used in adsorption tests had negative surface charges at around pH 9.5, ranging between -20 mV (for oleic acid coated MNP) to -32 mV (for levan coated MNP). Higher pH makes the biomass surface more negative. The more negative the surface charge of the sorbent, the faster the removal rate of Cu(II) in the aqueous phase, since the binding of cationic Cu(II) ions species with the negatively charged groups is enhanced [23].

The effect of pH on metal adsorption is also explained in relation with the pH of point of zero charge (pH_{pzc}) that is obtained from zeta potential analysis. pH_{pzc} represents the pH values where the net surface charge is zero. It is stated at pH higher than pH_{pzc}, the MNP surface is negative and metal adsorption is expected. But, when the pH is lower than pH_{pzc}, metal adsorption is reduced because the MNP surface is positive [24]. Based on the zeta potential results of Fig 3, the pH_{pzc} of the uncoated Fe_3O_4 MNP was found to be around 6.6, which was consistence with the values reported in literature. After coated with the polymers, the pH_{pzc} had been shifted to 6.4, 3.6 and 2.9 for the chitosan, levan and oleic acid coated MNPs respectively, showing that the coating of the polymers onto uncoated Fe_3O_4 MNP was successful. Moreover, magnetic nanoparticles modified with these polymers produce acidic surface since pH_{pzc} is lower than that of uncoated MNPs and this surface acidity is due to the introduction of several functional groups [25].

4. CONCLUSION

This study clearly reveals the potential of using bare and different polymer coated Fe_3O_4 MNPs as an excellent adsorbent for the removal of Cu (II) from aqueous solutions. The adsorption capacities of Fe_3O_4 nanoparticles were enhanced upon the surface modification polymers. The adsorption results showed that the highest copper ions adsorption was observed by the chitosan coated MNP, which was 125mg g^{-1}. This is due to the electrostatic attraction and complexation of copper ions with amine groups on the surfaces of the chitosan molecules. Moreover, zeta potential results showed zeta potential of the MNPs decrease with increasing pH and higher pH values is preferred for adsorption of copper ions on the surface of MNPs. In general the results obtained in this study were comparable with the literature values. Therefore, it is concluded that chitosan coated Fe_3O_4 MNP can be widely used in the removal of copper and other heavy metals from water and wastewaters.

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RESEARCH ARTICLE

A comparison of bioethanol and biochar production from various algal biomass samples and sweet sorghum energy crop

Anil Tevfik Kocer[1], Benan Inan[1], Didem Ozcimen[*,1]

[1] Yildiz Technical University Department of Bioengineering, 34220 Esenler, Istanbul, TURKIYE

ABSTRACT

In this study, bioethanol and biochar production from various algal biomass samples (*Chlorella minutissima, Chlorella vulgaris, Nannochloropsis oculata* microalgae *and Laminaria digitata, Codium fragile, Ulva lactuca* macroalgae*)* and an energy crop sample (sweet sorghum bagasse) were investigated. In bioethanol production, acid pre-treatments were performed with 2 N H_2SO_4 solution at the temperature of 100°C, and pre-treatment time of 60 minutes. Fermentation was carried out in erlenmeyer flasks which were placed in a shaking incubator set to the 150 rpm at the temperature of 30°C for 48 hours. The highest bioethanol yield was obtained as 44% by utilizing sweet sorghum. Biochar production was carried out at a heating rate of 20°C min^{-1}, 250 ml min^{-1} nitrogen flow rate and temperature of 400°C in a carbonization retort. The characterization of biomass samples were performed, and all biofuel yields were compared. Although sweet sorghum as an energy crop has higher bioethanol production potential than micro and macroalgae sources, especially macroalgae can be a remarkable solution of waste utilization as a new generation feedstock of biosorbent and biochar production.

Keywords: Biochar, bioethanol, biomass, algae, sweet sorghum

1. INTRODUCTION

Nowadays high amount of energy demand and carbon emissions which cause global warming lead the world to use renewable energy. Especially bioethanol and biodiesel production have increased rapidly due to meet this energy requirement. Bioethanol can be produced from sugar-based feedstocks which are also food source and lignocellulosic biomass which are not used for food requirements. Crop plants like sweet sorghum and algae which are third generation biofuel feedstock are seen as alternative feedstock for bioethanol production [1].

Sweet sorghum is a C4 crop and has a high photosynthetic efficiency [2]. It has high biomass and sugar yield and it is resistant to drought, salinity and alkalinity, it can remain dormant during these conditions [1], [2]. Therefore, it can be cultivated in both irrigated and non-irrigated environments [3-4]. Due to this characteristic, it can grow everywhere and there are no competition between food growing and biofuel feedstock growing for lands. It contains soluble carbohydrates such as glucose, fructose and sucrose and insoluble carbohydrates like cellulose and hemicelluloses [1]. In addition to these carbohydrates, sweet sorghum juice contains some nutrients for microorganisms which produce ethanol and this can increase the process yield [5].

High sugar content of sweet sorghum makes it an interesting feedstock for bioethanol production. There are remains obtained after extraction of its juice and it should be utilized in different ways in concept of waste management and also to reduce energy cost in the process. In large scale production of bioethanol from sweet sorghum, high amount of sweet sorghum remains can become available raw material for another usage [6].

As third generation biofuel feedstock, algal biomass becomes very popular in biodiesel production in the last decade because of its high lipid content [7]. On the contrary, recent studies show the increase in bioethanol production from algal biomass instead of

Corresponding Author: ozcimen@yildiz.edu.tr (Didem Ozcimen)

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biodiesel production, considering the world's renewable energy trends. Macroalgae which are often located in coastal areas can be a good solution for both disposal of waste and economically viable bioethanol production. While microalgae mostly stand out as biodiesel feedstock with the ability of high lipid production and photosynthetic efficiency in the last decade, macroalgae are utilized for biogas or bioethanol production due to their high carbohydrate content [8].

In the concept of using renewable energy, many researchers investigate different biofuels such as biochar, bio-oil and syngas which is obtained by the conversion of biomass. Biochar is a carbon rich product which produced from biomass in absence of oxygen by thermal decomposition and it can be used as fuel due to its high fixed carbon content and high calorific value, a soil amendment, a soil carbon sequestration and a raw material for activated carbon production [9][10][11]. In order to reduce the biofuel production cost and apply waste management, it is important to utilize waste products or biomass which considered as waste for biofuel productions.

In the literature, there are many studies which investigate bioethanol and biochar production from different biomass sources. It is especially important to compare biofuel yields of algae and energy crops to be able to decide true raw material for biofuel production. For this reason, bioethanol and biochar production from various algal biomass samples (*Chlorella minutissima, Chlorella vulgaris, Nannochloropsis oculata* microalgae and *Laminaria digitata, Codium fragile, Ulva lactuca* macroalgae*)* and an energy crop sample (sweet sorghum bagasse) were carried out to compare biofuel yields.

2. EXPERIMENTAL

2.1. Materials

In the experiments, *Chlorella minutissima, Chlorella vulgaris, Nannochloropsis oculata, Ulva lactuca, Laminaria digitata, Codium fragile* algae and sweet sorghum bagasse were used as raw materials (Fig 1.). Microalgae species were cultivated in Bioengineering Department of Yıldız Technical University. In the cultivation step, BBM culture media and F/2 media were used for marine and fresh water microalgae species. *Ulva lactuca* and *Codium fragile* were obtained from coastal regions of Marmara Sea, and *Laminaria digitata* was collected from the coastal regions of Mediterranean Sea. Sweet sorghum was obtained from Adana region of Turkey. As for the pre-treatments, H_2SO_4 (98% concentrated, Merck) was used. Luria Broth (LB) medium (Merck) was supplied to use in fermentation step, and 96% purity ethanol (Merck) was used for gas chromatography analysis.

2.2. Preparation and Characterization of Biomass Samples

Microalgae cultures were cultivated in 500 mL Erlenmeyer flasks in BBM and F/2 mediums at pH 7.8 in a shaking incubator set to 150 rpm at 25±3°C under continuous illumination. As for macroalgae samples, they were washed with tap water to remove impurities such as sand, shellfish and other materials. Microalgae samples were centrifuged and dried with macroalgae samples in an oven for 24 h at 70°C. Dried samples were stored in a clean air-tight container. Harvested sweet sorghum plants were cut to the smaller pieces and then they were smashed in a mixer for creating larger area for fermentation and carbonization.

Fig 1. Biomass samples used in biofuel production

YL 6100 gas chromatography (GC) was used to evaluate bioethanol concentration. Samples from fermentation process were taken and prepared for GC instrument for further analysis. Firstly, samples were filtered using 0.45 µm filters to avoid blocking in column. The GC contains flame ionization detector (FID) and 30 m x 0.32 mm x 0.25 µm ZB-FFAP column. The temperature of injector, detector and oven were maintained at 150°C, 250°C and 100°C, respectively. Hydrogen was used as carrier gas. Bioethanol concentration was calculated using calibration curve that was prepared by the different concentration of bioethanol standards (0.1% -10% (v/v)).

Proximate analysis of the raw materials were carried out using the thermogravimetric analyzer (TA Instrument, SDT Q600) [12]. The functional groups of the raw materials were determined by FTIR spectroscopy (Bruker, Alpha).

2.3. Bioethanol Production

Biomass samples were pre-treated with dilute acid to degrade the biomass for fermentation process. Acid pre-treatments were performed with 2 N H_2SO_4 solution at the temperature of 100°C, and pre-treatment time of 60 minutes. After pre-treatments, samples in flasks were cooled down to the room temperature. The liquid from pre-treatment was neutralized before the fermentation. pH was maintained at 4.8 by alkaline/acid solutions. *Saccharomyces cerevisiae* yeast was chosen for the fermentation process of bioethanol production. The yeast was cultured in Luria Broth medium. Yeast suspension was aseptically transferred to 150 ml of sterilized LB medium and cultured in an incubator set to 150 rpm at the temperature of 30°C for 24 h, and 3% (v/v) of *Saccharomyces cerevisiae* was inoculated to the working medium. Fermentation was carried out in Erlenmeyer flasks which were placed in a shaking incubator set to the 150 rpm at the temperature of 30°C for 48 hours. Aliquots of 5 ml were taken to determine the concentration of ethanol by gas chromatography (GC) analysis.

2.4. Biochar Production

In this experiment, a split furnace (Protherm, ASP 11/100/500) was used as carbonization retort. The split furnace is in dimensions of 51 cm × 40 cm × 50 cm and pipe diameter is 10 cm. The temperature control is provided by the Honeywell DC1010 PID controller. The experimental set-up was shown in Fig 2. Experimental conditions for carbonization process were selected as temperature of 400°C, heating rate of 20°C min^{-1}, retention time of 30 min and nitrogen flow rate of 250 ml min^{-1}.

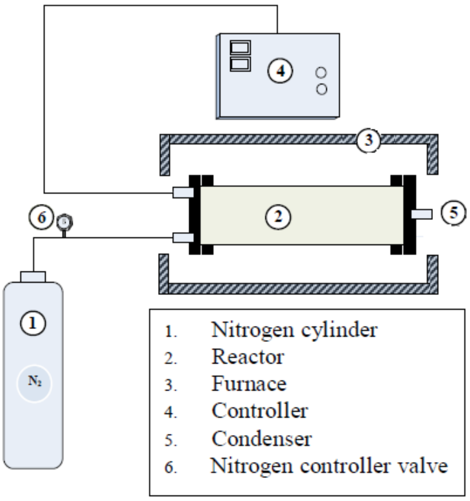

Fig 2. A schematic sketch of the carbonization experimental set-up

3. RESULTS

3.1. Characterization of Biomass Samples

Proximate analysis results of algae and sweet sorghum were shown in Table 1. As it can be seen in Table 1, *U. lactuca* has maximum moisture content (12.27%), *C. minutissima* has minimum moisture content (4.71%). Besides, moisture content of microalgae was found as lower than macroalgae. Ash content of *N. oculata* was found higher than other biomass samples due to the absorption of salts from seawater. The amounts of volatile substances of algal samples were very high, which was an expected result, because of the high carbohydrate content of macroalgae and high lipid content of microalgae [13]. The FTIR results of the raw materials used in the experiments were shown in Fig 3. When the obtained spectrums were examined, it was seen that the structure of the raw materials (especially algae) was similar, yet, the content ratios of the samples were different. The absorption between the range of 3300 and 3200 cm^{-1} can be assigned to the stretching vibrations of the OH groups which might be responsible for the moisture content [14][15] and this peak also appeared in three spectrum. Aliphatic C-H stretching at 2930 cm^{-1} and 2917 cm^{-1} caused by cycloparaffin structure [16]. The peaks at 1635 and 1626 cm^{-1}, which were determined in all raw materials, were presence of the protein content [17]; and the peaks at the range of 1100-1000 cm^{-1} in all biomass species, were determined because of the presence of the carbohydrate content [18].

3.2. Bioethanol Production

In order to make a comparison between results of the literature studies and this study, results were given in the Table 2. In this study, the highest bioethanol yield was obtained with sweet sorghum bagasse (SW) as 44%. This was an expected result, because of the carbohydrate content of sweet sorghum bagasse. Studies showed that, various sweet sorghum samples were resulted with 90-42% bioethanol yields by using different pre-treatment methods such as physical, acid and enzymatic. In this study, only 2 N acid pre-treatment was applied to the sweet sorghum samples. When considered the literature studies, it can be said that, acid+enzymatic pre-treatment is more efficient method than only acid pre-treatment. Bioethanol yield of *U. lactuca* was the second highest among them, and the lowest bioethanol yields were obtained with *L. digitata* and *C. fragile*. It was seen that bioethanol yields of microalgal samples were quite similar. According to the literature studies, carbohydrate content of *U. lactuca* generally constitutes of 55-60% of the biomass [19]. On the other hand, although carbohydrate content can be changed in seasons, 38-50% were reported for *L. digitata* and *C. fragile,* respectively [19][20]. When these samples were analyzed for carbohydrate content, the contents were found as 63%, 44%, and 36% for *U. lactuca, L. digitata* and *C. fragile.* This may be the reason of the bioethanol yield difference between these macroalgal samples. As in stoichiometric aspects, it can be commented that, the higher carbohydrate content will increase the bioethanol yield. In comparison with other macroalgal biomass, similar results were obtained in this research. As for the microalgal samples, bioethanol yields of *C. vulgaris, C. minutissima* and *N. oculata* were quite similar. Harun et al. reported that the highest bioethanol production from *Chlorococcum infusionum* was found as 26.13% under the conditions of 0.75% NaOH pre-treatment at the temperature of 120°C for 30 min [21]. In another study, bioethanol yield of *C. reinhardtii* was found as 29.10% after 3% H_2SO_4 pre-treatment in 110°C for 30 min by using modified yeast in fermentation. These studies show that, higher concentrations of acid pre-treatment can reduce bioethanol yield due to the formation of toxic molecules such as furaldehyde, acetate and hydroxymethylfuraldehyde which inhibit the fermentation [22]. In addition to this, concentration of bioethanol can increase in progress till there is no left convertible carbohydrate in the fermentation medium. The results obtained from this study are in agreement with these studies for bioethanol production.

Table 1. Proximate analysis of biomass samples

Biomass	*Moisture (%)*	*Volatile Matter (%)*	*Fixed Carbon (%)*	*Ash (%)*
Ulva lactuca	12.27	66.31	13.99	7.43
Laminaria digitata	10.89	55.85	24.95	8.31
Codium fragile	9.04	65.45	13.64	11.87
Chlorella vulgaris	6.77	76.68	11.62	4.93
Chlorella minutissima	4.71	75.29	10.55	9.38
Nannochloropsis oculata	4.87	68.06	12.88	14.19
Sweet sorghum	8.27	74.49	11.54	5.77

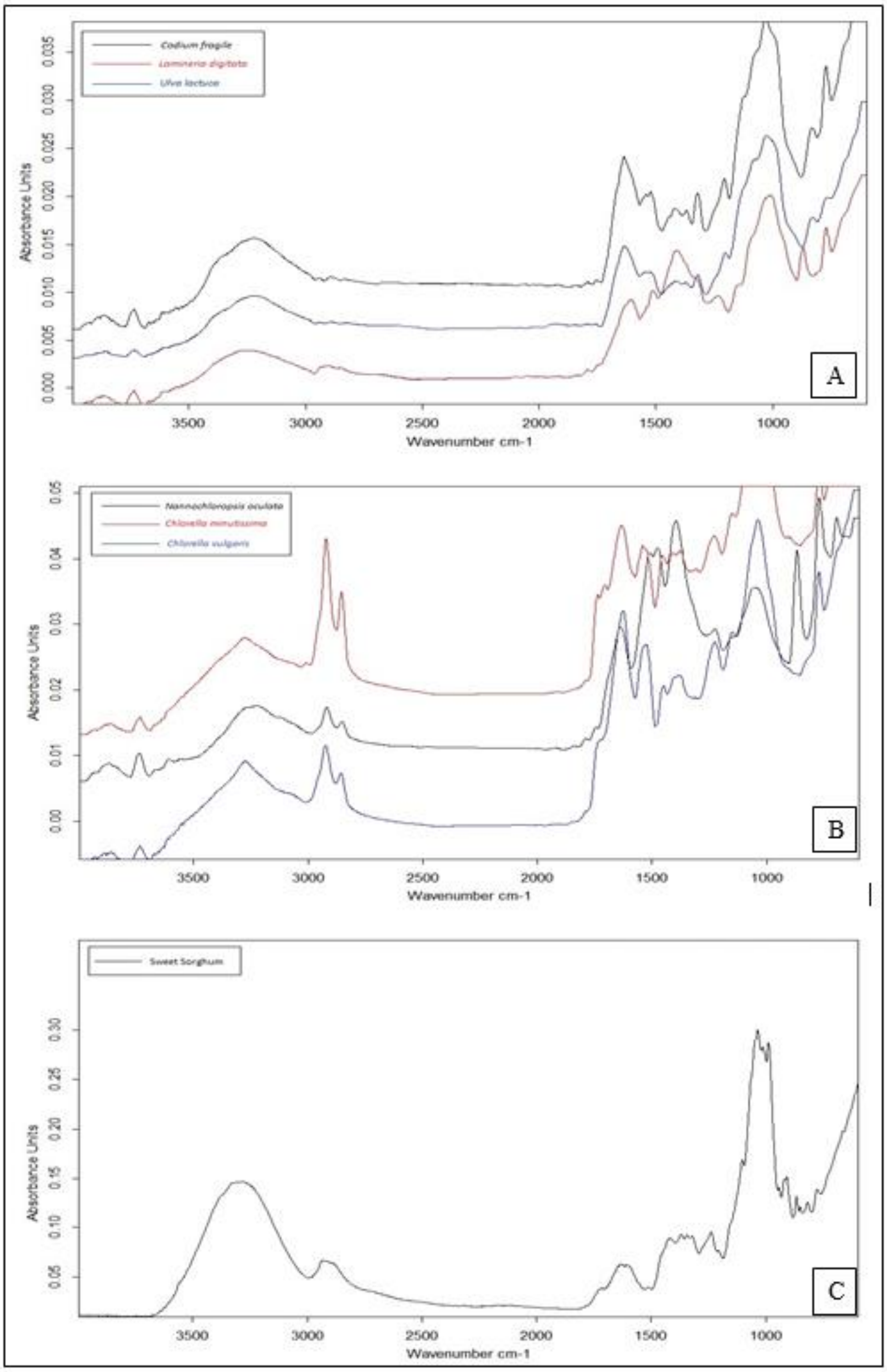

Fig. 3. FTIR spectrums of (A) macroalgae, (B) microalgae and (C) sweet sorghum

Table 2. Studies for bioethanol production from different biomass samples

Pre-treatment Method	*Sample*	*Time (h)*	*Ethanol yield (%)*	*Ref.*
Physical	SW-Stem	24	90.5	[6]
Physical	SW-Juice	40	50	[23]
Acid and enzymatic	SW-Stalk	24	42-45	[9]
Acid and enzymatic	SW-Bagasse	168	89.4	[10]
Alkaline	*C. infusionum*	72	26.00	[21]
Acid	*C. reinhardtii*	24	29.10	[24]
Hydrothermal and enzymatic	*Schizochytrium sp*	72	5.51	[25]
Acid	*C. humicola*	50	48	[26]
Physical	*L. japonica*	36	11.3	[27]
Acid and enzymatic	*G.verrucosa*	96	43	[28]
Acid	*G. corneum*	48	5.8	[29]
Alkaline	*N. oculata*	48	2.96	[30]
Acid	*U. lactuca*	48	26.52	*This study*
Acid	*Laminaria sp.*	48	9.88	*This study*
Acid	*C. fragile*	48	8.72	*This study*
Acid	*C. vulgaris*	48	15.20	*This study*
Acid	*C. minutissima*	48	14.46	*This study*
Acid	*N. oculata*	48	14.22	*This study*
Acid	SW-Pulp	48	44	*This study*

Table 3. Studies for carbonization process of different biomass samples

Species	*Conditions*	*Char yield (%)*	*Ref.*
Macroalgae			
Ulva flexuousa	450 °C	50	[31]
Cladophora sp.	550 °C, 60 min	31.0	[32]
Mix macroalgae species	500 C	29-36	[33]
Saccharina japonica	450^{0}C	33	[34]
Gracilaria gracilis	400-600 °C	26-32	[35]
Ulva lactuca	400°C	58	*This study*
Laminaria digitata	400°C	49	*This study*
Codium fragile	400°C	45	*This study*
Microalgae			
Arthrospira platensis	550 °C, 60 min	31.0	[32]
Chlamydomonas reinhardtii	350 °C, 20 min	44.0	[36]
Chlorella vulgaris	350 °C	31.0	[37]
Nannochloropsis sp.	400, 500, and 600 °C, 60 min	24.8-33.5	[38]
Tetraselmis sp.	500 °C, 1 h	~20	[39]
Chlorella vulgaris	400°C	34	*This study*
Chlorella minutissima	400 °C	32	*This study*
Nannochloropsis oculata	400°C	35	*This study*
Sweet Sorgum			
Raw sweet sorghum	427	21,4	[6]
Sweet sorghum bagasse	500	13,4	[6]
Sweet sorghum bagasse	500	28,8	[40]
Sweet sorghum bagasse	400 C	34	*This study*

3.3. Biochar Production

In order to make a comparison between the results of the some literature studies and this study, results were given in the Table 3. As it can be seen in the Table 3, the biochar yields of macroalgae were higher than those of microalgae. The main reason for this is the volatile matter ratios were lower in macroalgae. In addition, macroalgae collected from the seas have structures such as silica and lignin which degrade at very high temperatures. So, this has led to a higher yield of the solid. The microalgae used in this study have no silica and lignin content, because they are single cell microorganism and grown in fresh and marine water. In addition, due to high lipid content of microalgae was degraded in the temperature range of 250-350°C, the percentage of solid product was lower than the macroalgae.

As a result of the literature study, it was seen that, the yield of biochar obtained from micro- and macroalgae ranged from 20.0-63.0% to 8.1-62.4%, respectively [41]. Ronsse et al. [42], reported that the yield of algal biochar is lower than those of other lignocellulosic biomass. In addition, algal biochar yield was inversely proportional to temperature and residence time.

As a result of the carbonization process, char yields of *U. lactuca, L. digitata* and *C. fragile* were found as 58%, 49% and 45%, respectively. This result seems to be similar to the other studies in the literature. Bird et al. [31] calculated the yield of char obtained from *Ulva flexuosa* at the temperature of 450 °C as 50%. Yanik et al [33] found that the yields of chars produced from macroalgae (*Laminaria digitata, Fucus serratus* and *mix macroalgae species*) which collected from Black Sea, were 29-36% at the temperature of 500°C. Choi et al. [34] calculated to biochar yield that produced from *Saccharina japonica* as 33% at 450°C.

The char yields obtained from the carbonization of *C. vulgaris, C. minutissima* and *N. oculata* in our study were calculated as 34%, 32% and 35%, respectively. Wang et al. [37], in their study, found that *C. vulgaris* had a char yield of 31% at temperature of 350°C. Adamczyk and Sajdak [43] calculated that char yield of *Nannochloropsis sp.* at temperature of 400°C was about 55%; Aysu and Sanna [38] also calculated as 33.5%. The difference between two yields can be explained with their ash contents.

In our experiments, biochar yield of sweet sorgum bagasse was found as 33%. In the literature, Yin et al [40] found that the solid yield obtained from pyrolysis of sweet sorghum bagasse was 28.8% at temperature of 500°C. Piskorz et al. [6] used raw sorghum and sorghum bagasse in pyrolysis experiments and calculated their biochar yields as 21.4% and 13.4%, respectively. As can be seen in these studies, biochar production from sweet sorghum can be varied by pyrolysis conditions and raw materials used.

4. DISCUSSION AND CONCLUSIONS

Today, demand for fossil fuels cannot be met with current reserves and increasing oil prices with economic and political crisis and effects of global warming are led countries to use renewable energy sources. Currently, biodiesel and bioethanol are the lead biofuels. However, the high operational cost of the production of these biofuels led the researchers to utilize different raw materials and waste products to reduce the cost. In this study, sweet sorghum bagasse, *U. lactuca, L. digitata, C. fragile, C. vulgaris, C. minutissima* and *N. oculata* were utilized for bioethanol and biochar production. Bioethanol and biochar yields of these biomass samples were compared. As the highest bioethanol yield was obtained as 44% by utilizing sweet sorghum; the highest char yield was obtained from *U. lactuca* as 58%. As can be seen that, ethanol production potential from sweet sorghum has higher than algal biomass due to its high carbohydrate content. On the contrary, biochar production yields of algal biomass gave better results than sweet sorghum bagasse. Although sweet sorghum as an energy crop has higher bioethanol production potential than micro- and macroalgae sources, especially macroalgae can be a remarkable solution of waste utilization as a new generation feedstock of biosorbent and biochar production.

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RESEARCH ARTICLE

Development of velocity sensor to optimize the energy yield in a biogas plant

Abdullah Nsair*[,1], Olaf Bade[1], Kerstin Kuchta[1]

[1]Hamburg University of Technology, Institute of Environmental Technology and Energy Economics, Hamburg, GERMANY

ABSTRACT

The number of biogas plants has increased worldwide making the energy from Biomass one of the main renewable energy resources. Along with the increase of number of biogas plants, the prices of the substrates have been increased. Therefore, the optimization of the energy efficiencies in biogas plants has become a crucial subject. An option to improve the efficiency of the biogas plants is by optimizing their stirring system, where up to 51% from the internal energy consumption in biogas plants might be caused by the stirrers. The evaluation of the current mixing performance is done by performing velocity testing with a reliable technology - the bending beam-. The main advantages of this sensor in advance to the simple technology are the cost reliability, accuracy, resistivity against foul and ability to be installed inside the fermenters. The results showed the efficient use of the sensor and an inaccuracy of the range (4-6) %. The effect of the Total Solids content (TS) of the digestate on the mixing inside the fermenter was determined; at higher TS values, the flow of the substrates becomes more uniform than at lower TS values.

Keywords: Bending beam, biogas, optimization, sensor & velocity

1. INTRODUCTION

Worldwide the importance of renewable energy resources has increased over the recent years; the generated power by renewable energies (including hydropower) share of global energy production by the end of 2015 reached around 24% [1]. In Europe, the installed biogas plants by the end of 2015 reached 17,358 biogas plants, 10,846 of them were installed in Germany. The total capacity reached around 8,728 MW_{el} [2]. To reach the targets of the Kyoto protocol, Germany set a reduction aim of at least 40% of CO_2 emissions by 2020 and up to 80 to 90 percent by 2050 in comparison with 1990. These targets shall be achieved by supporting new renewable energy systems and the optimization of the energy efficiency for the installed systems [3].

The increasing substrate costs leads to difficulties in the economic operation of biogas plants. It is necessary for operators to achieve higher gas yields with lower internal energy consumption. One approach to increase the profitability is optimizing of the stirring performance. The reason for this is stirrers have a significant share of the internal energy consumption in biogas plants; the share of the stirrers might reach up to 51% from the internal energy consumption in biogas plants [4].

The reduction of the consumed energy by the stirrers is not always a good factor in the optimization of the energy yield; this has been noticed from the experience. In case of insufficient mixing, sinking layers and floating covers might be formed. That will prevent the anaerobic microorganisms from having the ability to get in contact with the substrates. Thus, the biogas production will decrease or stop entirely [5], [6], [7] and [8]. On the other hand, the aggressive stirring (the high velocities of the stirrers or long operation times) might form high shear forces. These forces can affect the acetic and methane producing bacteria negatively. Therefore, it is important to find the most suitable mixing conditions to avoid the formation of sinking layers and the floating covers as well high shear forces [9].

This project takes place in a biogas plant near to Hamburg – Germany. The biogas plant consists of two fermenters with a volume of 2659 m^3 each. Every fermenter has two submersible agitators and one Hydro-mixer agitator. In addition, inside the mixing tank and digestate storage one submersible and three

Corresponding Author: abdullah.nsair@tuhh.de (Abdullah Nsair)

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submersible agitators are assembled respectively (status March 2015). As substrates for the fermentation process dairy and swine manure, poultry manure and maize silage are used.

2. MATERIALS AND METHODS

To develop the velocity sensor and check its reliability, different technologies were evaluated according to several criteria. Then the sensor was tested in a biogas plant.

2.1. Methods

The choice of the concept to be used for the velocity sensor was done with attention on the needs of the sensor. Mechanical and chemical measurement concepts were chosen to be evaluated with regards to the cost, resistivity against foul, place requirements and the accuracy. The concepts doubling of ultrasonic, doubling of laser, X-Ray and tracer particles were excluded due to the available budget and the fact the measurements will be done inside a fermenter that has a concrete thickness of around 20 cm.

2.2. Mechanical Measurement Methods

The focus here is on the methods in which the forces or the effects of the forces are measured. The evaluation for the mechanical measurements method was done for two main concepts; the anemometer and the bending beam. Anemometer has been developed for measuring the flow field velocities. The main anemometer concepts, which were studied, are: Vane wheel anemometers, in which the speed of the rotating of the vane wheel is determined by the angle of the vane and the speed of the fluid flow [10]. Pitot tube anemometers rely on measuring the variances between the static pressure values and the dynamic pressure values to obtain the velocity of the fluid flow [11]. The rotating cup anemometer was the third type of anemometers that have been evaluated. This principle (rotating cup) is considered as a simple one and depends on counting the number of revolutions that the cups are having during the flow of the fluid [12]. The bending beam concept depends mainly on measuring the absorbed and forwarded forces which are applied by the flow hitting the plate, where a strain gauge (DMS) is assembled.

2.3. Chemical Measurement Methods

These methods focus on the differences of the substrates concentrations, the calorific properties or chemical concentrations between different points in the flow to measure the velocity. Three concepts can be used are: pH value and the Redox potential differences as well as calorimetric measurements. Based on the pH value measurements (the technology of ISFET array), a sensor for flow velocity measurements was designed and implemented [13], it depends on measuring the difference of the pH value at two different points. The measurements of velocity depending on the Redox potential values follow the same principle in the previous mentioned technology.

After carefully evaluating the mentioned concepts previously according to their costs, accuracies, resistivity against fouling and their suitability to fit inside the fermenter, the choice was made to use the bending beam concept. Table 1 summarizes the evaluation of the concepts.

Table 1. Summary of the evaluation of the main methods for velocity measurements

Method	Place requirement	Resistance Against fouling	Accuracy	Cost
Doubling of Laser	-	+	+	-
Doubling of Ultrasonic	-	+	+	-
X-rays	-	+	+	-
Tracer particles	0	+	+	-
Vane wheel anemometer	0	-	-	0
Pitot pipe impeller	0	0	+	+
Rotating cup anemometer	0	0	0	+
Bending beam	+	0	+	+
pH value difference	-	0	0	+
Redox potential difference	0	+	0	+
Calorimetric measurements	+	+	0	0

where:

- : Not or low competent,
0 : Medium competent,
\+ : Very competent.

2.4. Materials

The test of the sensor took place at a commercial size biogas plant locates near Hamburg – Germany. This biogas plant consists of two fermenters and digestate container. The fermenters have identical sizes (2659 m^3) and three stirrers; two movable submersible mixers (TMRW) and one Hydro mixer (GFRW) in each. The operating time for the mixers was five minutes every half an hour. The digestate container has a volume of 6514 m^3 with three submersible mixers. There is a possibility to insert the velocity sensors in the fermenters at twelve different locations; every 90° at the levels of 1, 3 and 5 m (normally at the level of 5m, there is just gas). Fig 1 represents the design of the fermenters (1 and 2 are identical) and the meaning of the levels (heights), angles and the depth.

The materials used for the measuring device were designed to last for the expected speed inside the fermenters; it was provided by the biogas plant operator that is in the range (0 – 0.4) ms^{-1}. The measuring device consists mainly from two parts; the measuring rod and the measuring sensor. Their design was done to fit to the gauge size at the chosen biogas plant. In this biogas plant, the operator designed gauges to simplify the sampling and the velocity measurements. The radius of the gauges is 38.5 mm.

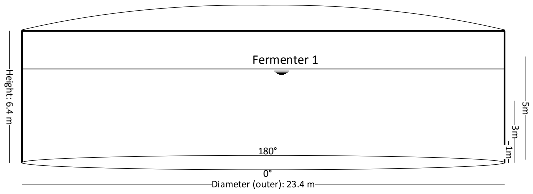

Fig 1. Design of fermenter 1 representing the possible sampling (measurements) points

2.5. Measuring Rod

The rod was designed to sustain the conditions in the fermenters with different substrates; Total Solids contents (TS), pH values, densities and velocities. For the conditions of the chosen biogas plant, the maximum reached TS value was around 10.5% (w/w), the rod designed to handle at least a velocity of 2 m s^{-1} at this value. The used material is stainless austenitic chromium – nickel steel (1.4301). The rod specifications are summarized in Table 2. Fig 2 represents the measuring rod connected to the fermenter.

Table 2. Specifications of the measuring rod

Parameter	Unit	Value
Length	m	1.5
Outer radius	m	0.019
Inner radius	m	0.014
Density	kg m^{-3}	7900

Fig 2. Measuring rod used for the velocity measurements

2.6. Measuring sensor

A plate from Aluminum alloy was used to build the sensor that can sustain bending corresponding to the velocity of 1 m s^{-1} at TS of 10.5% (w/w), its main specifications can be represented as following:

Table 3. Specifications of the measuring sensor

Parameter	Unit	Value
Length	m	0.200
Width	m	0.030
Thickness	m	$0.5 * 10^{-3}$
Density	Kg m^{-3}	2670

A resistance strain gauges (DMS) was built at Hamburg University of Technology. In this sensor, the resistance changes with the expansion. DMS consists from a carrier film and a meander inductor measurement grid. The carrier material is glued onto the surface of the aluminum plate. If the DMS stretched in the direction of measurement, the electrical resistance of the conductor increases, and it can be measured at constant amperage a change in voltage. The strain is proportional to the voltage change and enables the calculating of the force applied by the flow. This strain has a full bridge circuit consists of four units. It also has a resistance of 320 Ω. Thereafter, the terminals are electrical connected and to a 7-pole plug cable. Subsequently, the components have been sealed with clay. Fig 3 shows the measuring sensor.

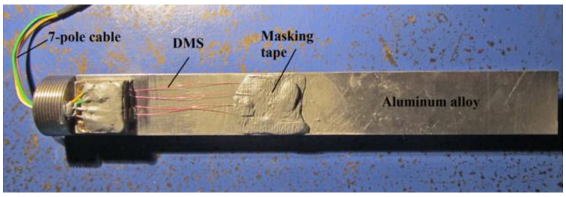

Fig 3. The velocity sensor designed at TUHH

The calibration of the sensor was done at The Hamburg Ship Model Basin (HSVA), where the measurements of the voltage generated were taken at different times and different velocities. A quadratic approximation (equation 1) can be used to show the relationship between the voltages (y) and fluid velocity (x).

$$y = 2.8219x^2 + 8.7681x \tag{1}$$

The sensor was used to measure the velocity inside a cylindrical fermenter. It could measure for around 75 seconds, but it started to show noise due to the high velocities exceeding 1 m s^{-1} and the aggressive environment inside the fermenter, which destroyed the DMS. Therefore, further improvements were needed. A new sensor from Aluminum alloy was developed has same specifications as the previous one, except increasing its thickness to 1.5 mm.

The sensor was isolated by using masking tape so-called ABM 75. This sensor operated for short time due to the insufficient isolation. Following further another sensor was designed, this sensor has a size of (180 mm * 20 mm * 1.5 mm) from the same material.

Then it was coated by a layer of masking tape ABM 75. After that and before any measurement, the sensor is coated with 3 layers from the insulation material Plasti Dip liquid rubber. The calibration was done at HSVA as before. The calibration curve can be seen in Fig 4 and the relationship between the voltage and flow velocity from equation 2.

$$y = 0.9887x^2 + 0.1088x + 0.0007 \tag{2}$$

y: the voltage in V

x: the flow velocity in m s^{-1}

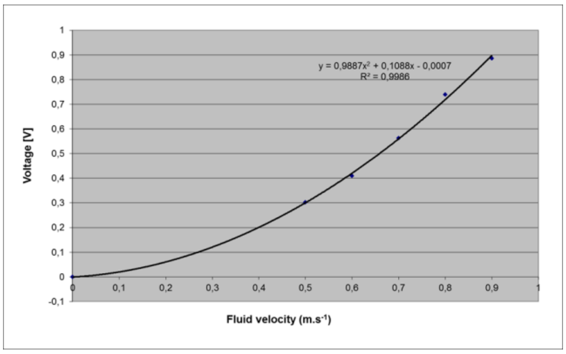

Fig 4. Calibration of the velocity sensor done at HSVA

The measuring rod was improved as well, by using a 6 m of rod of stainless austenitic chromium – nickel steel (1.4571). This rod was divided into three parts of 1m, 2m and 3m with the ability to be connected to allow further measurements at deeper points inside the fermenters with more flexibility in the measuring depth.

3. RESULTS AND DISCUSSION

The frequency of the measurements per second was decided after experimental trials; it was done for three different frequencies (two measurements per second, one measurement per second and one measurement every two seconds). The conclusion was to run the measurements with a frequency of one measurement per second. Fig 5 represents measurements of the flow velocity inside fermenter 2 in a biogas plant at a height of 1m, depth of 0.75 m. An example of the measurements of the velocity and its relationship with the measured voltage (the relationship can be seen from equation 2) can be seen from Fig 5. The harmonies and avoidance of the noise can be noticed as well. The changes of the measured voltage were not occurring dramatically within very short period (up to 10 seconds).

The velocity sensor has been used for the measurements at different points (heights 1m and 3m, depths of 0.75m, 1.25m and 1.75m, and angles of 0°, 90°, 180° and 270°) in two fermenters (fermenter 1 and fermenter 2). It showed stability and flexibility for the measurement at different depths inside the fermenters without any difficulties. The values of velocity inside the fermenter were changing for the different measuring locations according to the distance from the stirrers and the wall. The points next to the walls showed higher velocity values and longer time to reach the non-movement velocity after switching the stirrers off. The effect of the distance from the wall appeared stronger at lower TS values.

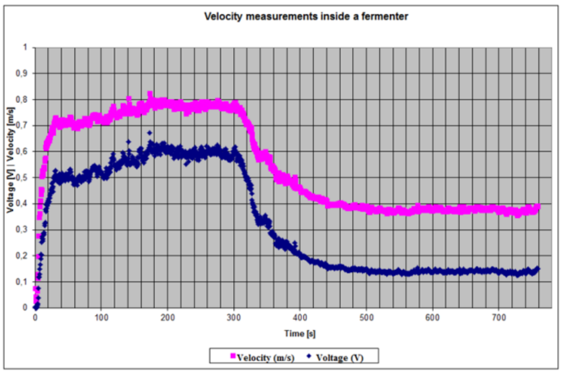

Fig 5. The velocity measurements at a biogas plant after the calibration [8]

A comparison was done for the velocities inside fermenter 2 at the same point (level 1 m and depth 0.75 m) at different times (different feeding scenarios), where the values of the Total solids content were different, refer to Fig 6. The measurements were done while the stirrers were on for 300 seconds, and while the stirrers were turned off. The Total Solids content played a big role in the changes of the velocity; at higher TS values the velocities were more stable and following a more uniform shape.

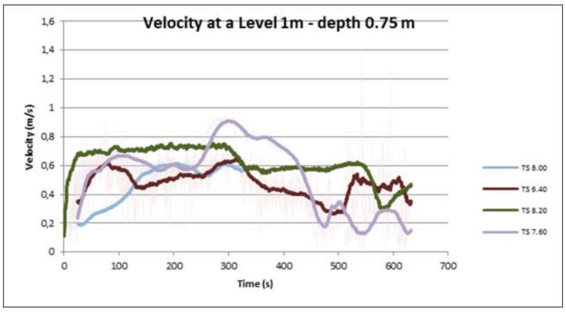

Fig 6. Velocity at different TS values

The TS value could be considered as one of the main factors controlling the mixing inside the fermenters. TS value is the main factor controlling the viscosity of the digestate. Therefore, it has an effect on creating foaming layers or causing an inadequate mixing or even breaking down the stirrers [14]. Brehemer studied the effect of the TS value on the viscosity and its effect on the mixing. He concluded that the viscosity is highly affected by the feeding substrates (TS values). To avoid the dead zones formation, increasing the viscosity can be chosen as an option, this increase leads to a strong reduction in the mixing time. At the same time if the viscosity increases too strongly, a stall and cavities are formed [15].

The results of the measurements showed that at higher TS values, the stability of the flow of the digestate is increasing and also the velocities are higher. Furthermore, it takes longer time to reach the phase of non-movement and starting the creation of dead-zones after turning off the stirrers, at higher TS values. The effect of the TS values on the velocity of digestate flow is comparable with the effect of the viscosity on the velocity flow from other studies [16], [17] and [18].

4. CONCLUSION

The principle of bending beam might be used in velocity measurements inside fermenters, where it is cost reliable, accurate and can be installed in any biogas plant. This only requires the adaption of the size of the gauges at the biogas plants. The resistivity against fouling can be improved by using isolation materials such as Plasti Dip liquid rubber. The inaccuracy of this sensor is dependent on the flow velocity, where it is in the range of (4-6) %. The relationship between the velocity of the flow and the sensor accuracy is proportional. As a result, this accuracy is satisfactory for the improvement of the mixing performance in biogas plant.

In the measurements done at the biogas plant, the stability of the velocity and the changes were highly dependent on the TS value due to the changes these values on the viscosity. Therefore, it is recommended to do further measurements in different biogas plants with different substrates and TS values. This will highly help in finding optimum conditions for the mixing in biogas plants and avoid the creation of floating layers and sedimentations.

The improvement of the mixing performance can be achieved by the help of simulation programs such as Computational Fluid Dynamics (CFD) and practical part using the flow sensor. This improvement and evaluation should consider the feeding substrates, the hydraulic retention time as well the stirrer models and their locations in the fermenters. The evaluation can be based on examining the homogeneity of the digestate from different locations in the fermenter and the effect of mixing on the energy yield and the consumed energy.

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