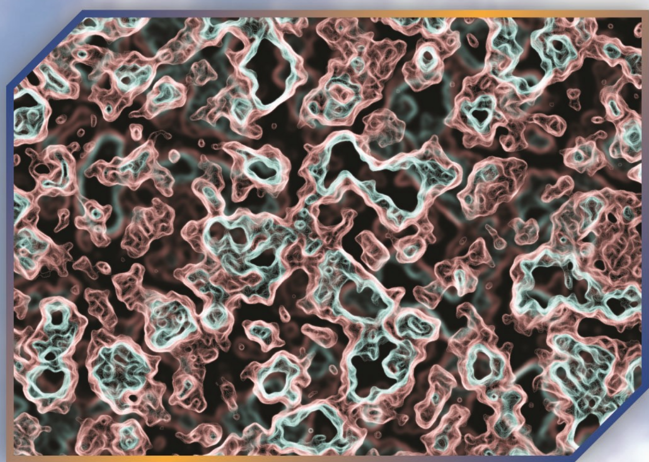
Environmental Research & Technology

YEAR : 2019 | VOLUME : 02 | ISSUE : 03

e-ISSN: 2636-8498



Turkish JournalPark ACADEMIC

Environmental Research & Technology

http://dergipark.gov.tr/ert

CONTACT

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

Environmental Research & Technology, Vol. 2 (3), 2019

Environmental Research & Technology

http://dergipark.gov.tr/ert

Environmental Research & Technology

http://dergipark.gov.tr/ert

Editorial Board

Environmental Research & Technology, Vol. 2 (3), 2019

Turkish JournalPark ACADEMIC

Environmental Research & Technology

http://dergipark.gov.tr/ert

TABLE OF CONTENTS

Environmental Research & Technology, Vol. 2 (3), pp. 103-111, 2019

Turkish JournalPark ACADEMIC

Environmental Research & Technology

http://dergipark.gov.tr/ert

RESEARCH ARTICLE

Effect of stirring device on CuO dissolution by glycine

Nadir Lakhel[1], Souad Djerad[1,*]

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

ABSTRACT

In this study the leaching of CuO particles by glycine, an environmentally friendly leachant, was investigated under different conditions. It was found that the variation of glycine and NaOH concentrations as well as CuO loading influenced slightly the dissolution of CuO while temperature, the volume of solution and the nature of stirring impacted greatly the dissolution process. Magnetic and mechanical stirring registered inverse effects. In fact, increasing the volume of solution from 105 to 405 mL decreased the dissolution of CuO from 100% to 26.2% registered after 180 min respectively under magnetic stirring, while it increased from 43.5% to 91.7% respectively under the same conditions with mechanical stirring. Thus, the nature of stirring is a crucial parameter that may radically change the dissolution results. The dissolution was found to be controlled by chemical reaction.

Keywords: CuO particles, glycine, dissolution, hydrodynamics, stirring device

1. INTRODUCTION

Copper is one of the most studied metals in the literature because of its large utilization in domestic and industrial fields [1, 2]. In hydrometallurgy, lot of research is conducted to optimize copper extraction from ores or secondary resources using different leaching reagents. However, many of these reagents pose potential environmental risks [3, 4]. Nowadays, efforts are made for the implementation of sustainable processes through the use of environmentally benign and renewable products such as organic acids and amino acids [5-8].

Glycine is a natural product which is non-toxic, non-volatile and non-flammable. In human body, glycine acted as precursor to proteins and is found in high concentrations in the skin, connective tissues of the joints and muscle tissue and in bone broth. Glycine is produced relatively cheaply. It is used in food, metal plating, animal feed, pharmaceutical industries, for the production of glyphosate herbicide, fertilizers and explosives [9, 10].

In the literature, several studies were reported dealing with the leaching of copper from different sources using amino acids. Tanda et al. [9] studied the leaching of copper oxide from different ores. They found that the optimum leaching conditions are pH 11 and glycine to copper ratio of 4:1 thereby they extracted 95%, 91%, 83.8%, and 17.4% of copper after 24 h from azurite, malachite, cuprite and chrysocolla respectively. Oraby and Eksteen [11] studied the selective leaching of copper from a gold-copper concentrate in glycine solutions in the presence and absence of peroxide. They found that 98 % of copper can be selectively leached in glycine-peroxide solution in 48 h at ambient conditions and a pH of 10.5-11. Feng and Deventer [12] studied the role of amino acids such as glycine, L-valine, DL-α-alanine, and L-histidine in the ammoniacal thiosulphate leaching of a pyrite concentrate. They found that amino acids enhanced the leaching of copper species from the pyrite concentrate and that thiosulphate consumption decreased from 12.6 kg t^{-1} to 6.6 kg t^{-1}, 6.3 kg t^{-1}, 5.2 kg t^{-1} and 4.5 kg t^{-1} after 24 h with the addition of 10 mM L-valine, glycine, DL-α-alanine and L-histidine, respectively.

Mixing operations are encountered widely throughout productive industry in processes involving physical and chemical change. Many sectors carry out mixing operations on a large scale such as in food,

Corresponding Author: s_djerad@hotmail.com (Souad Djerad)
Received 5 August 2018; Received in revised form 3 September 2019; Accepted 9 September 2019
Available Online September 2019
Doi: https://doi.org/10.35208/ert.450874

pharmaceutical, paper, and plastics industries [13]. As a result, the financial investment in both the capital and running costs of mixing processes is considerable. In fact, it was estimated that the cost to the process industries due to an inadequate understanding of mixing varied from 1 to 10 billion dollars per year [14].

Mixing is carried out usually to increase the homogeneities, and to enhance the rate processes. Understanding how the solids and liquids move to achieve these requirements is an essential prerequisite for a successful mixer design [13, 15, 16]. In the field of hydrometallurgy, metal dissolution testing is a fundamental part of mineral extraction and manufacturing. Tests are usually focused on the effect of parameters such as concentration, liquid/solid ratio, temperature and stirring speed. These parameters are often investigated with only one mixing device. Testing the nature of mixing may bring useful data that can be further exploited for any leaching system. Only limited information on the impact of mixing equipment on leaching process was generated to date in hydrometallurgical field [17].

The work described in this paper is an attempt to address the factors governing the dissolution process of pure CuO particles by glycine with a particular attention given to the effect of stirring device.

2. MATERIALS & METHOD

Powder of CuO (black color) with a mean size of 3 µm was purchased from Fluka (≥98%). Glycine (99%, Fluka) and NaOH (99%, Biochem) were used as received. Distilled water was used for the preparation and washing in all experiments. In a typical experiment 0.05 g of copper oxide (CuO) was contacted at 25 °C with a solution containing glycine and NaOH. The mixture was magnetically stirred. During CuO dissolution a deep blue solution is produced indicating the formation of copper (II)-glycinate complexes which are stable over a broad pH range (2.8-12) [9, 18, 19] and can be analyzed by molecular spectrometry. In this study a JENWAY 6705UV/VIS spectrometer was used at 640 nm found as the maximum absorbance of the complexes formed. Cupric sulphate pentahydrate (98%, Fluka) was used at different concentrations to generate a calibration curve (Fig.1). In this work, different parameters were investigated such as the concentration of glycine and NaOH, CuO loading, temperature, and stirring device (magnetic and mechanical). The results are presented below.

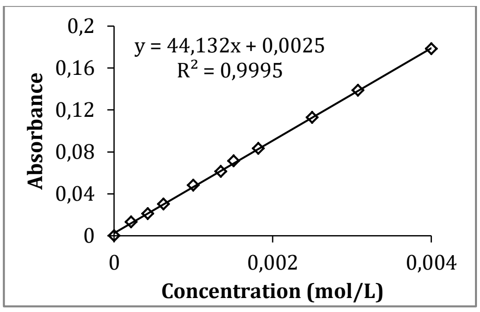


Fig 1. Calibration curve

3. RESULTS & DISCUSSION

3.1. Effect of the operation conditions on CuO dissolution

The glycine molecule (H_2N-CH_2-COOH) contains carboxylic and amino functional groups and is itself amphoteric. In aqueous solutions it can be in two forms depending on the pH [9]:

H_3^+N-CH_2-COOH↔ H_2N-CH_2-COOH + H^+ pKa=2.47 (1)

H_2N-CH_2-COOH ↔ H_2N-CH_2-COO^- + H^+ pKa=9.66 (2)

The amine group is protonated at pH below 2.47 and glycine is in an anionic form at pH above 9.66. In the intermediate interval the neutral form of glycine is in equilibrium with the zwitterion H_3^+N-CH_2-COO^-.

The effect of glycine concentration was studied by contacting 0.05 g of CuO with 200 mL of glycine at different concentrations: 0.1-0.5-1 and 1.5 M at 25 °C and 250 rpm. To each solution 5 mL of NaOH at 0.5 M were added (V_{total}=205 mL) thereby the pH of the solutions was 8.9. At this pH value it is the zwitterion which is the predominant specie. Thus, it can be supposed that the reaction of CuO dissolution occurred as follows:

CuO+2(H_3^+N-CH_2-COO^-)→Cu(H_2N-CH_2-COO)$_2$+H_2O (3)

The results show that the extent of CuO dissolution increased slightly with increasing glycine concentration. It attained 12.3-17.6 -23.3 and 29% after 1 min of contact and increased to 70.9- 79.7-92.2 and 96.8% after 180 min with 0.1-0.5-1 and 1.5 M respectively (Fig.2a).

The effect of CuO loading was studied by testing 3 values 0.03-0.05 and 0.07 g. The other parameters were kept constant ($C_{0(glycine)}$ = 0.1 M, 25 °C and 250 rpm). The results (Fig. 2b) show three curves fused together up to 90 min beyond which the effect was more visible. The dissolution rate decreased with increasing CuO loading attaining 58.1-70.9 and 77.6 % with 0.07 g-0.05 g and 0.03 g respectively after 180 min.

The same slight effect was also observed when the concentration of NaOH was varied (Fig.2c) while maintaining the other parameters constant ($C_{0(glycine)}$=0.1 M, m_{CuO}=0.05 g, 25 °C and 250 rpm) reaching 66.8 % with 0.1 M and 83.4 % with 2M after 180 min.

Figure 2d shows the effect of temperature (25-30-40-50 and 60 °C) tested under the conditions ($C_{0(glycine)}$=0.1 M and m_{CuO}=0.05 g and 250 rpm). On the contrary of the previous parameters, temperature had an important effect on the dissolution of copper oxide. At 25 °C it reached 70.9% after 180 min and at 60 °C total dissolution was obtained after only 20 min of reaction.

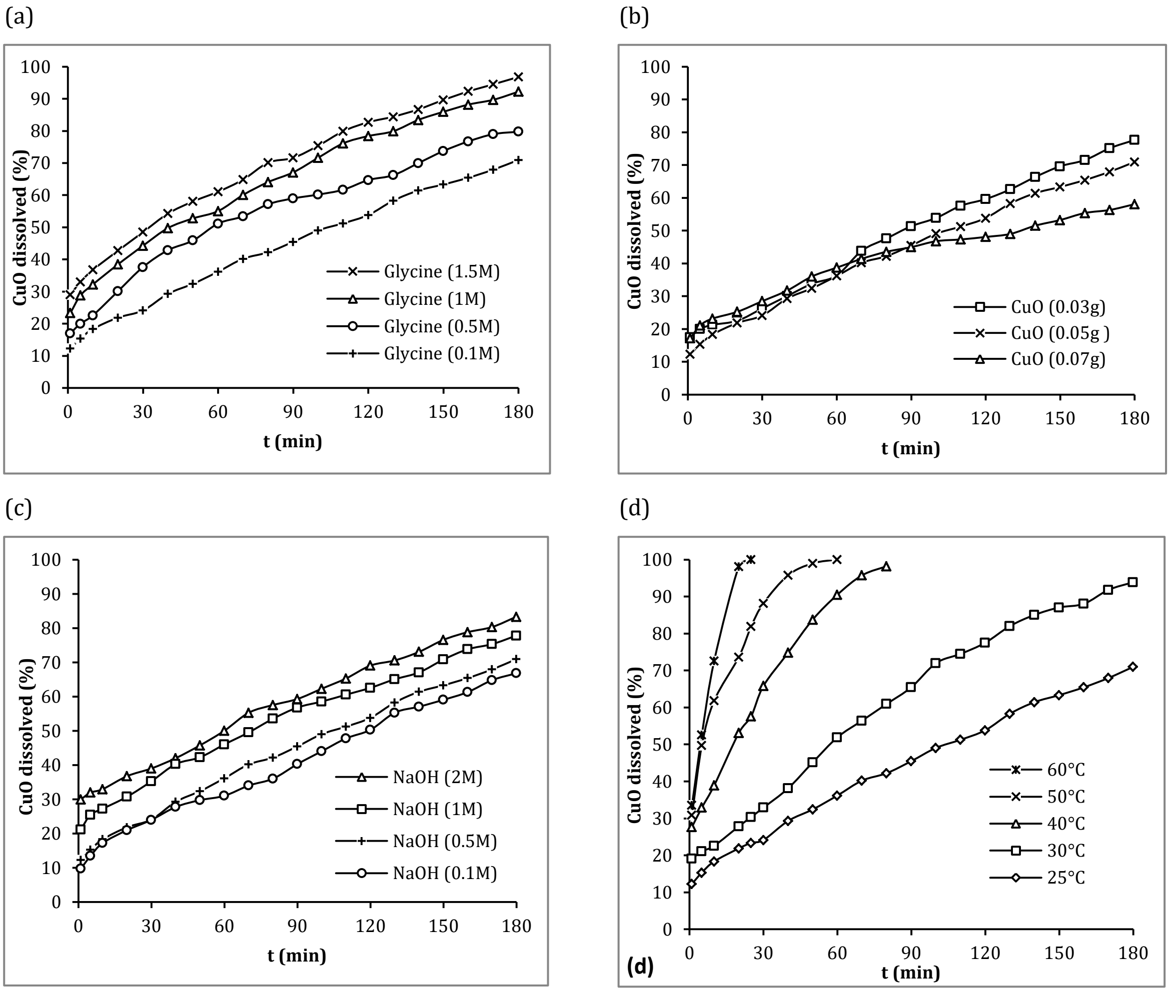


Fig 2. Effect of glycine concentration (a), the amount of CuO (b), NaOH concentration (c) and temperature (d) on the rate of CuO dissolution by glycine

In a previous study we investigated the leaching of CuO from CuO/α-Al_2O_3 catalyst in the presence of different acids (HCl, HNO_3, H_2SO_4, and $C_6H_8O_7$) [20]. It was found that hydrochloric acid yields the highest CuO dissolution efficiency, followed by sulfuric acid, nitric acid and citric acid. Citric acid was the weakest leachant because of the absence of aggressive anions in the systems (Cl^-, SO_4^{2-}, NO_3^-) which were found to be effective in the dissolution process. The time for total dissolution was about 14 min with inorganic acids at ambient temperature using an acid concentration of 0.5 M at 25 °C while 2 h at 80 °C were necessary to reach the same dissolution efficiency with citric acid solution. In this study the dissolution of CuO by glycine at 0.1 M was total after 25 min at 60 °C but took up to 3 h at ambient temperature. However, despite their lower efficiencies compared to mineral acids, the use of organic leachants such as glycine or citric acid remains more interesting from economical and environmental point of views.

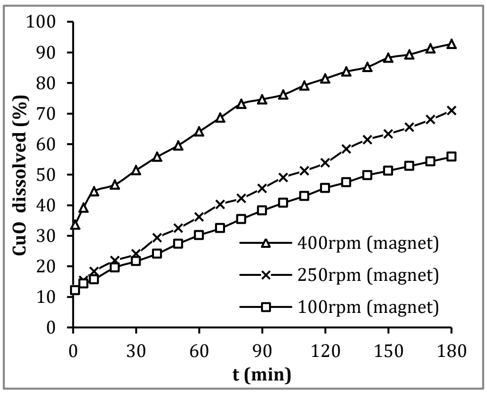
3.2. Effect of mixing device

Two kinds of stirrers were used to homogenize the solutions (magnetic and mechanical). The mechanical stirrer was formed by a pitched blade turbine (5 cm of diameter and inclined with 45°) while magnetic stirring was carried out with a magnetic bar with 2 cm in size. Mechanical stirrers or impellers are often used in industry. They are classified in two general types; axial flow and radial flow. Axial flow impellers impose essentially bulk motion to the fluid. They are very useful in mixing solid-liquid suspensions. They promote a downward velocity profile and are characterized by low shear and high axial dispersion, they create good top to-bottom motion in a tank, which results in good mixing. Radial impellers discharge fluid radially outward to the vessel walls and impose essentially shear stress to the fluid. Mechanically agitated tanks have been studied over a wide range of laboratory and industrial conditions, in order to improve the agitation energy efficiency [21-27] but less in hydrometallurgical field to optimize the extraction efficiency of minerals. In this study a pitched four blade turbine (axial flow) was used. A pitched blade turbine consists of a hub with an even number of blades bolted and tack-welded on it [13]. The blades can be at any angle between 10 and 90° from the horizontal [28-30], but the most common blade angle is 45° as that used in this study.

3.2.1. Effect of stirring speed

The effect of stirring speed was studied with both mixing devices by testing three values: 100-250 and 400 rpm while maintaining the other conditions constant ($C_{0(glycine)}$=0.1 M, m_{CuO}=0.05 g, 25 °C and 205 mL). In both cases, increasing stirring speed led to improve the dissolution rate. It attained 55.8-70.9 and 92.7 % with magnetic stirrer (Fig. 3a) and 50.2-57.2 and 80 % with mechanical one (Fig. 3b) at 100-250 and 400 rpm respectively after 180 min.

(a)



(b)

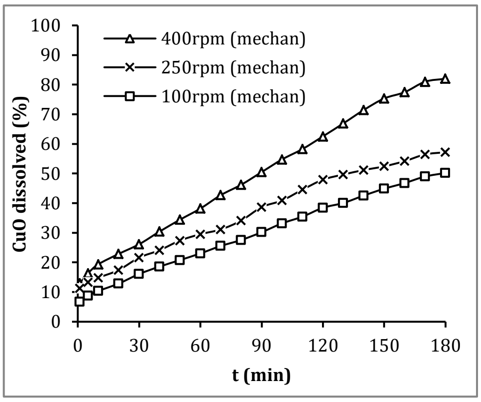


Fig 3. Effect of magnetic (a) and mechanical (b) stirring on CuO dissolution by glycine

3.2.2. Effect of the volume of solution

The volume of solution inside which the reagents react together may influence the rate of the reaction. In this work, the effect of the volume of solution was studied by maintaining the mol numbers of the reagents constant (0.02 mol of glycine and $6.28.10^{-4}$ mol of CuO (0.05 g)) and varying the volume of water (100-200-300 and 400 mL). To each volume of solution 5 mL of NaOH at 0.5 M were added ($2.5.10^{-3}$ mol). The dissolution reaction was studied with both mixing devices at a constant stirring speed of 250 rpm and 25°C.

a. Magnetic stirring

A magnetic bar of 2 cm in size was used. The results show that the rate of dissolution increased when the volume of solution decreased (Fig.4a). In fact, total dissolution was achieved with 105 mL after 120 min while only 26.2 % were dissolved with 405 mL after 180 min. These results can be explained by the increase in the frequency of reactive collisions between the reagents occurring in small volumes resulting in the acceleration of the dissolution reaction. An induction period (where no dissolution occurred) of 30 min was observed with 405 mL.

- Effect of the size of the magnetic bar

In magnetic stirring, the size of the bar may influence the rate of the chemical reaction. To investigate this parameter, a second magnetic bar with 6 cm in size was tested and the results were compared to those of 2 cm. The longer bar obviously gave the best results (Fig. 4b). With the volume of 105 mL, total dissolution was obtained after 75 min with bar 6 cm and after 120 min with bar 2 cm. With 405 mL, 72.5 % and 26.2 % were reached with bars 6 cm and 2 cm respectively after 180 min. On the other hand, it can be observed that plots obtained with bar 6 cm were closer to each other than those obtained with 2 cm and no induction period was observed in this case. The bar 6 cm involved higher turbulence than bar 2 cm so that the decrease in the volume of solution impacted less the dissolution results.

b. Mechanical stirring

The effect of the volume of solution was investigated with mechanical stirrer under the same conditions used for magnetic one. The mechanical stirrer was centrally located and placed in the middle height of the solutions.

The results show that on the contrary of magnetic stirring, increasing the volume of the solution led to increase the dissolution of copper oxide (Fig. 5). In fact, after 180 min, 91.6% of CuO were dissolved with 405 mL and 43.47% with 105 mL. During the experiments, it was observed that CuO particles settled at the bottom of the vessel and that increasing the volume of the solution led to partially disperse the particles into the bulk. In the literature, it was reported that there is a location under the paddle in the central position of the vessel where the velocity of the fluid is minimal leading to accumulate the particles in the form of aggregate [31]. The formation of agglomerate reduced the surface of the particles exposed to the fluid and hence decreased the dissolution rate. On the other hand, CuO density (6.31 g cm^{-3}) is important and needs high turbulence to maintain the particles in suspension.

The increase in the dissolution rate of CuO with increasing the volume of solution under mechanical stirring may be explained by the fact that an important volume of water may remove more efficiently the aggregate located under the paddles and drag the particles to the main stream where the turbulence is higher increasing consequently the dissolution rate. In a reduced volume, the capacity to move the same amount of solid is lowered leading to settle the particles as aggregate and decrease the dissolution rate.

- Effect of the position of the impeller inside the vessel

The impeller positioning is an important factor impacting hydrodynamics. In order to study this parameter, the impeller was disposed at different heights measured from the base of the vessel: 1 cm, 4.5 cm and 7.5 cm (Fig.7). The experiments were carried out with 205 mL (total height of the liquid =8.5 cm).

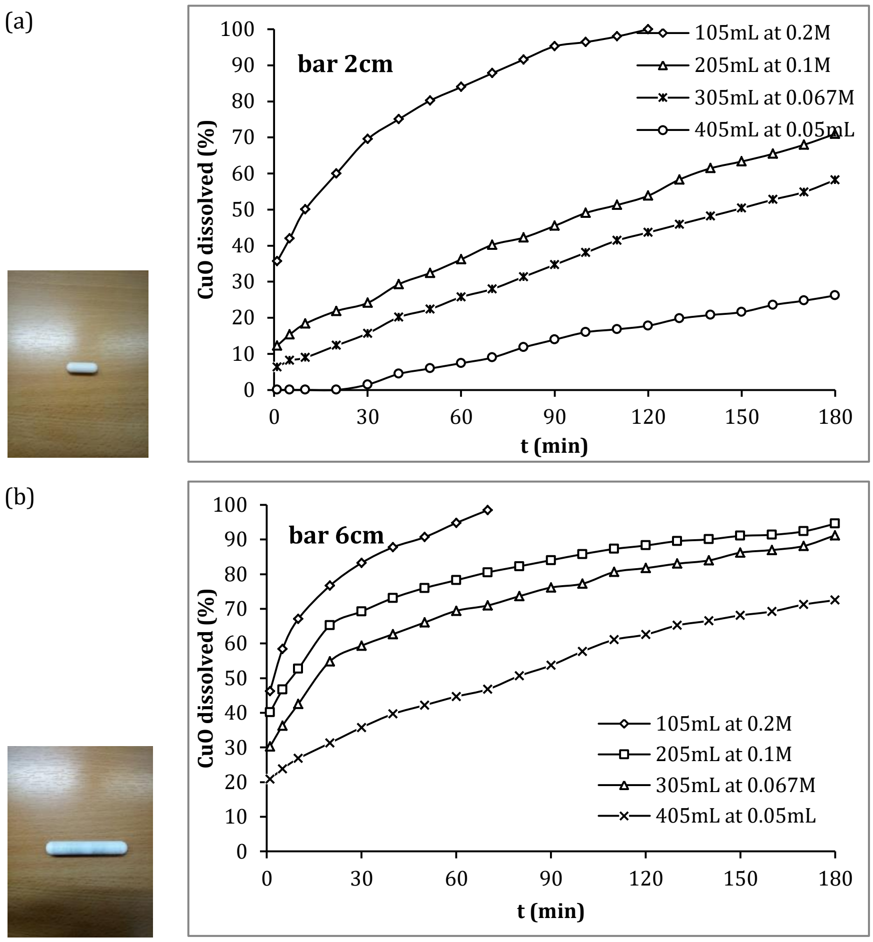


Fig 4. Effect of magnetic bar size 2 cm (a) and 6 cm (b) on CuO dissolution by glycine

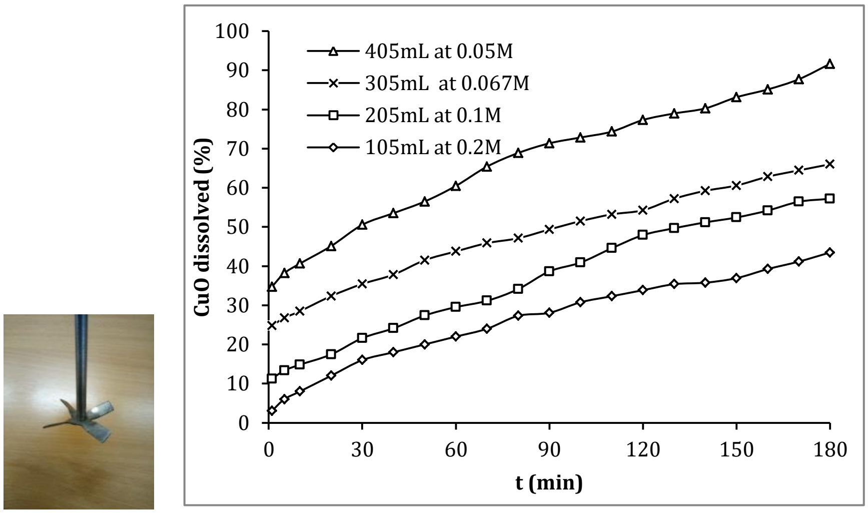


Fig 5. Effect of mechanical stirring on the dissolution of CuO by glycine

The results show that the lowest dissolution efficiency (50.3%) was obtained when the paddles were close to the upper surface (7.5 cm). The dissolution was slightly improved (57.2%) when the paddles were placed very close to the bottom of the vessel (1 cm) while the best results were obtained at middle height (4.5 cm) reaching 76.7% after 180 min (Fig. 6).

In the literature, the suspension of particles in tanks stirred by different types of impeller was investigated. It was reported that axial flow impeller generates an axial jet that sweeps the vessel bottom of settled solids and that the flow at the bottom is mainly directed outward [27]. When the distance of the impeller-bottom increased, a flow transition occurs. The outflow of the impeller becomes more radial and the jet from the impeller is directed towards the vessel wall. The flow direction at the vessel bottom is reversed and is directed inward, rather than outward as was the case with the axial flow pattern [32]. Furthermore, the velocities at the bottom are lower than with the axial flow pattern. As a result, complete solids suspension is much more difficult to obtain in this case and the solids mainly move around at the tank bottom, instead of being suspended throughout the vessel [31]. The settling of particles when the impeller was positioned at 7.5 cm height was visually observed confirming the explanation given above. Thus, there is an optimal position of the impeller inside the vessel where the suspension of particles is maintained and their dissolution favored.

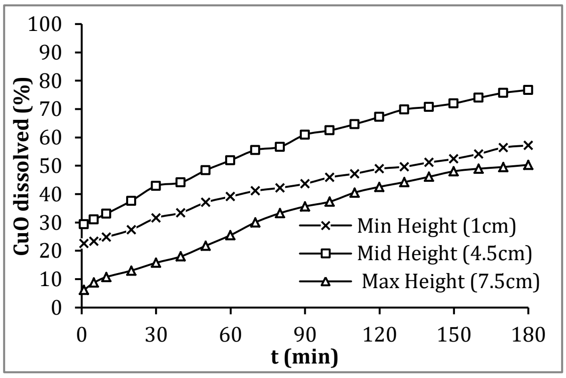


Fig 6. Effect of the position of paddles inside the reactor on the dissolution of CuO by glycine

It is worth noting that the position of the impeller at 1 cm height (very close to the bottom) approaches the conditions of magnetic stirring. A comparison of the results between magnetic and mechanical stirring under the same conditions (200 mL of glycine at 0.1 M+5 mL of NaOH at 0.5 M, 0.05 g of CuO, 25 °C, 250 rpm) shows that magnetic stirring was more efficient in CuO dissolution despite the small size of the magnetic bar used (2 cm) compared to that of the impeller (diameter 5 cm) dissolving 70.9 % versus 57.2 % respectively after 180 min. It can be supposed that since the magnetic bar is disposed at the bottom of the vessel, it enters into contact with the powder and disperses the particles more efficiently during rotation, while the region of low velocity still exists with mechanical stirring leading to agglomerate the particles and hinders the dissolution rate. The settling of particles at 1cm height of impeller was also visually observed. Thus, stirring device may cause a radical change in flow dynamic and consequently in dissolution rate. This was highlighted by the effect of the volume where opposite effects were observed between magnetic and mechanical stirrers.

3.3. Kinetic study

Leaching kinetic is often described by the Schrinking Core Model where the reaction between solid and fluid reactants occurs on the outer surface of the solid [33]. The solid reactant is initially surrounded by a fluid film through which mass transfer occurs between the solid and the bulk fluid. As the reaction proceeds, the unreacted core of the solid shrinks toward the center of the solid and a porous product layer forms around the unreacted core. This heterogeneous model stipulates that the rate of a reaction can be controlled either by diffusion through the liquid film or by diffusion through a layer of products or by the chemical reaction. Thus, for a spherical, nonporous particle, the fraction x of the solid dissolved as a function of time t is given as follows:

$$x = k.t \qquad (4)$$

for control by diffusion through the liquid film

$$(1\text{-}x)^{2/3} + 2\,(1\text{-}x) = k.t \qquad (5)$$

for diffusion control through the product layer

$$1\text{-}\,(1\text{-}x)^{1/3} = k.t \qquad (6)$$

for control by the chemical reaction

where k is the rate constant (min^{-1}). The rate of dissolution is controlled by the slowest process.

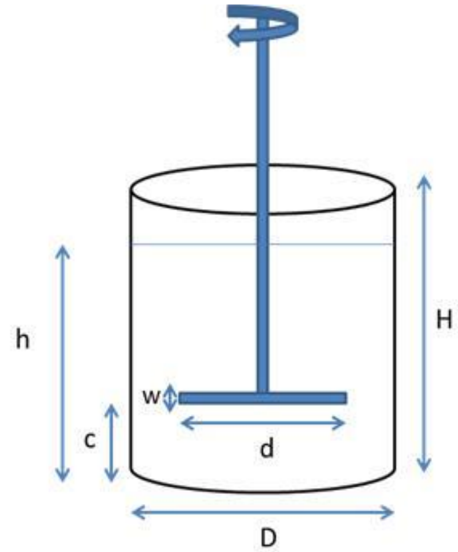


Fig 7. Characteristics of the mixed system. It consists of a flat bottomed cylindrical vessel of diameter D = 6 cm and height H = 12 cm. The liquid height is h = 8.5 cm. Mixing is ensured by a four-bladed impeller of diameter d = 5 cm and height w = 7 mm with blade attack angle of 45°. The clearance between the vessel base bottom and the middle of the impeller blades (variable) c = 1 cm, 4.5 cm and 7.5 cm

Levenspiel model was applied for the dissolution of copper oxide by glycine at different temperatures under magnetic stirring (results of figure 2d) in order to determine the rate constants and the activation energy.

The rate constants were determined by plotting the left side of equations (4-6) versus reaction time. Thus, the three expressions [(x), (1- $3(1\text{-}x)^{2/3}$ + 2(1-x)) and (1- $(1\text{-}x)^{1/3}$)] were reported on the y axis as a function of time (t) which was reported on the x axis. The slopes of the straight lines were equal to the rate constants (k). The application of the model reveals that equation (6) gave straight lines with linear regression coefficients close to 1 indicating that the dissolution of copper oxide was controlled by the chemical reaction (Fig. 8a).

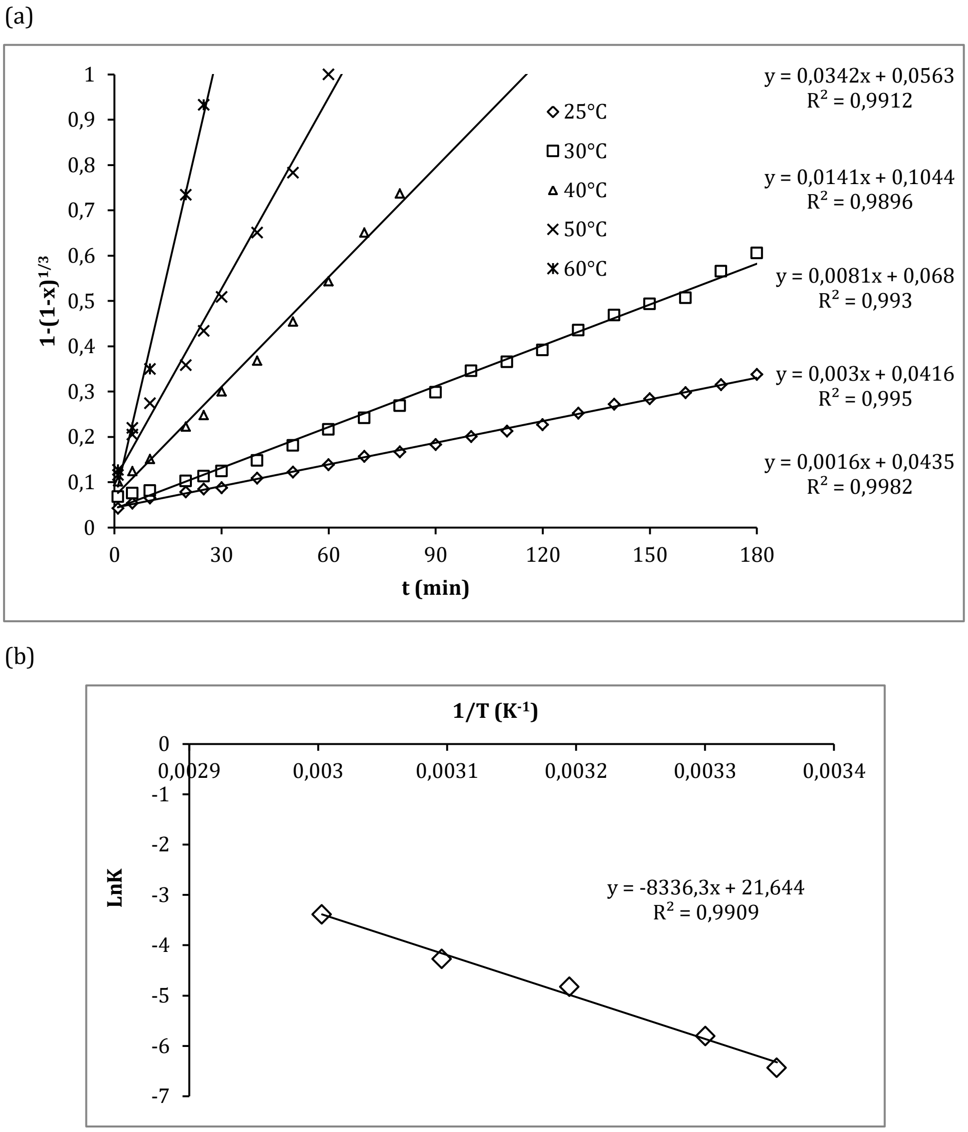


Fig 8. Fitting the experimental data obtained at different temperatures by Levenspiel Model (a) and determination of the activation energy for the dissolution reaction of CuO by glycine (b)

The values of the rate constants were used to calculate the activation energy by using the Arrhenius equation ($k = A.e^{-Ea/RT}$). By taking the logarithm of both sides the equation became: Lnk=LnA-(Ea/R)T and it is possible by plotting Lnk as a function of 1/T to determine the value of slope Ea/R and calculate the activation energy (Ea) of the reaction (Fig. 8b). Under the conditions used in this study Ea value was found to be equal to 69.31 kJ mol^{-1}. A chemically controlled reaction is generally a temperature dependent process and has activation energy higher than 40 kJ mol^{-1}. Our results have shown that the dissolution of CuO by glycine was greatly affected by temperature which agrees with this assumption.

4. CONCLUSIONS

This article is intended to share the preliminary results of a study that was conducted to gain a basic understanding of the role of hydrodynamics in dissolution testing for a pure component. The results for pure components are important as they may be used to evaluate leaching of more complex systems containing several mineral constituents such as in ores and mineral wastes.

The results obtained in this study show that glycine may be used as an eco-friendly reagent as it dissolved easily CuO under mild conditions and produced a non-pollutant effluent. Noticeable but small effects of reagent concentrations were observed while temperature, the volume of solution and the nature of stirring impacted greatly the dissolution process. The effect of the volume of solution depended on the nature of mixing device. In fact, the dissolution of CuO was enhanced by reducing the volume of solution under magnetic stirring and by increasing it under mechanical stirring. These differences in results were due to differences in fluid movements created by magnetic bar and the paddles inside the vessel. The results obtained underline the crucial effect of hydrodynamics created by mixing devices on the rate of chemical reactions. This should be more routinely monitored as a part of dissolution tests when projecting to design a reactor for leaching process.

ACKNOWLEDGEMENT

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

REFERENCES

[1]. M. Kermiche and S. Djerad, ″Facilitated transport of copper through bulk liquid membrane containing di-2ethylhexyl phosphoric acid,″ *Desalination and Water Treatment*, Vol. 36 (1-3), pp. 261-269, 2011.

[2]. T. Miyahara, H. Kanzaki, R. Hamadab, S. Kuroiwa, S. Nishiyama and S. Tsuruya, ″Liquid-phase oxidation of benzene to phenol by CuO-Al_2O_3 catalysts prepared by co-precipitation method, ″*Journal of Molecular Catalysis A: Chemical*, Vol. 176 (1-2), pp. 141–150, 2001.

[3]. N. Alane, S. Djerad and L. Tifouti, ″Acid Leaching of Zinc From ZnO/Al_2O_3 Catalyst,″ *Lebanese Science Journal*, Vol. 9 (2), pp. 63-74, 2008.

[4]. I. Boukerche, N. Habbache, N. Alane, S. Djerad and L. Tifouti, ″Dissolution of Cobalt from CoO/Al_2O_3 Catalyst with Mineral Acids,″ *Industrial Engineering and Chemistry Research,* Vol. 49 (14), pp. 6514–6520, 2010.

[5]. I. Boukerche, S. Djerad, R. Larba, L. Benmansour and L. Tifouti, ″Dissolution behavior of metallic zinc in organic acid,″ *Environmental Research and Technology,* Vol. 1 (3), pp. 11-18, 2018.

[6]. J.J. Eksteen and E.A. Oraby, ″The leaching and adsorption of gold using low concentration amino acids and hydrogen peroxide: effect of catalytic ions, sulphide minerals and amino acid type,″ *Minerals Engineering*, Vol. 70, pp. 36-42, 2015.

[7]. N. Habbache, S. Djerad and L. Tifouti, ″Optimization of the operation conditions for NiO dissolution with different leachants,″ *Process Engineering Journal*, Vol. 1 (2), pp. 59–67, 2017.

[8]. E.A. Oraby and J.J. Eksteen, ″The leaching of gold, silver and their alloys in alkaline glycine-peroxide solutions and their adsorption on carbon,″ *Hydrometallurgy,* Vol.152, pp. 199-203, 2015.

[9]. B.C. Tanda, J.J. Eksteen and E.A. Oraby, ″An investigation into the leaching behavior of copper oxide minerals in aqueous alkaline glycine solutions,″ *Hydrometallurgy*, Vol. 167, pp. 153-162, 2017.

[10]. V.Ya. Yablokov, I.L. Smel'tsova, I.A. Zelyaev and S.V. Mitrofanova, ″Studies of the rates of thermal decomposition of glycine, alanine and serine,″ *Russian Journal of General Chemistry*, Vol. 79 (8), pp. 1704-1706, 2009.

[11]. E.A. Oraby and J.J. Eksteen, ″The selective leaching of copper from gold-copper concentrate in glycine solutions,″ *Hydrometallurgy,* Vol.150, pp. 14-19, 2014.

[12]. D. Feng and J.S.J. Van Deventer, ″The role of amino acids in the thiosulphate leaching of gold,″ *Minerals Engineering*, Vol. 24 (9), pp. 1022-1024, 2011.

[13]. N. Harnby, M.F. Edwards and A.W. Nienow, ″Mixing in the Process Industries, ″Butterworth-Heinemann 2nd Ed, Oxford, 2001.

[14]. G. Tati'erson and R. Calabrese, (eds) ″Industrial Mixing Research Needs,″ AIChE, New York, 1989.

[15]. G. Daccord, ″Dissolutions, evaporations, etching,″ In: Avnir, D. (Ed.), The fractal approach to heterogeneous chemistry. John Willey and Sons, Chichester, 1989.

[16]. P.M. Armenante, E.U. Nagamine and J. Susanto, ″Determination of correlations to predict the minimum agitation speed for complete solid suspension in agitated vessels,″ *Canadian Journal of Chemical Engineering*, Vol.76 (3), pp. 413-419, 1998.

[17]. O. Akiti, A. Yeboah, G. Bai and P.M. Armenante, ″Hydrodynamic effects on mixing and competitive reactions in laboratory reactors,″ *Chemical Engineering Science*, Vol. 60 (8-9), pp. 2341- 2354, 2005.

[18]. S. Aksu and F.M. Doyle, ″Electrochemestry of copper in aqueous glycine solutions,″ *Journal of Electrochemical Society*, Vol. 148 (1), pp. B51-B57, 2001.

[19]. S. Aksu and F.M. Doyle, ″The role of glycine in the chemical mechanical planarization of copper, ″ *Journal of Electrochemical Society,* Vol. 149 (6), pp. G352-G361, 2002.

[20]. N. Habbache, N. Alane, S. Djerad and L. Tifouti, ″Leaching of copper oxide with different acid solutions,″ *Chemical Engineering Journal*, Vol. 152 (2-3), pp. 503–508, 2009.

[21]. M. Ammar, Z. Driss, W. Chtourou and M.S. Abid, ″Effect of the Tank Design on the Flow Pattern Generated with a Pitched Blade Turbine,″ *International Journal of Mechanics and Applications,* Vol. 2 (1), pp. 12-19, 2012.

[22]. S. Karray, Z. Driss, A. Kaffel, H. Kchaou and M.S. Abid, ″Fluid-structure interaction in a stirred vessel equipped with the Rushton turbine,″ *International Journal of Mechanics and Applications,* Vol. 2 (6), pp. 129-139, 2012.

[23]. J. Baldyga and J.R. Bourne, ″Turbulent Mixing and Chemical Reactions,″ Wiley, New York. 1999.

[24]. J. Aubin, D.F. Fletcher and C. Xuereb, ″Modeling turbulent flow in stirred tanks with CFD: the influence of the modeling approach, turbulence model and numerical scheme,″ *Experimental Thermal and Fluid Science,* Vol. 28 (5), pp. 431-445, 2004.

[25]. J. Kukura, P.C. Arratia, E.S. Szalai and F.J. Muzzio, ″Engineering tools for understanding hydrodynamics of dissolution tests,″ *Drug Development and Industrial Pharmacy*, Vol. 29 (2), pp. 231-239, 2003.

[26]. M. Kamba, Y. Seta, N. Takeda, T. Hamaura, A. Kusai, H. Nakane and K. Nishimura, ″Measurement of agitation force in dissolution test and mechanical destructive force in

disintegration test,'' *International Journal of Pharmaceutics*, Vol. 250 (1), pp. 99-109, 2003.

[27]. M. Higuchi, Y. Yoshihashi, K. Tarada and K. Sugano, ''Minimum rotation speed to prevent coning phenomena in compendium paddle dissolution apparatus,'' *European Journal of Pharmaceutical Sciences*, Vol. 65, pp. 74-78, 2014.

[28]. H. Ameur and M.D. Bouzit, ''3D hydrodynamics and shear rates, variability in the United States Pharmacopeia Paddle Dissolution Apparatus,'' *International Journal of Pharmaceutics*, Vol. 452 (1-2), pp. 42-51, 2013.

[29]. H. Ameur, ''Mixing of complex fluids with flat and pitched bladed impellers: effect of blade attack angle and shear-thinning behavior,'' *Food and Bioproducts Processing*, Vol. 99, pp. 71-77, 2016.

[30]. H. Ameur, ''Energy efficiency of different impellers in stirred tank reactors,'' *Energy*, Vol. 93 (2), pp. 1980-1988, 2015.

[31]. A. Bakker, J.B. Fasano and K.J. Myers, ''Effects of Flow Pattern on the Solids Distribution in a Stirred Tank,'' 8th European Conference on Mixing, Cambridge, U.K. IChemE Symposium Series No. 136, ISBN 0 85295 329 1, pp. 1-8, 1994.

[32]. Z. Jaworski, A.W. Nienow and K.N. Dyster, ''An LDA study of the turbulent flow field in a baffled vessel agitated by an axial, down-pumping hydrofoil impeller,'' *Canadian Journal of Chemical Engineering*, Vol. 74 (1), pp. 3-15, 1996.

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

Environmental Research & Technology, Vol. 2 (3), pp. 112-121, 2019

Turkish JournalPark ACADEMIC

Environmental Research & Technology

http://dergipark.gov.tr/ert

RESEARCH ARTICLE

Adsorption of Basic Blue 41 using *Juniperus excelsa*: Isotherm, kinetics and thermodynamics studies

Ali Riza Kul[1], Adnan Aldemir[2,*], Salih Alkan[3], Hasan Elik[1], Meliha Caliskan[3]

[1]Van Yüzüncü Yıl University, Faculty of Science, Chemistry Department, 65080, Van, TURKEY
[2]Van Yüzüncü Yıl University, Faculty of Engineering, Chemical Engineering Department, 65080, Van, TURKEY
[3]Ordu University, Faculty of Science, Chemistry Department, 52200, Ordu, TURKEY

ABSTRACT

In this study *Juniperus excelsa* shavings powder (JESP) was utilized as an adsorbent for the removal of Basic Blue 41 (BB 41) which is one of the common basic dyes, from aqueous solution. The adsorption experiments were carried out in a batch system and effects of initial concentration of dye, interaction time and temperature were investigated. Langmuir, Freundlich and Temkin adsorption isotherms were used to model equilibrium data. According to the results, Freundlich isotherm model becomes more convenient option compared with Langmuir and Temkin models. Freundlich model coefficients are raise as the temperature rises, showing that the adsorption process becomes favorable higher temperature. The kinetic parameters were determined by pseudo first order (PFO), pseudo second order (PSO) and intra-particle diffusion (IPD) models. Results indicated that experimental and calculated qe values are matched to each other. Thus the process fits PSO kinetic model with higher R^2 values than other two models. Kinetic constants become closer to both temperatures and initial concentrations and qe values are increases with increasing concentration of BB 41. Initial dye concentration elevates from 25 to 100 mg L^{-1}, dye adsorption capacity onto JESP from 3.06 to 16.53 mg g^{-1}, respectively. Thermodynamic parameters for instance free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were assessed. Enthalpy and entropy of this separation process are determined from 3081.91 J mol^{-1} and 12.33 kJ mol^{-1}, respectively. The negative values of $\Delta G°$ showed that this separation process was endothermic and natural. The research results demonstrate that JESP may be a substitute than pricey adsorbents for dye removal.

Keywords: Basic Blue 41, dye adsorption, *Juniperus excelsa*, isotherm models, kinetic and thermodynamic parameters

1. INTRODUCTION

The various pollutants such as dyes, pesticides, herbicides and pharmaceuticals should be remove the water systems because of these materials have a negative effect on human and animal health [1, 2]. Dyes released from various sources, e.g., textile industries, cosmetics, pharmaceuticals, paper and pulp industries are regarded as one of the potent pollutants being added to the natural water resources [3]. Dyes are stable, complex structure and very slow biodegradability materials with toxic to organisms in receiving waters and prejudicial to photosynthetic activities. Especially textile dyes are an important type of pollutants which occur in industrial wastewater and cause serious environmental problems. Among these textile dyes, basic dyes have brilliant and strong color intensity and are very detectable in a low concentration. Basic dyes are quaternary salts whose cations have the positive charge most often on the N, C, O and S atoms and anions are most frequently Cl^-, SO_4^{-2}, HSO_4^- or $(COO^-)_2$ ions [4-6]. In relation with their detrimental effects, it is essential to remove the dyes from wastewater. Several chemical and biological treatment technologies are applied to industrial wastewater such as aerobic and anaerobic microbial degradation, filtration, flocculation, softening, hydrogen peroxide catalysis, coagulation, chemical oxidation, membrane separation, electrochemical treatment, and reverse osmosis [7-10]. Among these methods, the adsorption technique which have relatively economical, flexible and simple

Corresponding Author: adnanaldemir@yyu.edu.tr (Adnan Aldemir)
Received 22 May 2019; Received in revised form 13 September 2019; Accepted 16 September 2019
Available Online September 2019
Doi: https://doi.org/10.35208/ert.568992

design, comfort in operation and efficient is proved to be an effective process for the treatment of color wastewater [11, 12]. Performance of adsorption process is related with adsorbent materials and several adsorbents have been used for the dyes removal from wastewater. Low cost and efficient, locally available materials are investigated for the removal of dyes as activated carbon which is commonly used adsorbent is very expensive with high operation costs and regeneration is needed after treatment process [13, 14].

Juniperus genus has too many species which just *J. oxycedrus*, *J. excelsa*, *J. communis* and *J. foetidissima* species are widely grown in Turkey. The chemical composition and the phytochemical characteristics of the principal compounds of *Juniperus* genus are summarized before. *Juniperus* genus has many biological effects which might be antifungal, antiviral, antimicrobial, anticancer, cytotoxic, antifungal and antioxidant [15, 16]. There are few studies and data on chemical compositions of the related *Juniperus* species because of widespread using *Juniperus* species in many areas. But there is no any research on heavy metal and/or dye adsorption capacity of these species in the literature. Therefore, the dye adsorption capacity was examined with *J. excelsa* shavings in this study.

The interference among the adsorbent and the adsorbate molecules is explained with the adsorption isotherms. A plot of adsorption isotherm associates with the quantity of substance adsorbed to the equilibrium concentration of the adsorbate molecules in the solution at an absolute temperature. The adsorbate nature changes the amount adsorbed and adsorbent affect the adsorption isotherm profile shape [17]. Different isotherm models involving in Langmuir, Freundlich and Temkin adsorption isotherms were utilized to investigate the result [18]. In this investigation, all mentioned ones are considered. Considering the Langmuir isotherm, the assumption was made that adsorption of monolayer and all the active sites on the surface of adsorbent are equal in energy. Freundlich isotherm clarifies the multilayer adsorption behavior. Temkin isotherm describes interaction of solute molecules in the aqueous phase with heterogeneous solid surface. The temperature effect on the adsorption process is determined with analyzed thermodynamic parameters like free energy, entropy as well as enthalpy [19]. The kinetic mechanism of the adsorption process is explained with calculated different equations such as PFO, PSO and IPD models [13].

In this research we studied the adsorption capacity of JESP from Balıkesir, Turkey, for cationic dye Basic Blue 41 (BB 41). By considering its toxicity, this dye was selected as adsorbate. For this aim kinetic, isotherm and thermodynamic studies of this dye adsorption on JESP was conducted.

2. MATERIALS & METHOD

2.1. Adsorbent (*Juniperus excelsa* shavings powder)

Adsorption experiments were carried out with shavings powder from *Juniperus* excelsa which grown on the Balıkesir region in Turkey. The shavings were washed with distilled water to remove dirt and then dried at 65 °C in an oven for 48 h. Then the dried shavings were grinded and passing through a 235 mesh sieve (61.75μm) with high speed disintegrator and named JESP. The chemical composition and the characteristics of the principal compounds of *Juniperus* genus are summarized before [16].

2.2. Adsorbate (Basic Blue 41)

The cationic dye BB 41, was used as the adsorbate in the current research. The IUPAC name of BB 41 is 2-[N-ethyl-4-[(6-methoxy-3-methyl-1,3-benzothiazol-3-ium-2-yl) diazenyl] anilino] ethanol. The formula of BB 41 is $C_{20}H_{26}N_4O_6S_2$ (molecular weight 482.57 g mol^{-1}) which was taken from Sigma-Aldrich Company and used without any purification. A stock solution with a concentration of 1000 mg L^{-1} was prepared by dissolving the required dye amount in distilled water. The required solutions concentration used at the adsorption process was prepared to dilute the stock solution of BB 41 with deionized water to obtain the suitable solution concentrations. 25, 40, 55, 70, 85, 100 ppm solutions of BB 41 were prepared for adsorption experiments using stock dye solution.

2.3. Adsorption experiments

In the batch adsorption experiments which were realized in a temperature-controlled water bath, 2 g of adsorbent was treated with 500 mL of the dye solution. The BB 41 concentration in the solution of dye determined for 180 min while the neutral pH was gradually adjusted by adding H_2SO_4 or NaOH solutions (0.1 M). All experiments were achieved in triplicate at the same conditions which were made for 298, 308 and 318 K temperatures in the water bath and the average values taken to represent the result with all data being calculated.

After adsorption experiments, immediately the suspensions were separated by centrifuge. The concentration of BB 41 in solution at a maximum absorption wavelength of 617 nm was evaluated the UV/VIS spectrophotometer (PG Instruments Ltd, T80 model). A calibration curve was obtained by plotting among absorbance and certain concentrations of the dye solution. Unknown BB 41 concentration was measured using a calibration curve. The dye adsorption capacity on the adsorbent is given Eq. (1):

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

where V symbolizes the solution volume (L), C_0 and C_e represent initial and the equilibrium concentration of dye (mg L^{-1}) and m denotes adsorbent mass (g). Ultimately, obtained data from this study were tested by fitting in isotherm, kinetic and thermodynamic relationships to design the appropriate BB 41 dye remove system using JESP adsorbent.

3. RESULTS & DISCUSSION

3.1. Effect of contact time on dye and initial dye concentrations

One of the critical physical parameters used economically is contact time for the plan and operating wastewater treatment plants. In Fig 1-3, the BB 41 removal from the solutions is rapid at the initial period and from the results that specific adsorption increases with increasing dye concentration at a constant temperature. In the beginning, the surface of the adsorption process is large, so the adsorption to this surface is fast. The equilibrium adsorption time was determined at 120 min for BB 41 removal.

Fig 1-3 demonstrates that the rise at the initial concentration of BB 41 caused the increment in adsorption capacity for three temperatures, respectively. As the initial dye concentration enhances from 25 to 100 mg L^{-1}, the adsorption capacity of dye onto JESP gets up from 2.73 to 15.66 mg g^{-1} for 298 K, 2.92 to 16.45 mg g^{-1} for 308 K and 3.06 to 16.53 mg g^{-1} for 318 K, respectively. These data show that the initial dye concentration plays a critical role in the dye adsorption capacity and that provides a driving force to the interaction between adsorbent and dye. Furthermore, a rise in initial dye concentration induces to elevate in the adsorption amount of dye. Based on the experimental results the maximum dye adsorption rate was obtained with 100 mg L^{-1} initial dye concentration. Previously reported results from various researchers were available for Basic Blue dyes adsorption on different adsorbents and biosorbents such as; activated carbon, inorganic oxide ($MgO-SiO_2$), natural zeolitic tuff, ground nut shells and Eichhornia charcoals, brick waste, nanoporous silica, alumino silicate, pineapple plant stem, black tea leaves, chitosan [1, 5, 7, 20-24]. Comparison of this research results with relevant results of literature, the dye adsorption capacity of JESP is good and JESP may be an alternative material in accordance with more expensive adsorbent used for dye removal.

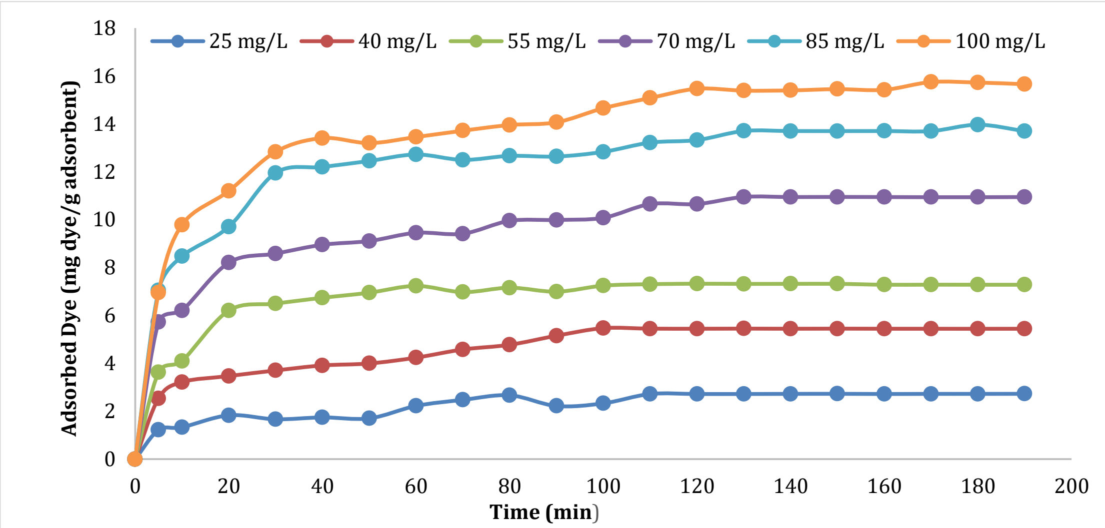


Fig 1. Effect of contact time and initial concentration on dye removal with JESP at 298 K

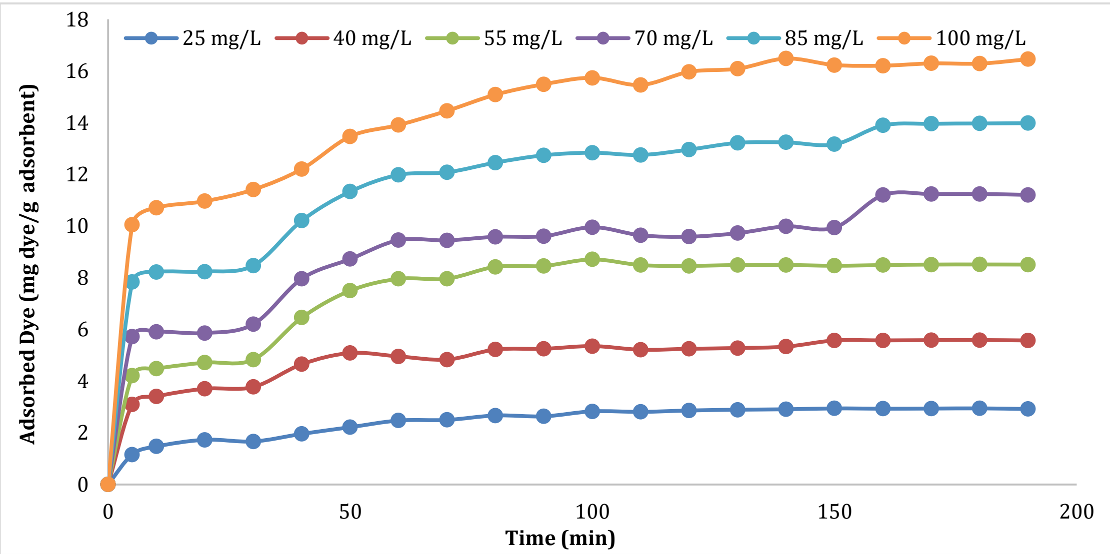


Fig 2. Effect of contact time and initial concentration on dye removal with JESP at 308 K

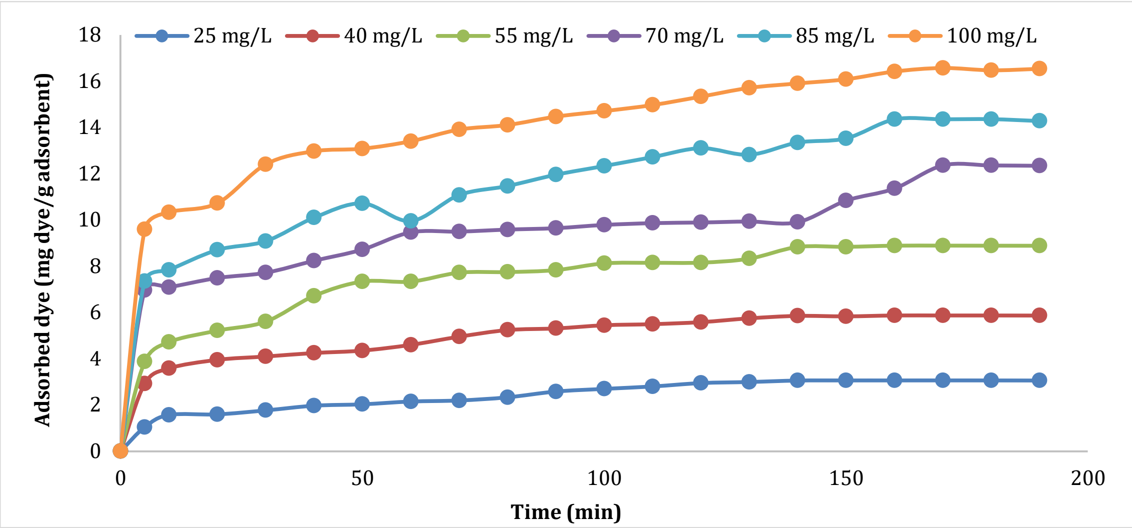


Fig 3. Effect of contact time and initial concentration on dye removal on JESP at 318 K

3.2. Adsorption isotherm studies

Many models used to identify the dyes adsorption on solid surfaces. For the interaction between adsorbate molecules and adsorbent surface investigations, three isotherm models (Freundlich, Langmuir and Temkin) were chosen to endeavor to simplify the interactions between BB 41 and JESP in this study. Three models were applicable for the descriptions of the experimental results obtained at three different temperatures. The parameters of these isotherm models were estimated by using linear regression of isotherms.

Langmuir isotherm has some assumptions for the adsorption occurrence on a homogenous surface with non-interaction adsorbates in the plane of the surface. Langmuir isotherm equation is given Eq. (2):

$$\frac{C_e}{q_e} = \frac{K_L}{q_{max}} + \frac{C_e}{q_{max}} \qquad (2)$$

where q_{max} denotes the maximum capacity of adsorption (mg g^{-1}), *Ce* represents the equilibrium concentration of the solution (mg L^{-1}), K_L is a Langmuir constant associated with the affinity of the binding sites and energy of adsorption (L g^{-1}). q_{max} and K_L values are determined from the slope and intercept of C_e/q_e versus C_e graph. The determination coefficient R^2 of the Langmuir equation demonstrates that the adsorption onto JESP tracks the Langmuir model and this isotherm results of BB 41 adsorption on JESP for 298, 308 and 318 K gives at Fig 4.

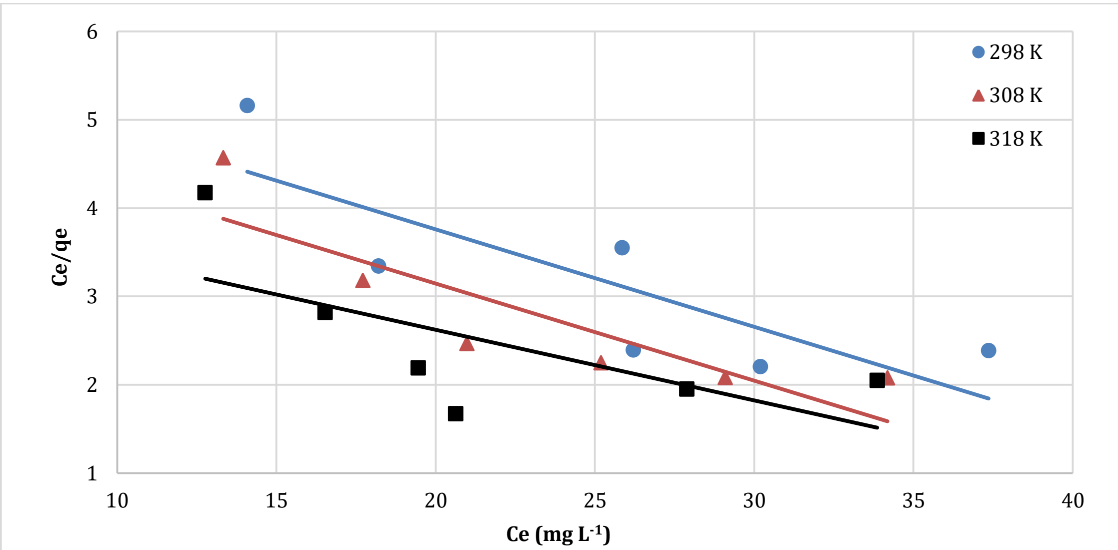


Fig 4. Langmuir isotherms of MB adsorption on JESP for different temperatures

Freundlich isotherm is the empirical one based upon adsorption on a heterogeneous surface and this isotherm equation is given Eq. (3):

$$lnq_e = lnK_F + \frac{1}{n}lnC_e \qquad (3)$$

where K_F is a Freundlich constant linked to adsorption capacity (L g^{-1}), *1/n* is an empirical parameter connected to adsorption intensity. The K_F and n values were determined from the intercept and slope of the plot between lnq_e against lnC_e, respectively. Freundlich isotherm results of BB 41 adsorption on JESP for 298, 308 and 318 K gives at Fig 5.

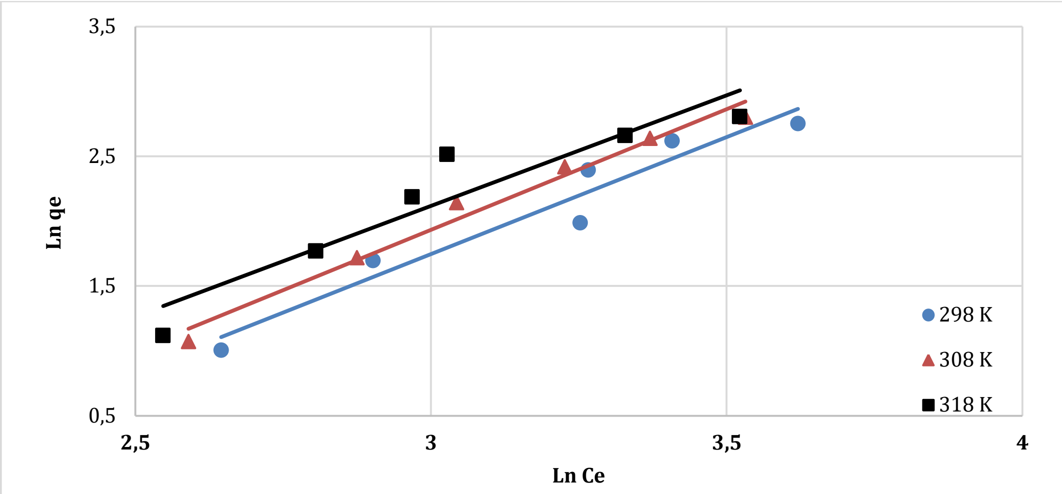


Fig 5. Freundlich isotherms of MB adsorption on JESP for different temperatures

Temkin isotherm represents solute molecule interaction from aqueous phase with heterogeneous solid surface. The isotherm is based upon the notion that heat of adsorption reduces on covering of solid surface. The Temkin equation used for the calculation of isotherm parameters is given Eq. (4):

$$q_e = \frac{RT}{b_T} lnK_T + \frac{RT}{b_T} lnC_e \qquad (4)$$

In the relationships binding energy and heat of adsorption, b_T and K_T are available and they can be determined from the slope and intercept of the *qe* line versus lnC_e respectively. Temkin isotherm results of BB 41 adsorption on JESP for 298, 308 and 318 K gives at Fig 6.

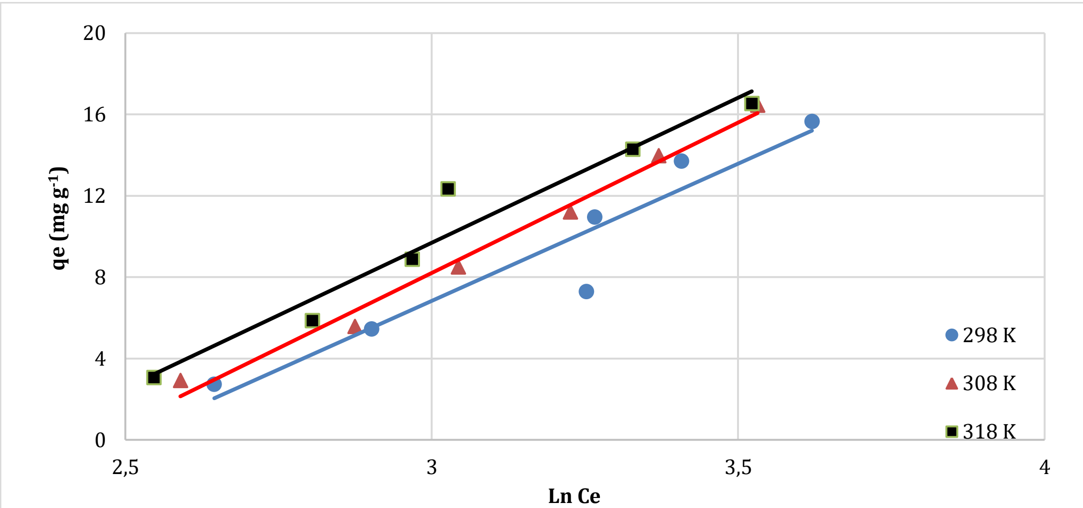


Fig 6. Temkin isotherms of MB adsorption on JESP for different temperatures

The calculated parameters of the Langmuir, Freundlich and Temkin isotherms for adsorption of BB 41 on the JESP were presented in Table 1. Concerning the coefficients determined, Freundlich model is more fitting than the Langmuir and Temkin model. It is noted that KF and n values elevate as the temperature rises, as well as, adsorption is approving at higher temperature. R^2 values of Freundlich model are higher than the other model values for JESP. The maximum adsorption value was improved by increasing the adsorption temperature; this value reached 22.5 mg g^{-1} at 318 K.

Table 1. Isotherm model parameters of BB 41 adsorption on JESP at different temperatures

Temp	Langmuir			Freundlich			Temkin		
(K)	K_L (L g^{-1})	q_m (mg g^{-1})	R^2	n	K_F (L g^{-1})	R^2	K_T (L g^{-1})	b_T (J mol^{-1})	R^2
298	0.0165	19.0661	0.6707	0.5494	0.0244	0.9409	0.0334	178.23	0.9067
308	0.0177	20.0912	0.7456	0.5645	0.0310	0.9722	0.0800	181.82	0.9492
318	0.0189	22.5156	0.7877	0.5813	0.0481	0.9986	0.1238	183.30	0.9891

3.3. Effect of Temperature and Adsorption Thermodynamics

The temperature effect on the BB 41 adsorption was investigated from the experiments executed with three different temperatures and results indicated that adsorption capacity decreases with rise in temperature. The trend was due to escaping of the adsorbed BB 41 ions on getting higher temperature or energy, indicating physical nature of the adsorption. The thermodynamic investigation is required to determine the importance of adsorption process. Thermodynamic parameters like free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) are significant to detect heat alteration in the adsorption process for dye and JESP. These parameters are calculated by the equations given with Eqs. ((5)-(8)):

$$K_e = \frac{c_{Ads}}{c_e} \quad (5)$$

$$\Delta G° = -RT lnK_e \quad (6)$$

$$\Delta G° = \Delta H° - T\Delta S° \quad (7)$$

$$lnK_e = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (8)$$

where, K_e is the equilibrium constant, C_{Ads} represents the dye amount adsorbed mg on the JESP per litter of the solution at equilibrium, the adsorbent of adsorbent per unit litter of solution. Furthermore, Ce represents the equilibrium concentration of dye in the solution. R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T denotes the temperature. From the graphical representation according to Eq. (8), namely $lnKe$ vs. $1/T$, a straight line is obtained in Fig 7. $\Delta H°$ and $\Delta S°$ parameters are analyzed from the slope and intercept of this figure and thermodynamic parameters were illustrated into Table 2.

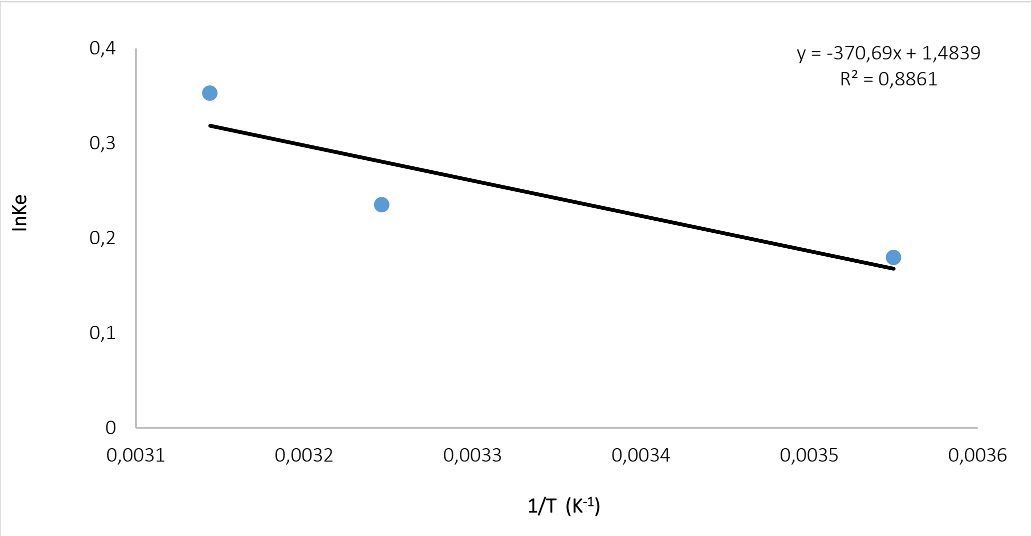


Fig 7. The plot of *ln Ke* vs. *1/T* for BB 41 dye onto JESP

Thermodynamic parameters of BB 41 adsorption onto JESP are calculated with using Eq. 5-8. The absolute values of free energy of BB 41 onto JESP obtained -447.57 J mol^{-1}, -582.20 J mol^{-1} and -902,90 J mol^{-1} for 298, 308 and 318 K temperatures respectively. Enthalpy and entropy values of BB 41 adsorption onto JESP determined 3081.91 kJ mol^{-1}and 12.33 kJ mol^{-1}K^{-1}respectively. The negative ΔG° values indicate that the adsorption is physisorption and ΔG° suggests the feasibility and the spontaneous nature of the adsorption. The absolute values of $\Delta G°$ are decreased as the temperature rises shown that this separation process is constructive at low temperatures. The positive value of $\Delta H°$ shows that the adsorption process is endothermic and the positive value of $\Delta S°$ establishes the enhanced entropy at the solid–solute interface and the affinity of the JESP for BB 41 [25].

Table 2. Thermodynamic parameters of BB 41 adsorption on JESP

Temp (K)	K_e	ΔG° (J mol^{-1})	ΔH° (J mol^{-1})	ΔS° (J mol^{-1} K^{-1})	R^2
298	0.1795	-447.57			
308	0.2350	-582.20	3081.91	12.33	0.8861
318	0.3526	-902.90			

3.4. Adsorption kinetics studies

Kinetic models have been applied for checking experimental results of BB 41 adsorption onto JESP. The adsorption kinetics is important to choose the best process conditions for the batch operating. The useful kinetic parameters for the estimation of adsorption rate, provides vital knowledge for designing and modeling adsorption processes [26]. In this study, BB 41 kinetics was calculated using three kinetic models (PFO, PSO and IPD). The most suitable model has been chosen depending on the linear regression coefficient of correlation coefficients R^2 values. These models have been investigated according to experimental data at varied temperatures and initial BB 41 concentrations.

Lagergren's first order rate equation which is named pseudo first order (PFO) kinetic model is to separate the kinetics equation depending the concentration of solution and solid adsorption capacity. This kinetic model can be the first for the characterization of the liquid-solid adsorption systems depending on solid capacity. This kinetic model is applied for sorption in liquid-solid system. It stated that number of unoccupied adsorptive sites specifies the adsorption rate [18]. The PFO kinetic model is given with Eq. (9):

$$\ln(q_e - q_t) = lnq_e - k_1 t \quad (9)$$

where, the adsorption capacities in time t are q_m and q_t (mg g^{-1}) at equilibrium respectively. k_1 (min^{-1}) is the rate constant of PFO adsorption. To achieve constants of this model, the straight line plots of $ln(q_e\text{-}q_t)$ against t are drawn. The constants detected from the slope and intercept of the line plotted [18].

The pseudo second order (PSO) kinetic model which explained with the chemical bond formation between adsorptive site and solute molecule is the rate-limiting step based on adsorption capacity is given Eq. (10):

$$\frac{t}{q_t} = \frac{1}{k_2 {q^2}_e} + \frac{1}{q_e} t \quad (10)$$

where k_2 represents adsorption rate (g mg^{-1} min^{-1}), q_m denotes adsorbate amount that adsorbed onto adsorbent at equilibrium (mg g^{-1}) and q_t is dye amount adsorbed at any time (mg g^{-1}). The plot of t/q_t vs. t has a linear link. Values of k_2 and equilibrium adsorption capacity q_e were identified from the intercept and slope of the plot of t/q_t versus t according to Eq. 10.

The PSO kinetic model could not identify the diffusion mechanism and the kinetic results were subsequently analyzed with the intraparticle diffusion (IPD) model. Adsorption of the dyes was more gradual when IPD was the rate controlling step. This model assumes that the physical or chemical bond created between solute and solid at solid interspatial sites dominate the overall speed of the adsorption. This was done by testing the possibility of intraparticle diffusion as rate limiting step using IPD model, which can be represented by an Eq. (11):

$$q_t = k_{ipd} t^{0.5} + C \quad (11)$$

where k_{ipd} (mg g^{-1} $min^{-1/2}$) denotes the intra-particle diffusion rate constant and C represents close relation with the boundary thickness. A plot of qt against $t^{0.5}$ at different BB 41 concentrations gave two phases of linear plots.

PFO, PSO and IPD kinetic model parameters of BB 41 adsorption on JESP are given in Table 3. The experimental results indicated that R^2 coefficients are higher than 0.99 with experimental and analyzed qe values close to each other explained that this process fits the PSO kinetic model. Usually the kinetic adsorption data is better represented by a PSO model for most dye adsorption systems [25, 27].

Experimental and calculated qe values of 318 K are higher than 298K and 308K values. According to these tables, it is noted that qe values increases with increasing BB 41 concentration. When kinetic constants are compared, it is seen that constant values are closer to both temperatures and concentrations for PSO model. This result exhibited that BB 41 adsorption kinetics on JESP results from the PSO and suggested that the step of rate-limiting can be the dye chemisorption [18].

Table 3. PFO, PSO and IPD kinetic model parameters of BB 41 adsorption on JESP

	Temp (K)		25 mg L^{-1}	40 mg L^{-1}	55 mg L^{-1}	70 mg L^{-1}	85 mg L^{-1}	100 mg L^{-1}
	298	$q_{e\,exp}$(mg g^{-1})	2.727	5.447	7.287	10.941	13.701	15.749
	308	$q_{e\,exp}$(mg g^{-1})	2.935	5.582	8.507	11.235	13.952	16.291
	318	$q_{e\,exp}$(mg g^{-1})	3.063	5.870	8.890	12.355	14.352	16.570
PFO kinetic model	298	k_1(min^{-1})	0.0225	0.0209	0.0216	0.0214	0.0435	0.0442
		$q_{e\,cal}$ (mg g^{-1})	3.339	3.575	3.777	5.007	5.494	7.588
		R^2	0.7750	0.8817	0.8755	0.8243	0.8801	0.8356
	308	k_1(min^{-1})	0.0295	0.0170	0.0202	0.0271	0.0307	0.0333
		$q_{e\,cal}$ (mg g^{-1})	3.202	3.459	6.285	7.019	8.138	10.939
		R^2	0.8360	0.7561	0.9029	0.5821	0.8147	0.8528
	318	k_1(min^{-1})	0.0191	0.0182	0.0244	0.0343	0.0390	0.0435
		$q_{e\,cal}$ (mg g^{-1})	4.934	5.6416	7.333	9.088	11.447	13.415
		R^2	0.7617	0.8532	0.7298	0.8636	0.5349	0.8973
PSO kinetic model	298	k_2(min^{-1})	0.0267	0.0208	0.0173	0.0089	0.0076	0.0059
		$q_{e\,cal}$ (mg g^{-1})	3.038	5.967	7.530	11.600	14.335	16.473
		R^2	0.9913	0.9926	0.9994	0.9977	0.9988	0.9981
	308	k_2(min-1)	0.0171	0.0164	0.0096	0.0089	0.0042	0.0033
		$q_{e\,cal}$ (mg g^{-1})	3.224	6.337	9.208	10.194	15.432	17.423
		R^2	0.9934	0.9972	0.9927	0.9943	0.9993	0.9971
	318	k_2(min^{-1})	0.0158	0.0123	0.0096	0.0086	0.0042	0.0033
		$q_{e\,cal}$ (mg g^{-1})	3.517	6.337	10.194	12.516	15.432	17.423
		R^2	0.9912	0.9947	0.9925	0.9961	0.9969	0.9947
IPD kinetic model	298	k_{id}(mg g^{-1} $min^{-0.5}$)	0.1407	0.2577	0.3414	0.4245	0.4838	0.6059
		C (mg g^{-1})	0.924	2.347	4.564	5.794	7.967	8.283
		R^2	0.8718	0.8184	0.7435	0.8048	0.8088	0.8571
	308	k_{id}(mg g^{-1} $min^{-0.5}$)	0.1574	0.2115	0.4112	0.5019	0.5834	0.6117
		C (mg g^{-1})	1.019	2.646	2.714	4.511	5.833	8.529
		R^2	0.9214	0.8742	0.7995	0.9036	0.9262	0.9369
	318	k_{id}(mg g^{-1} $min^{-0.5}$)	0.1779	0.2596	0.4534	0.5142	0.6187	0.6402
		C (mg g^{-1})	1.029	2.991	3.739	5.500	6.533	8.844
		R^2	0.9645	0.9608	0.8153	0.9125	0.9839	0.9831

4. CONCLUSIONS

The BB 41 adsorption on the JESP was examined at various experimental conditions. By examining the data it was shown that BB 41 adsorption elevates with initial dye concentration, contact time and temperatures for JESP. Dye adsorption capacity onto JESP gets up from 2.73 to 15.66 mg g^{-1}, 2.92 to 16.45 mg $g^{-1}$and 3.06 to 17.53 mg g^{-1} for 298, 308 and 318 K respectively as the initial BB 41 concentration rises from 25 to 100 mg L^{-1}. The equilibrium adsorption time was determined at 120 min for BB 41 removal.

Isotherm studies demonstrate that the Freundlich model shows more suitable profile for BB 41 adsorption on JESP than the Langmuir and Temkin models. It is noted that the parameters of these three isotherms are raise as the temperature increments, and also indicated that adsorption is approving at higher temperature. R^2 values of the Freundlich model are higher than other two model values for BB41 removal with JESP. The JESP monolayer adsorption capacity (q_m) was 19.066, 20.091, 22.516 mg g^{-1} for temperature tested at 298K, 308K and 318K respectively. This result revealed the endothermic adsorption process nature.

Kinetic studies displayed that adsorption of BB 41 process follows the pseudo second order and suggested that the step of rate-limiting could be the dye chemisorption. R^2 coefficients are higher than 0.99 with experimental and evaluated q_e values very close to each other. Kinetic constants are closer to both temperatures and concentrations, and q_e values are increases with increasing concentration of BB 41. During the adsorption of BB 41 on JESP the diffusion constant (k_{id}) and monolayer concentration (C) increases with the increase in temperature.

Thermodynamic parameters demonstrate that this adsorption occurred is endothermic. The negative $\Delta G°$ values indicate that the adsorption is physisorption and $\Delta G°$ suggests the feasibility and the spontaneous nature of the adsorption. The absolute values of ΔG° are decreased as the temperature rises shown that this separation process is constructive at low temperatures. The positive value of $\Delta H°$ shows that the adsorption process is endothermic and the positive value of $\Delta S°$ establishes the enhanced randomness at the solid–solute interface and the affinity of the JESP for BB 41. All of these results indicated that JESP could be used as an unconventional adsorbent for the cationic dyes removal in wastewater.

REFERENCES

[1]. F. Ciesielczyk, P. Bartczak, J. Zdarta and T. Jesionowski, "Active MgO-SiO2 hybrid material for organic dye removal: A mechanism and interaction study of the adsorption of C.I. Acid Blue 29 and C.I. Basic Blue 9," *Journal of Environmental Management*, Vol. 204, pp.123-135, 2017.

[2]. M.Z. Mehrizi and A. Badiei, "Highly efficient removal of basic blue 41 with nanoporous silica," *Water Resources and Industry*, Vol. 5, 49-57, 2014.

[3]. P.M.K. Reddy, P. Verma and C. Subrahmanyam, "Bio-waste derived adsorbent material for methylene blue adsorption," *Journal of the Taiwan Institute of Chemical Engineers*, Vol.58, pp.500-508, 2016.

[4]. I. Humelnicua, A. B˘aiceanu, M.-E. Ignat and V. Dulman, "The removal of Basic Blue 41 textile dye from aqueous solution by adsorption onto natural zeolitic tuff: Kinetics and thermodynamics," *Process Safety and Environmental Protection*, Vol. 105 pp.274-287, 2017.

[5]. M. Wawrzkiewicz, "Removal of C.I. Basic Blue 3 dye by sorption onto cation exchange resin functionalized and non-functionalized polymeric sorbents from aqueous solutions and wastewaters," *Chemical Engineering Journal*, Vol. 217, pp.414-425, 2013.

[6]. L. Laysandra, M. Sari, F.E. Soetaredjo, K. Foe, J.N. Putro, A. Kurniawan, Y.H. Ju and S. Ismadji, "Adsorption and photocatalytic performance of bentonite-titanium dioxide composites for methylene blue and rhodamine B decoloration," *Heliyon*, Vol.3, (12), 2017.

[7]. A. Regti, M.R. Laamari, S.-E. Stiriba and M.E. Haddad, "Removal of Basic Blue 41 dyes using Persea americana-activated carbon prepared by phosphoric acid action," *International Journal of Industrial Chemistry*, Vol. 8, pp. 187-195, 2017.

[8]. H. Luo, X. Huang, Y. Luo, Z. Li, L. Li, C. Gao, J. Xiong and W. Li, "Adsorption behavior and mechanism of acidic blue 25 dye onto cucurbit[8]uril: A spectral and DFT study," *Spectrochimicia Acta A Mol Biomol Spectroscopy*, Vol. 193, pp.125-132, 2018.

[9]. Y. Jin, C. Zeng, Q.F. Lu and Y. Yu, "Efficient adsorption of methylene blue and lead ions in aqueous solutions by 5-sulfosalicylic acid modified lignin," *International Journal Biological Macromolecules*, Vol. 123, pp. 50-58, 2018.

[10]. R. Hasan, C.C. Chong, H.D. Setiabudi, R. Jusoh and A.A. Jalil, "Process optimization of methylene blue adsorption onto eggshell–treated palm oil fuel ash," *Environmental Technology & Innovation*, Vol. 13, pp. 62-73, 2019.

[11]. I. Ali and V.K. Gupta, "Advances in water treatment by adsorption technology," *Nature Protocols*, Vol.1, pp.2661-2667, 2006.

[12]. E. Daneshvar, M.S. Sohrabi, M. Kousha, A. Bhatnagar, B. Aliakbarian, A. Converti and A.-C. Norrstro¨me, "Shrimp shell as an efficient bioadsorbent for Acid Blue 25 dye removal from aqueous solution," *Journal of the Taiwan Institute of Chemical Engineers*, Vol. 45 pp.2926-2934, 2014.

[13]. S. Basu, G. Ghosh and S. Saha, "Adsorption characteristics of phosphoric acid induced activation of bio-carbon: Equilibrium, kinetics, thermodynamics and batch adsorber design," *Process Safety and Environmental Protection*, Vol.117, pp.125-142, 2018.

[14]. V. K. Gupta, "Application of low-cost adsorbents for dye removal – A review, *Journal of Environmental Management,* Vol.90, pp.2313-2342, 2009.

[15]. J. Basas-Jaumandreu, J.F. López, F. Xavier and C.d.l. Heras, "Labdane-type diterpenoids from Juniperus communis needles," *Industrial Crops and Products*, Vol.76, pp.333-345, 2015.

[16]. A.S. Yaglioglu and F. Eser, "Screening of some Juniperus extracts for the phenolic compounds and their antiproliferative activities," *South African Journal of Botany*, Vol. 113, pp.29-33, 2017.

[17]. M. Yazdanshenas, A. Fazilat and S. Ahmadi, "Adsorption of Basic Blue 41 from Aqueous Solution onto Coconut Fiber Particles," *Journal of Applied Chemical Research*, Vol. 8(2), pp.15-28, 2014.

[18]. Y. Jiang, Y. Luo, F. Zhang, L. Guo and L. Ni, "Equilibrium and kinetic studies of C.I. Basic Blue 41 adsorption onto N, F-codoped flower-like TiO2 microspheres," *Applied Surface Science*, Vol. 273, pp.448-456, 2013.

[19]. M.A. Hossain and M. Mohibullah, "Kinetics and Thermodynamics of Adsorption of Basic Blue 41 on Used Black Tea Leaves," *International Journal of Scientific & Engineering Research,* Vol. 8(4), pp.995-1002, 2017.

[20]. S. Afshin, S.A. Mokhtari, M. Vosoughi, H. Sadeghi and Y. Rashtbari, "Data of adsorption of Basic Blue 41 dye from aqueous solutions by activated carbon prepared from filamentous algae," *Data Brief*, Vol.21, pp.1008-1013, 2018.

[21]. S. Rani and R.K. Mahajan, "Equilibrium, kinetics and thermodynamic parameters for adsorptive

removal of dye Basic Blue 9 by ground nut shells and Eichhornia," *Arabian Journal of Chemistry*, Vol.9, pp.1464-1477, 2016.

[22]. G. Crini, F. Gimbert, C. Robert, B. Martel, O. Adam, N. Morin-Crini, F. De Giorgi and P.M. Badot, "The removal of Basic Blue 3 from aqueous solutions by chitosan-based adsorbent: batch studies," *Journal of Hazardous Materials*, Vol. 153, pp.96-106, 2008.

[23]. S.S. Tahir and N. Rauf, "Removal of a cationic dye from aqueous solutions by adsorption onto bentonite clay," *Chemosphere,* Vol. 63(11), pp.1842-1848, 2006.

[24]. S.-L. Chan, Y. P. Tan, A. H. Abdullah and S.-T. Ong, "Equilibrium, kinetic and thermodynamic studies of a new potential biosorbent for the removal of Basic Blue 3 and Congo Red dyes: Pineapple (Ananas comosus) plant stem," *Journal of the Taiwan Institute of Chemical Engineers,* Vol. 61, pp.306-315, 2016.

[25]. L. Bulgariu, L. B. Escudero, O. S.Bello, M. Iqbal, J. Nisar, K. A. Adegoke, F. Alakhras, M. Kornaros and I. Anastopoulos, "The utilization of leaf-based adsorbents for dyes removal: A review," *Journal of Molecular Liquids*, Vol. 276, pp.728-747, 2019.

[26]. F. Kooli, L. Yan, R. Al-Faze and A. Al-Sehimi, "Removal enhancement of basic blue 41 by brick waste from an aqueous solution," *Arabian Journal of Chemistry,* Vol.8, pp.333-342, 2015.

[27]. M.T. Yagub, T.K. Sen, S. Afroze and H.M. Ang, "Dye and its removal from aqueous solution by adsorption: a review," *Advanced Colloid Interface Science*, Vol.209, pp.172-84, 2014.

Environmental Research & Technology, Vol. 2 (3), pp. 122-124, 2019

Turkish JournalPark ACADEMIC

Environmental Research & Technology

http://dergipark.gov.tr/ert

RESEARCH ARTICLE

Investigation of in-situ changes in electrical behavior during one day with environmental effects of *Spathiphyllum spp.* and African violet (*Saintpaulia ionantha*)

Ertugrul Osman Bursalioglu[1,*]

[1]Bioengineering Department, Faculty of Engineering, Sinop University, Sinop, TURKEY

ABSTRACT

Plants play an extremely important role in environmental cleanliness by reducing harmful gases in the atmosphere. *Spathiphyllum spp.* and African violet (*Saintpaulia ionantha*) plants are widely found in many countries of the world, decorative inside. Since these two plants are commercially propagated throughout the world, they have economic importance at the same time. *Spathiphyllum spp.* also has a separate prescription due to its ability to clean some air toxins in the interior. Simultaneously monitoring, the frequencies and electrical voltage values per hour were measured by using oscilloscope for during one day on the leaves of these plants. African violet plant decrease and *Spathiphyllum spp.* increase are showed in frequency values especially at night and in the near morning. The change in voltage values in the *Spathiphyllum spp.* plant was particularly reduced in the morning and the changes were clearer until the evening, and the voltage change in the African violet plant was at very low levels.

Keywords: Frequency, electrical voltage, *Saintpaulia ionantha*, *Spathiphyllum spp.*

1. INTRODUCTION

People prefer to live in multi-storey buildings for various reasons. Particularly in winter, since the houses are much less ventilated, the harmful gases inside reach much more. Therefore, a wide variety of indoor plants can be used to remove these harmful gases from the interiors of our living spaces. The aim of this study was to investigate the changes in frequency and electrical potential difference of these plants for 24 hours (night-day) indoors.

Spathiphyllum spp. is a plants species known as peace grass with attractive white leaves and dark green leaves. It is a monocotyledon plant belonging to the Araceae family and contains about 40 species [1]. These plants are known for their ability to remove toxins from. It is a popular plant in the world and in our country and it is preferred as a decorative plant in the interior. *Spathiphyllum* is an economically important ornamental plant native to the tropical regions of America and Southeast Asia and grown all over the world [2]. These plants are known for their ability to remove toxins from indoor air as well as attractive flowers [3]. Thus are rated as a top performer in NASA's clean air study. As with many other ornamental plants, plant propagation is also the main method in *Spathiphyllum*. Vegetative proliferation of these plants occurs with lateral and adventitious shoots [4].

African violet (*Saintpaulia ionantha*) is an important and popular species of *Saintpaulia*. It is domesticated, grown and commercialized and easily reproducible vegetatively [5]. African violets belong to Gesneriaceae, a large family of plants (about 2000 species, 125 genera), mostly tropical plants and shrubs, many of which are popular planted ornamental plants [6]. This plant has many different varieties in terms of flower color, leaf shape, vegetative structure, flowering time and flowering time [7,8]. Characteristic features such as visual appeal, ability to blossom under artificial light and vegetative propagationally ear round make the African violet popular indoor ornamental plant [9]. They have been subjected to intensive breeding by the horticultural industry for nearly a century and commercial *Saintpaulia* hybrids are popular ornamental plants in the rich parts of the World [10].

Corresponding Author: ebursalioglu@sinop.edu.tr (Ertugrul Osman Bursalioglu)
Received 3 September 2019; Received in revised form 12 September 2019; Accepted 16 September 2019
Available Online September2019
Doi: https://doi.org/10.35208/ert.615118

Electrical stresses and frequencies of plants may change at different times of the day depending on the sun, physical situations and some other factors. Frequency and electrical stress can also change in seasonal changes, flowering, fruiting, leaf casting and stress conditions. Therefore, measuring the set values may give us some clues. In addition to that, frequency and electrical voltage measurement may be important to follow the health of the plant.

2. MATERIALS & METHODS

In this study, *Saintpaulia ionantha* and *Spathiphyllum spp.* the measurement of frequency and electrical tension per hour in a 24 hour cycle on the leaves of plants was measured simultaneously in two plants. Measurement of frequency and electrical voltage was made simultaneously with AA TECH-1022B Digital Storage oscilloscope for 24 hours every hour. Besides, Origin Pro -2015 is used as the computer software (Fig 1).

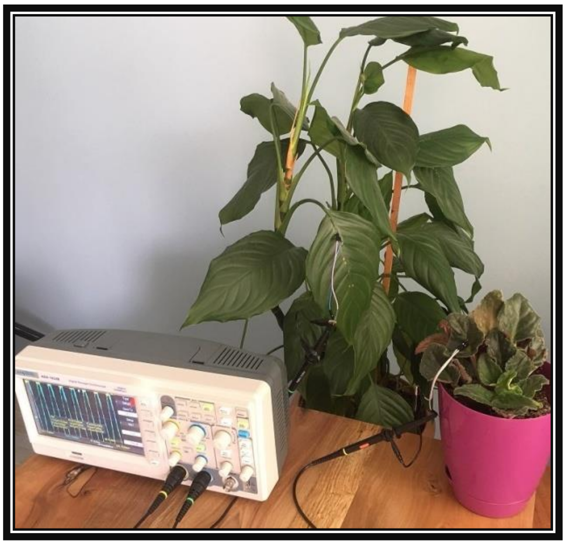


Fig 1. General image of frequency and electrical voltage measurement in plants of *Saintpaulia ionantha* and *Spathiphyllum spp.*

3. RESULTS & DISCUSSION

In *Saintpaulia ionantha* and *Spathiphyllum spp* plants, frequency and electrical stress measurements were made every 24 hours and recorded. No literature similar to this study was found.

The frequency and electrical voltage measurements of the leaves of *Saintpaulia ionantha* (African violet) plant and *Spathiphyllum spp.* plant were recorded for 24 hours. These measurements were made side by side every hour (Fig 1). Frequency values of these two plants showed different values. The wavier and various frequency values were measured in *Saintpaulia ionantha* plant than *Spathiphyllum spp.* plant. Frequency values were measured around 10-15 Hz between 2 am and 9 am, between 10 am and 9 pm and between 12 pm and 1 am at 50 Hz in *Saintpaulia ionantha* (African violet) plant. Besides, the frequency values at night 10-11 were measured as 100 and 80 Hz respectively (Fig 2a).

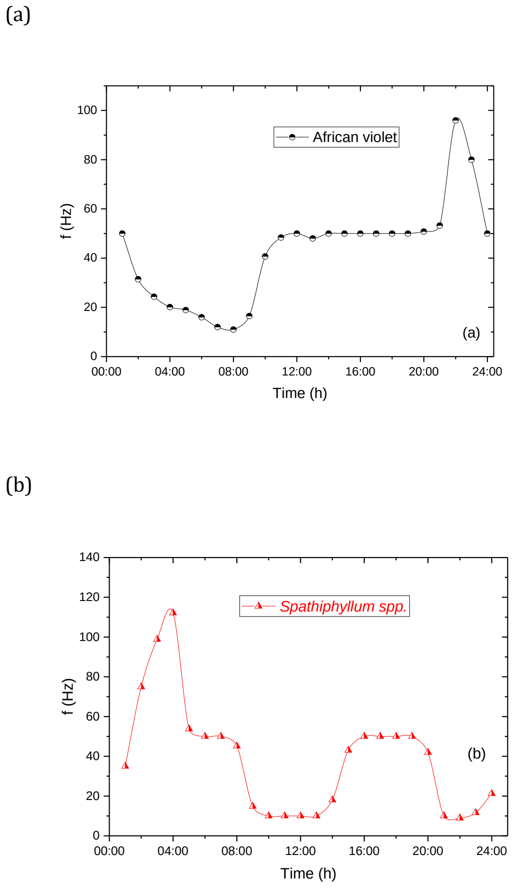
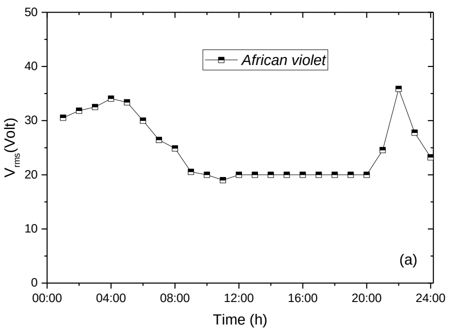


Fig 2. Time-dependent frequency change graph of a) *Saintpaulia ionantha* and b) *Spathiphyllum spp.*

The frequency measurements of *Spathiphyllum spp.* plant are shown in figure 2b. Frequency values between 9 and 2 in the day and between 9 and midnight were measured as 11 Hz. Frequencies between 3 pm to 8 pm and between 5 am to 8 am were measured at 50 Hz. Differently from these results, a value of about 80-125 Hz was measured between the night 2 and morning 4 (Fig 2b).

The electrical voltage measurements of *Saintpaulia ionantha* plant and *Spathiphyllum spp.* plant were as follows (Fig 3a and Fig 3b). Electrical voltage values in *Spathiphyllum spp.* plant were measured more fluctuated than *Saintpaulia ionantha* plant. The electrical voltage is usually measured at around 20 Vrms in *Saintpaulia ionantha* (African violet) plant. Differently, only around 35 Vrms at 5 am, 8 am and 60 Vrms at 10 am in the night were measured (Fig 3a). A fluctuating potential difference between 0-20 Vrms was generally measured in *Spathiphyllum spp.* plant. As a difference, only values between 80 and 120 Vrms were read at 9 and 10 in the morning. Additionally, low values such as 11-12 Vrms were measured between 11 am and 12 am in the day, between 2 pm and 4 pm, between 10 am and midnight (Fig 3b).

(a)



(b)

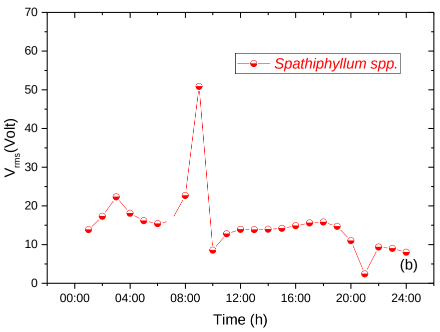


Fig 3. Time-dependent change electrical RMS voltage graph of a) *Saintpaulia ionantha* and b) *Spathiphyllum spp.*

4. CONCLUSION

Frequency and electrical voltage measurements made at each hour for 24 hours in the indoor environment generally showed an increase in frequency values near night and sunrise in the plants of *Saintpaulia ionantha* and *Spathiphyllum spp*. In African violet, frequency values generally decreased in the morning hours and increased at 10-11 at night. *Spathiphyllum spp.* the frequency values of the plant generally showed a decrease from morning to noon and from evening to night. Only an increase of 2-3 times in the morning hours was observed. The electrical voltage of this plant was increased 2-3 times in the morning and noon. Starting from this study, it is aimed to investigate the changes in frequency and electrical voltage by applying various stress conditions by increasing the number and variety of plants in subsequent experiments. After this study, a research will be conducted by increasing the parameters of the same species in the indoor and outdoor areas.

REFERENCES

[1]. D.B. Mc Connell, R.W. Henley and C.B. Kelly, "Commercial Foliage Plants: Twenty Years of Change," *Proceedings of the Florida State Horticultural Society*, Vol. 102, pp. 297-303, 1989.

[2]. R.J. Henny and A.R. Chase, "Screening Spathiphyllum species and cultivars for resistance to Cylindroclandiumspahy ll," *Hort Science*, Vol. 21, pp. 515-516, 1986.

[3]. K. Mounika, B. Panja and J. Saha, "Diseases of Peacelily [Spathiphyllum sp.] caused by fungi, bacteria and viruses, A review," *The Pharma Innovation Journal*, Vol. 6, pp. 103-106, 2017.

[4]. P.C.A. Debergh, "The in vitro techniques their contribution to breeding and multiplication of ornamentals," *Acta Horticulturae*, Vol. 353, pp. 122-133, 1994.

[5]. J.A. Teixeira da Silva, Y.H. Dewir, A. Wicaksono, M.M. Kher, H.H. Kim, M. Hosokawa and S. Zeng, "Morphogenesis and developmental biology of African violet (Saintpaulia ionantha H. Wendl)," *Journal of Plant Development*, Vol. 23, pp. 15-25, 2016.

[6]. V.H. Heywood, "Flowering plants of the world," London, England: BT Batsford Ltd, pp.335, 1996.

[7]. S. Al-Hussein, R. Shibli and N. Karam, "Regeneration in African violet (Saintpualia ionantha Wendl.) using different leaf explants, cytokinins sources and light regimes," *Jordan Journal of Agricultural Sciences*, Vol.2, pp. 361-371, 2006.

[8]. S. Jain, "Micropropogation of selected somaclones of Begonia and Saintpaulia," *Journal of Biosciences*, Vol. 22, pp. 585-592, 1997.

[9]. K. Sunpui and K. Kanchanapoom, "Plant regeneration from petiole and leaf of African violet (Saintpaulia ionantha Wendl.) cultured in vitro," *Songklanakarin Journal Science Technology*, Vol. 24, pp. 357-364, 2002.

[10]. R.A. Mittermeier, P.R. Gil, M. Hoffman, J. Pilgrim, T. Brooks, C.G. Mittermeier, J. Lamoureux and G.A.B. da Fonseca, "Hotspots Revisited: Earth's biologically richest and most endangered terrestrial ecoregions," Conservation International, Chicago, USA: University of Chicago Press, pp. 392, 2005.

Environmental Research & Technology, Vol. 2 (3), pp. 125-129, 2019

Turkish JournalPark ACADEMIC

Environmental Research & Technology

http://dergipark.gov.tr/ert

RESEARCH ARTICLE

Performance evaluation of two filter materials in intermittent sand filtration system

Ganiyu A. Sodamade[1,*], Ezechiel O. Longe[1], Odum L. Odum [1]

[1]University of Lagos, Civil and Environmental Engineering Department, Akoka, NIGERIA.

ABSTRACT

The environment is a treasure that needs to be protected from point and diffuse sources of pollution. Most wastewater treatment plants cannot attain 100% efficiencies and this call for tertiary treatment process before discharging final treated wastewater into the environment. The study focused on harnessing the locally available materials, sand and granulated Palm Kernel Shell (gPKS) as filters for treatment of wastewater from constructed wetland using intermittent filtration system in the laboratory. The filter depth and hydraulic loading rate was 650 mm and 0.135 L min^{-1}, respectively. Applied wastewater was effluent from the Constructed Wetland (CW) of wastewater treatment plant University of Lagos. The filtration system was dosed intermittently 6 hourly for 12 weeks. Experimental results showed that pH of the effluent from gPKS filter medium was slightly reduced to the influent due to acidic nature of the gPKS while effluent from sand filter slightly increased. The five day biochemical oxygen demand (BOD5) removal efficiency for the gPKS and sand filters were 59.2 and 69.08% respectively, while the corresponding average Dissolve Oxygen (DO) were 2.9 ± 0.6 mg L^{-1} and 3.4 ± 0.345. The percentage removal of *E. coli* in sand and gPKS filters are 69.34% and 87.49% respectively.

Keywords: Wastewater treatment plant, granulated palm kernel shells, intermittent sand filtration, *E. coli*

1. INTRODUCTION

It was estimated that 97% of the water in the earth is stored in the sea which is not suitable for consumption due to its high salinity; the remaining 3% that is fresh water is available as ice caps, surface and ground water. The anthropogenic activities that have resulted into the usage of part of the water have also resulted into the emanation of wastewater from different areas which if discharged directly into the environment will result into pollution of such environment and receiving water body. Towards protecting the environment, a number of ways has been adopted through construction of wastewater treatment plant such as onsite wastewater treatment plant, stabilization pond, construction wetland, trickling filter, activated sludge system among others.

Towards solving the problems that may emanate from discharging expected effluent from these treatment plants that does not meet the minimum quality requirement, researchers have studied need to provide tertiary treatment. In the course of doing this, most researchers have adopted the usage of sand as material for filtration. Reference [1] adopted the usage of sand for the treatment of synthetic effluent from an onsite wastewater treatment plant. References [2], [3] and.[4] used sand as filter for phosphate removal, disinfection of secondary clarifier effluent and dissolved substances removal in wastewater treatment respectively. Due to availability, accessibility and economical reasons [5]-[8] made use of sand in their studies of infiltration because sand material is stable and cannot be subjected to any chemical degration and physical abrassion.

The highest producing Palm Oil country in Africa is Nigeria. In 2016, the country was producing 970,000 metric tonnes in a year which was estimated as 55% of the entire Africa outputs (Palm oil in African I *SPOTT.org http.//www.spott.org*). This means that the tonnage of solid waste (PKS) from this production will correspondingly be high, hence, there is need to reuse it towards best solid waste management. One of the alternatives towards the reuse of this waste material is by investigating its usage as filter medium in an

Corresponding Author: gsodamade@unilag.edu.ng (Ganiyu A. Sodamade)
Received 14 December 2018; Received in revised form 25 September 2019; Accepted 25 September 2019
Available Online September 2019
Doi: https://doi.org/10.35208/ert.497511

area where sand material being used as filter medium is not available. It was reported in [9], that among the agro-based farm wastes and processing wastes in Nigeria that can serve as materials for Activated Charcoal production, PKS have the best adsorptive capacity. Through this, the stress and cost of transporting of the sand material to such wastewater treatment will be reduced while the environmental menace of the PKS solid waste shall be minimized. Therefore, this study investigates the performance evaluation of sand and gPKS as filter media.

2. MATERIALS & METHOD

This is a laboratory based experimental work to assess performance of two different filter media (PKS and sand) in the tertiary treatment of effluent from a constructed wetland of an educational institution. The sand medium was collected from Ilaje, a suburb of Lagos Mainland in Somolu Local Government Area, while the PKS was collected from Arigbajo community of Ogun State, Nigeria. The PKS was crushed and granulated to sizes relatively similar to the sampled sand filter from Ilaje of Lagos as shown in Figure 1.The hydraulic parameters of the two media were determined to confirm their relative suitability or otherwise with respect to specification recommended in [10]. The particle size distribution curves of the two media and their hydraulic parameters are presented in Figure 1 and on Table 1 respectively.

The sand medium has the effective size (d_{10}) of 0.28, coefficient of uniformity (C_u) of 2.85 and pore diameter (d_{15}) of 0.39. The d_{10}, C_u and d_{15} values respectively for gPKS are 0.34, 2.94 and 0.39. The values are all within the recommended values by [10] and shows that the materials can serve as filter media for intermittent sand filtration.

The experiment was setup in the Granulometric Laboratory of the Hydraulic Research Unit of University of Lagos, using two columns of Perspex material of 100 mm diameter and thickness of 5 mm. The columns were sealed at the bottom with 10 mm thick flat Perspex plate and filled with underdrain material of 7.5 cm and each of the columns was filled with separate filter medium (sand or gPKS) of 650 mm depth. The choice of 650 mm was based on [1], where it was reported that a depth of 500 mm and little above it will perform effectively in the removal of the organic load of wastewater through intermittent sand filtration. Also, in an earlier research, Prasad [11] reported removal of organic load 2 ft (0.6 m) depth.

Wastewater samples used for the study were collected from the effluent of the constructed wetland of the Wastewater Treatment Plant of University of Lagos, Nigeria using sterile container. The sewage quality of the university wastewater fluctuated during the operation period detailed whether the university was in session or not.

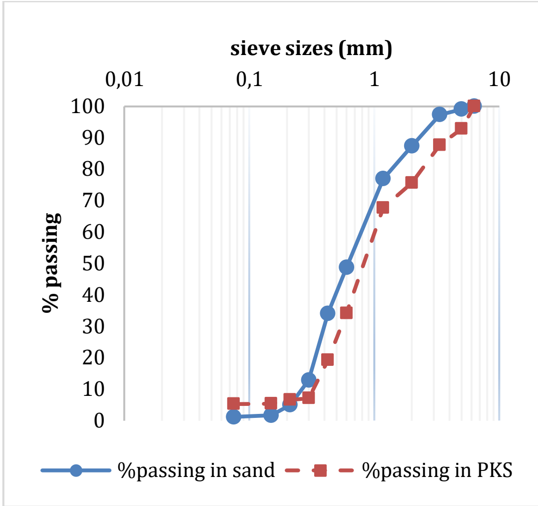


Fig 1. Particles size distribution curves of Ilaje sand and Arigbajo granulated palm kernel shell

Table 1. Granulometric properties of filter media

Property	Sand	PKS
D_{10}(mm)	0.28	0.34
D_{15} (mm)	0.31	0.39
D_{30} (mm)	0.40	0.55
D_{60} (mm)	0.80	1.00
C_u	2.85	2.94

The columns were first saturated by pumping water into it followed by draining prior performing the test. Effluent from the wetland that serves as influent to the SSF was collected and served as the influent for the laboratory intermittent sand filtration set up as shown in Figure 2. The sample was applied to the filter from the top through the use of peristaltic pump. The pump operation was for 15 minutes duration for each batch at the hydraulic loading rate of 0.135 L min^{-1}. The batching of the columns was 4 times a day as shown on Figure 3 for 90 days and was performed concurrently. Samplings of treated wastewater from columns were done once weekly for laboratory analysis. The parameters tested for were BOD, DO and *Escherichia coli* (*E. coli*) and were analyzed using standard methods of measurement [12].

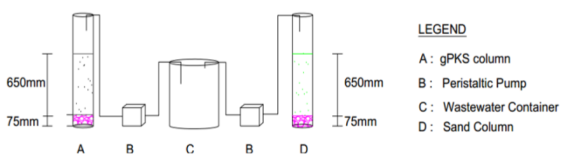


Fig 2. Filtration setup

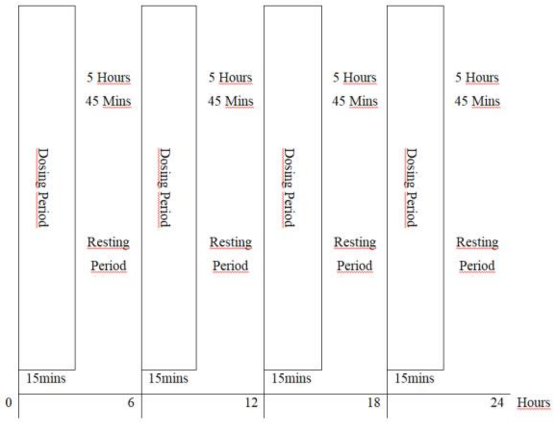


Fig 3. The dosing pattern of the columns

3. RESULTS & DISCUSSION

The average pH of the influents was 7.0 while that of effluents from the sand and gPKS filters were 7.1 and 6.7 respectively. The slight increase in pH in the sand filter column was due to biological activity and gas exchange as reported by Kim et al. [13] on one hand but that of slight decrease of the gPKS effluent may be due to the effect of traces of palm oil from the gPKS which contains higher proportion of saturated fatty acids[14] -[15], this could be responsible for the lower pH value of the effluent from the gPKS filter medium. Generally, the system pH values indicate that the system operated optimally for biological activities.

The BOD_5 of the wastewater and effluent from the filters are shown on Table 2. The average BOD_5 value of wastewater was 33.3 mg L^{-1} with the maximum BOD_5 of 90.4 mg L^{-1} measured in week 2 and the minimum of 4.2 mg L^{-1} measured in week 11. The value for week 11 was due to non-availability of the students in the hall of residence during the period. Though average value of 33.3 mg L^{-1} may be slightly higher than the minimum standard required by WHO [16], that may not necessarily need to be polished, the occurrence of higher values in weeks 2, 3, 6, 7 and 8 make it desirable and validate the essence of polishing the effluent from the constructed wetland before being discharged as corroborated by Longe and Ogundipe [17].

From Figure 4, it was shown that the sand filter gave an average of 69.08% removal efficiency of the organic load, BOD_5, while the gPKS filter recorded 59.2% removal. The average value recorded in sand filter was close to the 72.5 % recorded by Prasad et al. [11] that uses sand and soil in the treatment of domestic wastewater. The value recorded for gPKS was lower to that of sand; this may be due to larger d10 value of gPKS (0.34 mm) compared to that of sand (0.28 mm) which affects the porosity of the media and directly affect the detention of the wastewater in the filter and consequently organic matter removal. Generally, the performance of gPKS in organic load removal throughout the treatment period was relatively close to that of the sand as filter. Expectedly, the usage of raw gPKS without charring it could have also been a factor that contributed to the low BOD_5 and decrease in pH recorded. Further work need to be done to ascertained this.

Table 2. Result of BOD_5

Weeks	Wastewater	Effluent from Sand	Effluent from PKS
1	67.6	25.6	30.6
2	90.4	24.5	25.2
3	56.8	22.4	21.4
4	23	22.2	21.6
5	13.4	8.6	12
6	59.4	40.6	23
7	39.2	29.4	28.4
8	62.2	23	28.4
9	11	6.8	7.4
10	8	5.6	12.2
11	4.2	3.4	2.8
12	25.8	22.4	12.2
Average	33.34	19.49	18.76
Maximum	90.4	40.6	30.6
Minimum	4.2	2.8	2.8

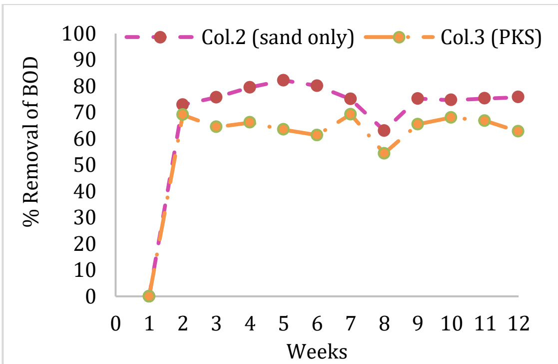


Fig 4. Percentage removal of BOD in sand and gPKS columns

The level of dissolved oxygen present in water is directly proportional to the quality of that water. That is, dissolved oxygen increases with increase in water quality and vice-versa. Bulley and Husdon [18] reported that most systems that are designed for the aerobic treatment of municipal waste recommend the dissolved oxygen concentration be maintained in the range of 0.5 – 2 mg L^{-1} this was supported by Awoyemi et al. [19]that reported a DO of 0.6 mg L^{-1} of a domestic wastewater. The level of DO in wastewater depicts the degree of contamination of the wastewater by organic matter. On examination, average DO value after 12 weeks of experiment was 2.48 ±0.56 from the wastewater and shows that the effluent from constructed wetland is relatively treated as shown on Table 3. The average DO recorded for the sand and gPKS columns respectively are 3.4 ± 0.345 and 2.9 ± 0.6 mg L^{-1}. This confirmed the reason why the organic load removal from the PKS filter material was averagely low compared to that of the sand filter because enhancement of dissolved oxygen in the sewage after treatment may be due to minimization of organic pollution load in the wastewater during treatment [11]. Though, the DO from the two filters is less than the recommended value of 4.0 mg L^{-1} before discharging to the environment, the table shows a consistency increase in DO values from week 8 to week 12, if this experiment is extended beyond 12 weeks duration, it is expected that the DO values would have reached the minimum standard expected of 4.0 mg DO L^{-1} because more slime would have developed around the filter that will aid the removal of organic matter and consequently increase the DO in the effluent.

Table 3. DO Improvement in the filters

Week	Influent	Effluent (Sand)	Effluent (PKS)
1	3.6	3	3
2	2.3	2.9	1.5
3	1.7	3.3	3.7
4	2.8	4.1	3.8
5	3.1	3.5	3.2
6	2.8	3.4	3
7	1.7	3.3	2.8
8	2.5	2.9	2.7
9	2	3.1	2.9
10	2.7	3.6	3.1
11	2.4	3.4	2.3
12	2.2	3.6	2.9
Ave.	2.48	3.34	2.91
STDV	0.56	0.34	0.60

The *Escherichia coli* in the wastewater were within 65 and 90 cfu 100 mL^{-1}, these values shows that the constructed wetland of the university has greatly removed the E. coli from the wastewater. Figure 4 shows the trend of *E. coli* removal in the sand and gPKS columns. From the figure, the number of *E. coli* in the wastewater ranged between 63 and 89 cfu 100 mL^{-1} that of the effluent from sand was between 10 and 35; while gPKS effluent has values that ranged 0 and 30.

The gPKS column performed better than the sand column is *E. coli* removal, which may portends that the gPKS, though have higher d_{10} but has more adsorption characteristic to *E. coli* which made the removal better than the sand filter. Generally, the removal of the *E. coli* by the sand and gPKS filters was efficient enough and requires only little chlorination for reuse of the treated water or discharging into the environment where necessary. Also it is expected that increasing the duration of the experiment could have eliminate the total removal of the *E.coli*.

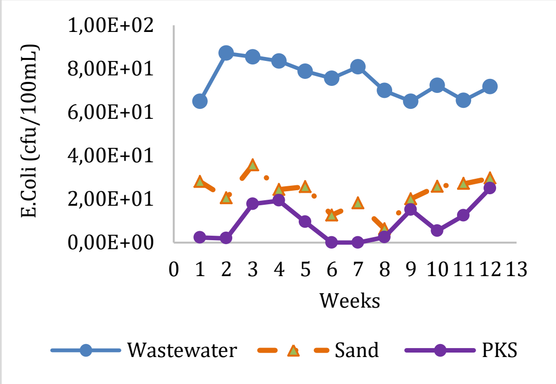


Fig 5. Percentage of *E. coli* removal in the filter

4. CONCLUSION & RECOMMENDATION

The tertiary treatment of effluent from the constructed wetland of University of Lagos, Nigeria was done through Intermittent Sand Filtration using sand and gPKS as different filter medium to ascertain the level of performance of the filters and their suitability as filter material. The pH of the effluent from the sand filter slightly increased from 7.0 to 7.1 while that of the gPKS filter was slightly reduced to 6.7 due to the traces of fatty acid that may be present around the gPKS surface. The DO of the gPKS effluent is 2.9 ± 0.6 mg L^{-1} and it's lower than that of sand filter effluent that if 3.4 ± 0.345 mg L^{-1}. This directly was related to removal of organic matter from the wastewater with the removal of 59.2% and 69.08% BOD_5 efficiency for gPKS and sand media respectively. The removal of *E. coli* was 69.34% in sand filter and 87.49% in PKS filter. The effluent from the filter has between 0 and 30 cfu 100 mL^{-1}, this is greater than the recommended value of Nigeria Standard for Water Quality (2007). This can be removed through little chlorination during the early part of the experiment, As the experiment progresses beyond the 12 weeks, there is possibility of the microorganisms to be removed completely. The renovated water from this system can be re-used in an area where scarcity of water prevails.

It is recommended that further work should be done to look at the use of charring PKS for the study and a long period of time for the experiment to assess the degree of improvement of the quality of the effluent properties.

ACKNOWLEDGEMENT

We acknowledge the Works Department of University of Lagos for the opportunity given to us in using wastewater treatment plant and the laboratory equipment for the experiment. The contribution of Dr. Mrs. Aina of Works and Services Department, University of Lagos; Mr. Kazeem Orebiyi and Mr. Taofik Yusuf is highly appreciated.

REFERENCES

[1]. G. Sodamade, E. Longe and A. Sangodoyin, "Depth and performance evaluation of a laboratory scale sand filtration system for wastewater treatment," *Turkish Journal of Engineering & Environmental Sciences,*Vol. 38(2), pp. 209-216, 2014.

[2]. M. Valentukeviciene, and G. Ignatavicius, "Improvement of phosphorus removal in the wastewater treatment," *Ekologija,* Vol. 60(4), pp. 65–72, 2014.

[3]. K. Langenbach, P. Kuschk, H. Horn and M. Kästner, "Modeling of slow sand filtration for disinfection of secondary clarifier effluent", *Water Resources*, Vol. 44, pp. 159–166, 2010.

[4]. A. Renman, L.D. Hylander, and G. Renman, "Transformation and removal of nitrogen in reactive bed filter materials designed for on-site wastewater treatment", *Ecological Engineering,* Vol. 34, pp. 207–214, 2008.

[5]. T.K. Stevik, G. Ausland, P.D. Jenssen and R.L. Siegrist, "Removal of *E. coli* during intermittent filtration of wastewater effluent as affected by dosing rate and media type", *Water Resources,* Vol. 33, pp. 2088-2098, 1999.

[6]. G. Ausland, T.K. Stevik, J.F. Hanssen, J.C. Kohler and P.D. Jenssen, "Intermittent filtration of wastewater-removal of fecal coliforms and fecal Streptococci", *Water Resources*, Vol.36, pp. 3507-3516, 2002.

[7]. S.J. Rooklidge, L.H. and Ketchum Jr.,"Corrosion control enhancement from a dolomite-amended slow sand filter", *Water Resources,* Vol.36, pp. 2689-2694, 2002.

[8]. M.L. Weber–Shirk, "Enhancing slow sand filter performance with an acid-soluble seston extract", *Water Resources*, Vol. 36, pp. 4753-4756, 2002.

[9]. I.K. Adewumi and M.O. Ogedengbe, "Optimising conditions for activated charcoal production from palm kernel shells", *Journal of Applied Sciences,* Vol. 5, pp. 1082-1087, 2005.

[10]. U.S. Environmental Protection Agency (EPA), "Design manual – onsite wastewater treatment and disposal systems", Office of Water Program Operations, Office of Research and Development - Municipal Environmental Research Laboratory; 1980.

[11]. G. Prasad, R. Rajput and A.K. Chopra, "Sandintermittent filtration technology for safer domestic sewage treatment", *Journal of Applied Science and Environmental Management,* Vol. 10 (1), pp. 73 – 77, 2006.

[12]. American Public Health Association (APHA), Standard Methods for Examination of Water and Wastewater. 21stEdn., pp. 1368, 2005.

[13]. D. Kim, M. Gautam, W.A. Sack and D. Gera, "Estimation of fecal coliform removal from domestic sewage in two sand filter columns systems", *Toxicological and Environmental Chemistry,* Vol. 71, pp. 421-434, 1999.

[14]. R. Manorama and C. Rukmini, "Nutritional evaluation of crude palm oil in rats", *American Journal* of *Clinical Nutrition*, Vol. 53, pp. 1031S-1033S, 1991.

[15]. M.O. Aremu, A. Olonisakin, D.A. Bako and P.C. Madu, "Compositional studies and physicochemical characteristics of cashew nut (*Anarcadiumoccidentale*) flour", *Pakistan Journal of Nutrition*, Vol. 5, pp. 328-333, 2006.

[16]. World Health Organization (WHO) standard: Guidelines for drinking waters, 2006.

[17]. E.O. Longe and A.O. Ogundipe, "Assessment of wastewater discharge impact from a sewage treatment plant on lagoon water, Lagos, Nigeria", *Journal of Applied Sciences, Engineering and Technology,* Vol. 2(3), pp. 274 – 282, 2010.

[18]. N.R. Bulley and J.T.R. Husdon, "Effect of dissolved oxygen concentration on the aerobic stabilization of swine waste", *Canadian Agricultural Engineering,* Vol. 20(1), pp. 60-63, 1978.

[19]. O.A. Awoyemi, A.C. Achudume and A.A. Okoya, "The physicochemical quality of groundwater in relation to surface water pollution in Majidun Area of Ikorodu, Lagos State, Nigeria", *American Journal of Water Resources,* Vol. 22 (5), pp. 126-133, 2014.

Environmental Research & Technology, Vol. 2 (3), pp. 130-140, 2019

Turkish JournalPark ACADEMIC

Environmental Research & Technology

http://dergipark.gov.tr/ert

RESEARCH ARTICLE

A guide to theory and practice of drinking water: PURE-H2O approaches

Neslihan Dogan-Saglamtimur[1], Fehiman Ciner[1,*]

[1]Nigde Omer Halisdemir University, Environmental Engineering Department, 51240, Nigde, TURKIYE

ABSTRACT

The quality of drinking water that is essential for life is a powerful environmental determinant of health. Engineering works in all fields have been constructed to distribute water from places of abundance to places in need. All water sources contain suspended and particulate inorganic/organic substances that must be dispelled during water treatment process to yield pure water that is fit for drinking and any other usage. Treatment procedures should be chosen in order to improve water stability. Many treatment processes (sometimes called unit processes and unit operations) are linked together to form a treatment plant in order to produce water of the desired quality. Unit operations, which are physical and chemical (aeration, adsorption, membrane processes, ion exchange, coagulation and flocculation, chemical oxidation and water softening) and mechanical (sedimentation and filtration) should be taken into consideration for producing clean drinking water. Choosing the suitable treatment process is a critical step in the procurement of safe, reliable, high quality drinking water at a cost-effective price for green/sustainable engineering.

As a main part of the EU Project titled as "Implementation of ECVET for Qualification Design in Drinking Water Treatment Plants and Sanitation for Pure Drinkable Water-PUREH2O" that includes environmental planning, training in the field of drinking water, sustainable development, sound practices not only in the field of drinking water but also affiliated treatment facilities, this study focuses on selection of the water source, unit operations for drinking water and choosing water treatment processes.

Keywords: Drinking water, environmental engineering, PURE-H2O project, sustainable development, unit operations

1. INTRODUCTION

Recently, the state of the infrastructure has been extensively accentuated in light of the significance of safe drinking water for the necessities of society and industrial development [1]. The environmental impact of water production industry in coming few years will be higher due to population growth. Therefore, most developed countries interest with the sustainability as an environmental protection strategy to increase the efficiency of environmental preservation and energy [2].

Water called the universal solvent that can be consumed in any desired amount without concern for adverse health impacts is termed *potable* water. As production increases, while plant capacity remains the same, the task of producing potable water becomes increasingly difficult. The scientific community is continually making advances in identifying contaminants and discovering potential long-term health effects of constituents that had not been previously identified [3].

By 2050, with an additional 2.3 billion people living on earth, the expected scenario of global freshwater resource consumption is estimated to present that 40% of the population will be living in acute water stress situation [4]. Several treatment processes can be applied to obtain water for consumption with various qualities. The source of water such as groundwater, seawater and surface freshwater reservoir each have different qualities together with the adopted treatment methodology [5].

Water generally hosts biological and chemical agents that impact the environmental health. A wide range of communicable diseases can be spread through elements of the environment by animal and human

Corresponding Author: fciner@ohu.edu.tr (Fehiman Ciner)
Received 8 March 2019; Received in revised form 29 August 2019; Accepted 3 September 2019
Available Online September 2019
Doi: https://doi.org/10.35208/ert.537341

waste products. In order to protect the environment from its adverse effects, water quality standards have been designated, treatment facilities have been built up, and treatment technologies have been discovered [6]. Variability of water treatment technologies between countries based on a wide range of factors such as water resources, geographical location, climate conditions, style of culture, and economical issues [2].

On the other hand, lifelong learning is perceived as a lifestyle, a profession based training which is one of the cores of lifelong learning perception is accepted as being important by workers, employees, and companies. Profession's training and education contain all the activities so that one person gets the necessary skills, knowledge, competencies, and information for a job or job group. Individual profession's training enables an individual get ready for work-life, increase his/her eligibility for companies by bridging theoretical education and the occupational area. Beyond working life, it supports the development of the individuals in other areas of life and supports their active skills in life. For this reason, in order to develop partnerships for professional training in Europe, some instruments have been developed. Europass [7], Youthpass, European Qualification Framework (EQF), Educational Credit Transfer in Vocational Education Training (ECVET), Educational Quality Assurance in Vocational Educational Training (EQAVET) [8], and networks through EU in order to support these materials can be counted, between these instruments. The basic idea behind these transparent instruments is to develop policies in order to increase the number of these for lifelong education and training, to apply and assess them; to continue to give extensive education and training and distant training services [9, 10].

In the direction of these facts, the project titled as "Implementation of ECVET for Qualification Design in Drinking Water Treatment Plants and Sanitation for Pure Drinkable Water-PUREH2O" was promoted to maintain an instrument that advances straightforward environmental planning and training in the improvement of manageable and sound practices in the field of drinking water and related treatment plants. The PURE-H2O project came about with the comprehension that advanced water technology enables a rise of green jobs and the coveted improvement of the sector's training capacity and employability. An investigation concerning the drinking water supply division indicated that in Turkey and many EU nations, including PURE-H2O partners, the national educational module for professional instruction needs educational means to furnish target mass with the necessary green competencies. The justification of the project is upgrading the quality and execution of VET system enhancing training in drinking water supply and improvement. It would be accomplished through advancing imagination, novelty and transfer of EQF/NQF principles in the instruction of the primary target group in the sector [10].

PURE-H2O project's main focus is to develop and launch a strategic partnership in the field of sustainable development of drinking water & treatment plants sector, establish a joint trans-European innovative competency-based training VET model and develop VET courses in accordance to the definition of qualification model and implement EQF/ISCO/ESCO principles [10].

To facilitate the improvement of VET system in Europe, the PURE-H2O consortium brings together six partners from Turkey, Bulgaria, and the Netherlands. The participating universities, R&D centers, and SMEs provide the PURE-H2O partnership with expertise, enriched by the competence of the associated members [9, 10].

In this study, the PURE-H2O Project that includes environmental planning to strengthen cleaner production principles, training in the field of drinking water sustainable development, sound practices not only in the area of drinking water and but also related treatment plants were given in detail from the perspective of Environmental Engineering approaches in pure water (selection of the water source, unit operations for drinking water and choosing water treatment processes, Fig. 1).

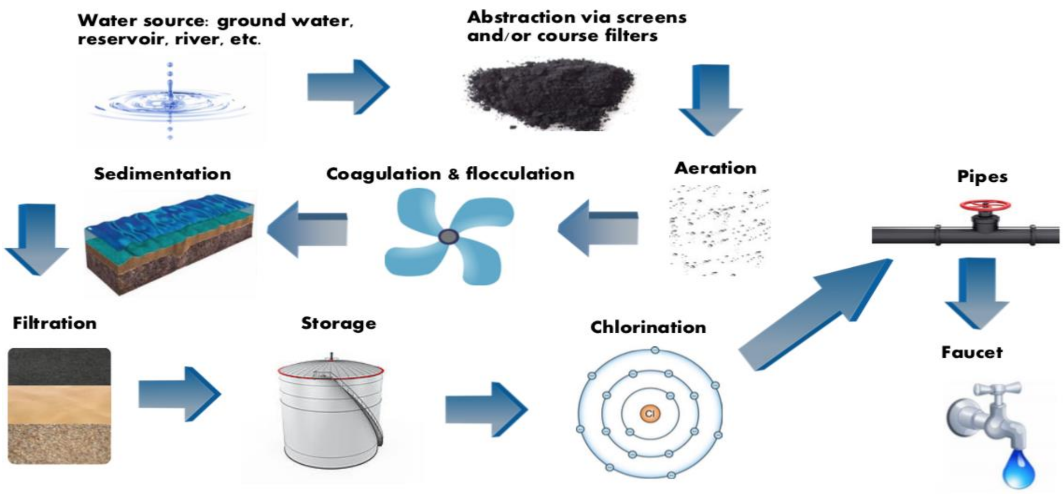


Fig 1. Drinking water processes [9]

2. WATER: SOURCES, QUALITY AND STANDARDS

Water is a substantial resource [11, 12] that can be crystal-clear, icy green in a mountain stream, whereas dark and opaque in a still water swamp. Approximately 2 billion people, one-third of the world's population, reside in countries with an inadequate amount of drinking water. Some experts estimate this figure would be twice as much within the next 25 years [13].

The materials found in water may be divided into living organisms and solid or dissolved organics and inorganics. Not all of these are harmful, and some may even be desirable for health, aesthetic, or technical reasons. Potable water is one that is reliable to drink, pleasant in taste, and suitable for domestic purposes. Contaminated or polluted water is one that contains suspended or dissolved material which makes it inappropriate for its intended usage. Potable water may be considered contaminated concerning some industrial uses [14].

The nature of water conveyed to consumers can be significantly impacted by different segments of a water-distribution system. The key variables influencing water quality in distribution systems are the nature of the treated water sustained into the system; the material and state of the pipes, valves, and storage facilities that make up the system; and the duration that the water is kept in the system. The main procedures that influence water quality inside the distribution system, for the most part, incorporate the loss of disinfection residual, with resulting microbial regrowth, and the development of disinfection by-products such as trihalomethanes. The deterioration of water-quality is frequently commensurate with the time during which water is resident in the distribution system. The longer the water is in contact with the pipe walls and held in storage plants, the higher the probability for water-quality to vary [15].

Water quality of both surface and groundwater can be affected by many things. Natural forces such as rainfall, geological characteristics, and seasonal changes can have a significant impact. Human activities, including overuse, pollution, changes in water-flow patterns, the introduction of non-native species, and dams on rivers can have unintended consequences. These factors can affect how water is treated and the results of water treatment [16].

Water-quality requirements transmute in accordance with the intended usage of the water. They should not be confused with water-quality standards. Determined by the prospective user, water-quality requirements depict an obvious or assumed necessity on the basis of the water user's prior experiences. Water-quality standards are prepared by a governmental agency and embody a legal requisition [17].

The quality of water in a lake or reservoir depends considerably on the season of the year. Municipal water-quality control starts with management of the river basin to protect the source of water supply. Highly polluted waters are both difficult and costly to treat [18]. The uses we make of water in lakes, rivers, ponds, and rivers are significantly affected by the water quality they acquire. Activities such as fishing, swimming, boating, shipping, and waste disposal have quite different requirements in terms of water quality. The water of particularly high quality is needed for potable water supplies. Water quality management involves the control of contamination from human actions with the goal that the water would not be degraded to the point that is not appropriate for intended usages [3].

One of the key factors that affect the quality of water is the geological nature of the area where the groundwater or surface water exists. Surface water composition is affected by contact with the soil or rock of the watershed that supplies either a river or lake. Groundwater is dependent on the type of rock through which rainwater permeates when entering the aquifer [16].

Drinking water standards around the world are in a continuous state of evolution as more information becomes available and is evaluated. No single standard for drinking water quality suffices for all countries, but there is a considerable degree of agreement on contaminants and their allowable concentrations. Different approaches to regulation and different conditions in countries will maintain differences in standards currently enforced. Although standards and monitoring programs are in place for most public water supplies around the world, bottled water, which is increasingly popular, is often not regulated [19].

Water quality criteria do not offer the same degree of protection for all forms of life in an ecosystem. Large degrees of response variation occur in different life forms and among different individuals of a species. Therefore, testing must include a wide range of biological processes. Values of society as well as scientific information influence standards. Often there is a conflict between the desire for a more comfortable existence for humans and the preservation of part of an ecosystem. Complex interrelationships among species and the environment market the task of establishing environmental standards very difficult [19].

3. SELECTION OF THE WATER SOURCE

The source of the raw water may be a river, lake, artificial reservoir, groundwater, and in some cases, reclaimed sewage or seawater. Data on the surface water quality, taken over a sufficient period (5 to 10 years), should be both reviewed and evaluated to assess the physical, chemical, microbiological and radiological properties of the raw water. A risk assessment must also be made regarding possible contamination of the water supply by chemical spills of radioactive wastes. Moreover, the degree of present and future land development in the watershed must be studied [20].

Raw water quality is a variable issue that depends on water sources. If the source is surface water, the water quality will change seasonally [2, 21]. If groundwater is selected as the source of the raw water, the same considerations associated with surface water applications [20]. The identification of potential ground-water sources for a public water supply broadly involves the following three steps: (1) identifying regions that have low pollution potential, high recharge capability, and a favourable location to the utility and its customers; (2) performing field investigations to confirm site-specific characteristics; and (3) dealing with land-use and wellhead-protection issues [15].

Even though iron and manganese are most regularly found in groundwater, surface waters may sometimes contain considerable amounts [14, 22]. They are minerals that cause staining of plumbing fixtures and laundered clothes as well as produce distinct tastes and odors in a drinking water. Iron and manganese also increase the hardness of water. These are aesthetic problems; there is no health risk associated with excessive amounts of iron and manganese [19].

Hardness in water is related to divalent cations such as calcium and magnesium and a lesser extent to aluminium, iron, and other divalent and trivalent cations resulting from water coming in contact with geologic formations. These, while not undesirable from a health standpoint, may make the water less suitable for some non-potable uses. Hardness concentration also influences the tendency of water to protect or corrode distribution pipes. Industries are especially concerned with the scale formation potential of water. Hardness ions can also contribute to color or taste of products made out of the water, which are important considerations for certain industries [18, 19].

Physical features characterize those properties of water that react to the faculties of sight, touch, taste, or smell. Suspended solids, turbidity, color, taste and odor, and temperature fall into this classification [17].

Suspended solids in water may be comprised of organic/inorganic particles or immiscible fluids. Inorganic solids and organic material are common in surface water. Suspended solids (organics) are regularly normal contaminants associated with the erosive activity of water flowing over surfaces. On account of the filtering capability of the soil, the suspended materials are rarely the components of groundwater. Most suspended solids can be removed from water via filtration [17].

Turbidity is a measure of the degree to which light is either absorbed or scattered by the suspended materials in water. Virtually all surface water sources contain perceptible turbidity. Most turbidity in surface waters is due to the disintegration of colloidal materials such as clay, silt, rock fragments, and metal oxides from the soil [17].

Pure water is colorless; however water in environment is regularly colored by foreign substances. Color contributed by dissolved solids that stay present after the removal of suspended material is known as true color [17]. Dissolved organic material from decaying vegetation and certain inorganic material cause color in the water. In certain occasions, excessive phytoplankton blooms or the growth of aquatic microorganisms may also impart color. Although color itself is not typically questionable from the aspect of health, its presence brings forth the necessity of proper water treatment [3].

Taste and odor of water can be caused by a foreign material, for example, organic compounds, inorganic salts, or dissolved gases which may have been originated from domestic, agricultural, or natural sources. Drinking water must be free from any repulsive taste or odor at the point of utilization [3].

Temperature is not utilized to assess specifically either potable water or wastewater. Nonetheless, it is a standout amongst the most imperative parameters in natural surface-water systems. The temperature of surface waters regulates the presence and activity rates of the biological species to a large extent. Temperature influences most chemical reactions taking place in natural water systems. In addition, it pronouncedly affects the solubilities of gases in water [17].

The evaluation and selection of the proper water source should be based on the following issues: (i) quantity of water required, (ii) quality of the raw water, (ii) climatic conditions, (iv) potential difficulties in constructing the intake, (v) operator safety, (vi) providing minimal operations and maintenance costs for the treatment plant, (vii) possibility of future contamination of the water source, and (viii) ease of enlarging the intake if required at a future date [20].

4. UNIT OPERATIONS FOR DRINKING WATER

There are two main unit operations for producing clean drinking water. These are physical-chemical processes and mechanical processes. Physical and chemical processes divide mainly seven parts that are aeration, adsorption, membrane processes, ion exchange, coagulation and flocculation, chemical oxidation, water softening and disinfection. On the other hand, mechanical processes consist of sedimentation and filtration.

4.1. Physical-chemical processes

Aeration is a process sometimes used in preparing drinking water. It is used in water treatment to change the concentration of dissolved gases, to strip volatile organics, and to reduce tastes and odors. The last generally involves removal of dissolved gases (such as hydrogen sulfide or chlorine) or volatile organic materials. The tastes and odors associated with algal growth are not appreciably reduced by aeration [14, 17].

Adsorption is generally utilized as a part of water treatment. It is a phase transfer process that is generally utilized as a part of dispelling substances from gases or liquids. Likewise, it can be seen as a characteristic process in various environmental compartments. Adsorption has been demonstrated as an effective removal process for a variety of solutes in water treatment [23]. Recently, the applications of adsorption in water treatment are predominately for taste and odor removal. However, adsorption is increasingly being considered for removal of synthetic organic chemicals (SOCs), volatile organic compounds (VOCs), and naturally occurring organic matter, such as trihalomethane (THM) precursors and disinfection by-products (DBPs) [3].

Membrane processes are utilized to separate dissolved and colloidal constituents from water. Water or constituents in it are forced through a membrane under the driving force of pressure, electrical potential, or concentration gradient in membrane treatment. Necessarily particulates are also trapped in the fine openings of membranes. Significant advances have been made in the design of membranes for selectivity and efficiency over the past two decades. The main application of membrane technology in water treatment is in the desalination of brackish waters, with over 4000 land-based plants. However, membrane treatment has been used for filtration, extraction of microorganisms, hardness, volatile organics and other dissolved organics, and biological treatment [19].

Ion exchange is primarily used for hardness removal in water treatment. Ion-exchange processes look much like filters in that they contain a bed of granular material, an influent structure which distributes the flow, and an effluent structure which collects the product. In the ion exchange process, an insoluble resin removes ions of either positive or negative charge from solution and releases other ions of equivalent charge into solution with no structural changes in the resin [19]. A wide variety of dissolved solids, including hardness, can be removed by ion exchange [17].

Coagulation and flocculation are utilized as parts of both water and wastewater treatment processes. It is generally cost-effective for performing coagulation and flocculation to dispel colloidal and little particles that settle gradually in water treatment. Also, coagulation-flocculation can be conducted to improve the removal of solids. Usually, pre-sedimentation without coagulant addition or a roughing filter is utilized to remove high concentrations of settleable solids prior to coagulation-flocculation-sedimentation [19].

Chemical oxidation is a process involving the transfer of electrons from an oxidizing reagent to the chemical species being oxidized. Oxidation-reduction (redox) reactions that may always be coupled establish the basis for many water treatment processes tending to an extensive variety of water quality goals. These reactions may consist of removal of iron, manganese, sulphur, color, tastes, odor, and synthetic organics such as pesticides and herbicides. Oxidants such as chlorine, chlorine dioxide, permanganate, oxygen, and ozone utilized as a part of water treatment processes [24].

Water Softening or the reduction of hardness, a process commonly practiced in water treatment process [17, 25], is the removal of certain dissolved minerals in water that results in scaling in boilers, from deposits on pipes, and cause excessive consumption of soaps made out of natural animal fats. The minerals responsible for these phenomena are referred to as hardness ions [19].

Disinfection is the process of utilizing chemical or physical methods to deactivate detrimental microorganisms that could be detected in water and to eliminate distributed water from pathogen (disease-causing microorganisms) regrowth or recontamination [26]. In the process, coliform bacteria and other indicator species will be killed as well, and the total bacterial count will be substantially reduced [14]. Unlike disinfection, sterilization is inferred as the destruction of every single living organism. Drinking water is not required to be sterilized [3]. The eradication of waterborne pathogens is the most imperative phase in water treatment [19].

4.2. Mechanical processes

Screening and sedimentation are inexpensive physical processes that are widely incorporated into treatment operations for water, wastewater, and storm water runoff. Screens and bar racks are placed at outlets from rivers, lakes, and reservoirs for water treatment plants or at the wet well into which the primary trunk sewer discharges for a wastewater treatment plant [19].

Sedimentation or clarification, is the removal of particulate material, chemical floc, and precipitates from suspension through gravity settling. This process is a standout amongst the most vital phases in the treatment of raw water [18, 27]. Sedimentation in drinking water treatment process is usually the next phase after chemical coagulation and flocculation, which leads to the grouping of particles together into a bigger size flocculent mass. This expands the settling velocity of suspended solids and permits settling colloids [9, 11].

Filtration is the principal treatment of raw water with the content of high suspended solids. Removal in a filter is exceedingly reliant on the surface area of the media particles. In the filtration process, the water is passed through permeable filter layers [19, 27]. While bigger particulates are restrained by a sedimentation process, the colloidal matter is held by adsorption, or coagulation and sedimentation [28].

5. CHOOSING WATER TREATMENT PROCESSES

The basis for selecting treatment process alternatives is established by the properties of the raw water and the finished water quality goals [20]. Choosing the suitable treatment process is a crucial phase in giving safe, reliable, high-quality drinking water at financially effective cost. The data on raw water quality is required for an adequately long period to demonstrate seasonal and extraordinary events to settle on a steady choice of suitable treatment procedures. Prior to any procedure is eventually chosen, it is vital to conduct treatability testing on the actual source water [29].

The choice of water treatment process is an unpredictable assignment. Conditions are probably diversified for each water utility, and it might be distinctive for each source used by one utility. Determination of at least one water treatment processes to be utilized at a given region is impacted by the requirement of compliance with administrative quality objectives, the desire of the utility and its clients to meet other water quality objectives, and the necessity to procure water service at the minimum rational cost [30].

The selection of treatment operations relies upon the quality and variability of the raw water source and the treatment goals, which may differ for industrial rather than municipal needs. An intensive study of the quality and amount of every single conceivable source is the first and most imperative phases in outlining a water supply process. Water treatment operations must be outlined to deal with the extreme cases of raw water quality variability to procure the adequate amount of water constantly [19].

Nowadays, water treatment plants are designed to meet potable water quality standard. The chosen source, water quality protection, treatment technologies and prevent re-pollution are the main considerations to achieve the optimum design of water treatment plants.

Factors that influence process selection are contaminant removal, source water quality, reliability, existing conditions, process flexibility, utility capacities, costs, environmental compatibility, distribution system water quality and issues of process scale.

Surface water must be treated for removal of turbidity, color, and bacteria [3]. The purpose of the municipal water treatment is to procure both chemically and microbiologically safe, potable water supply usage of population. Domestic consumption of treated water requires aesthetical convenience -lack of eminent turbidity, color, odor and objectionable taste [18]. Conventional surface water treatment plants are built based on three crucial assumptions. Firstly, the source water inflow arriving at the treatment plant merely contains naturally developed biological and chemical pollutants (for instance, total dissolved solids, turbidity, and some bacterial species). Secondly, they are observed in source waters (typically a reservoir, lake or a river) mainly due to (1) surface water runoffs, (2) existing local conditions in the source waters and (3) cross contamination due to the disposal of untreated sewerage. Thirdly, the contaminants present in source water would be totally removed through simple treatment practices following an order of phases such as coagulation-flocculation, filtration and disinfection [31].

Evaluation of the treatment plant site is based primarily on the distance from the intake, the layout of the treatment processes units, the environmental impact of the treatment plant and method of the water distribution. The following items must be included in evaluation of this site: (i) geographical location, (ii) information obtained from the geological study, (iii) availability of electric power and utilities, (iv) accessibility to major highways, (v) history of flooding or presence of earthquake faults, (vi) construction costs, (vii) site maintenance costs, (viii) operator safety, (ix) provisions for future plant expansion, and (x) environmental impact study [20].

Water supply approaches, factors affecting the choice of process, selection of appropriate processes for water treatment should be considered for choosing of water treatment processes.

5.1. Water supply approaches

Utilization of the best source water quality that can be achieved economically is an idea that has been supported by public health authorities. The principal idea of obtaining the top-quality source water that is financially plausible is a critical factor in making choices on source selection and treatment method [30].

Water utilities and their engineers need to take utilization of optional sources into consideration when another treatment facility or a noteworthy capacity expansion to a current facility is being assessed, or when an alternative and more expensive means to deal with treatment is under investigation. In case of very high level of treatment costs, improvement of a water source of higher quality might be financially appealing. The options are as follows [30]:

- Alternative surface water or groundwater source
- Groundwater as an alternative to surface water
- Riverbank infiltration as an alternative to direct surface water withdrawal

Well supplies usually yield cool, unpolluted water with the uniform quality for municipal use. If necessary, groundwater may require processing to remove toxic contaminants or to improve aesthetic quality. On the other hand, river supplies regularly require the broadest treatment plants with most prominent operational adaptability to deal with the day-to-day varieties of raw water quality [18].

At the point when distribution systems have high rates of water loss, a program of leak detection and repair may bring about expanding the measure of water accessible to customers without an expansion underway. Examination of other options for treatment may in numerous cases disclose the nonexistence of any practical or lucrative options regarding treatment of a currently utilized or new water source. In such conditions, modified, expanded, or new water treatment plants would be crucial [30].

5.2. Factors influencing process selection

All engineering, economic, energy and environmental factors will be taken into consideration by preliminary feasibility workouts in determining the design of treatment plants.

Contaminant removal is the ultimate objective of treatment for many source waters, especially surface waters. The quality of treated water must be in compliance with the requirements of effectual drinking water regulations [32]. Much is known in general about the capabilities of various water treatment processes for removing both regulated contaminants and contaminants conducting to aesthetic problems [30].

Comparison of **source water quality** and the desired/finished water quality is fundamental for the choice of the treatment process. With the knowledge of the adjustments in water quality that must be achieved, the engineer can define at least one or more treatment processes that would fit for accomplishing the improvement of quality [30]. The source of raw water can be an attractive target for an adversary. Whether it is a lake, river, or well field, many sources are remote can offer an attacker numerous opportunities to attempt contamination or physical attack [33].

Process reliability is a critical notion and at times could be a primary viewpoint in choosing the procedure. Disinfection of surface water is obligatory, so this is an example of a treatment process that must be basically safeguarded [30].

Existing conditions - The selection of processes to join into treatment train might be impacted firmly by the current procedures when a treatment facility is assessed for redesign/upgrading or expansion. Site constrains might be essential in choosing the process, particularly in pre-treatment when optional clarification methods are accessible, some of which require just a little portion of the space needed for a conventional settling basin [30].

Process flexibility - The capacity of a water treatment facility to oblige changes in future laws or amendments in source water quality is very imperative. Source water quality ought to be entrenched when a treatment facility is arranged, with the objective that good decisions on treatment procedures can be made. Most treatment facilities are established to endure for a very long time, and changes can happen in the quality of source waters with the progression of time [30].

Utility capabilities - Following the choice and outline of treatment procedures, the water utility must have the capacity to conduct them effectively to achieve the desired water quality. Accessibility to maintenance and repair of equipment includes contemplations of time and distance to service representatives, and this might be doubtful for some small-sized, exceptionally remote water utilities [30].

Cost considerations are mostly the main factor in process choice. Assessment of expenses for optional process trains utilizing standards of engineering economics may at first appear to be direct, yet this may not be the situation [30]. The cost of water treatment is dependent on three factors: (1) quality of the raw water, with costs increasing as raw water quality deteriorates, (2) the degree of treatment required, so that the purer the finished water required, the more it will cost to produce it, and finally (3) the volume of water required and hence the size of the treatment plant, with the cost of water per unit volume decreasing as the capacity of the treatment facilities [34].

Environmental compatibility issues involve a broad range of concerns that include residual waste management, the fraction of source water wasted in treatment processes, and energy requirements for treatment. The impacts of water treatment surpass the treatment facility. The advantages of procuring safe drinking water are extremely noteworthy, however certain level of caution must be taken when it comes to choose water treatment methods that would not result in severe environmental issues [30].

Distribution system water quality - The impact of treatment processes on desired water-quality in the distribution system is a factor to be taken into consideration in process assessment, and it includes the following [30]: (i) Chemical and microbiological stability of water outflowing from the treatment facility**,** (ii) elimination of internal corrosion and deposition, (iii) microbiological control in the distribution system, (iv) congruity of the quality of water from alternative sources and (v) minimization of formation of disinfection by-products in the distribution system.

Issues of process scale - Feasibility to scale procedures up to vast sizes or to scale them down to little sizes can be vital at times. Complicated treatment processes, e.g., coagulation, and filtration of surface water or precipitative lime softening, can be downsized physically. However, the expenses of hardware and the requirement for a profoundly prepared administrator may make the downsizing process unrealistic [30].

5.3. Source dependent treatment process selection

The basis for selecting treatment process alternatives is established by the properties of the raw water and finished water quality goals. Consideration must be given to the future implementation of more stringent drinking water quality standards and possible changes and variability in the raw water quality [20]. Engineers with expertise in water treatment facility design are expected to decide the best treatment system for a specific circumstance, and their recommendation ought to be considered in preliminary phases of project planning [35]. Raw water characteristics vary widely, the major differences being between surface and groundwater, hard and soft water, and river water compared to reservoir water. Therefore, groundwater systems are more prevalent than surface water, but more people drink water from surface water systems [16]. If groundwater is selected as the source of the process water, the same considerations associated with surface water apply [20].

Surface water treatment can be performed by a variety of process trains (Fig. 2), contingent upon source water quality. Since all surface waters require disinfection, process train must involve disinfection regardless of the selected treatment method. Disinfection is a part of the conventional treatment process, with the point or points of addition of disinfectant transmuting at different treatment facilities [30].

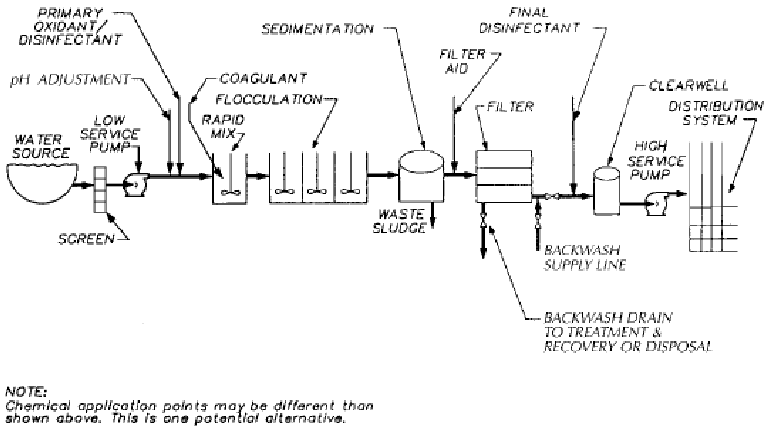


Fig 2. Conventional treatment, surface water [30]

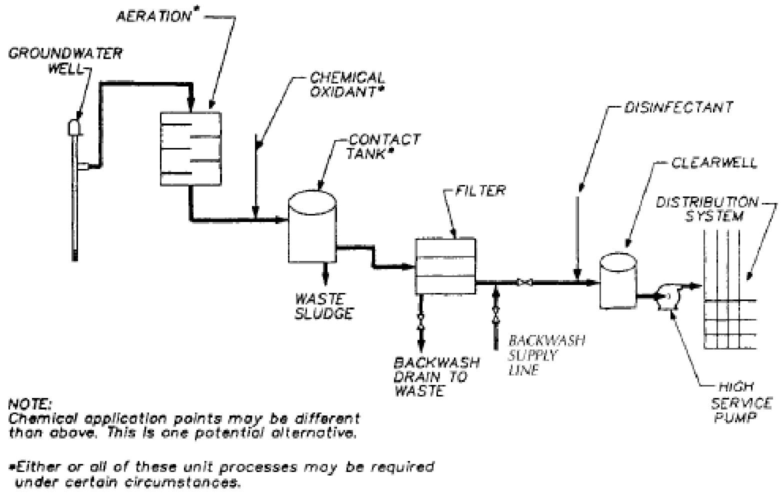


Fig 3. Iron and manganese treatment, groundwater [30]

Groundwater treatment - Many groundwaters provided from deep wells have high quality with respect to turbidity and microbiological contaminants. They may be convenient for consumption as soon as disinfection process is completed unless they have mineral components that would require extra treatment. The extra treatment process is mostly required due to the minerals in the aquifer incorporate iron or manganese. For removal of iron and manganese (Fig. 3), oxidation, precipitation, and filtration are normally utilized [30].

Hard water contains calcium and magnesium in excess concentration. Both ground and surface water can be processed by precipitative lime softening to remove hardness. The most common ion exchange softening resin is a sodium cation exchange (zeolite) resin that exchanges sodium for divalent ions, including calcium, magnesium, and radium (Fig. 4) [30].

5.4. Selection of appropriate processes for water treatment

The main function in determining the water treatment technology relies on the source of water and water quality required by the consumers. There are several types of water resources for supplying drinking water treatment plant as surface water, groundwater, and seawater. Each sort of water resources has variable characteristics depending on surrounding conditions playing a big role in selecting water production systems [36]. The problem is that numerous treatment processes are unsuitable for their usage and/or their vicinity. The spare parts, maintenance, and power consumption required by all treatment procedures render them impractical alternatives. The objective of the treatment process must be determined [12]. There may be a necessity to prioritize the issues.

Treatment procedure should be chosen to improve water stability. The basis for selecting treatment process alternatives is established by the properties of the raw water and finished water quality goals. Surface and groundwater treatment can be achieved by a variety of process trains, depending on source water quality. For analysis purposes, the problems to be addressed into the "SHTEFIE (Social, Health, Technological, Economic, Financial, Institutional and Environmental)" criteria can be grouped as an instrument to help with analysis of development programmes [12].

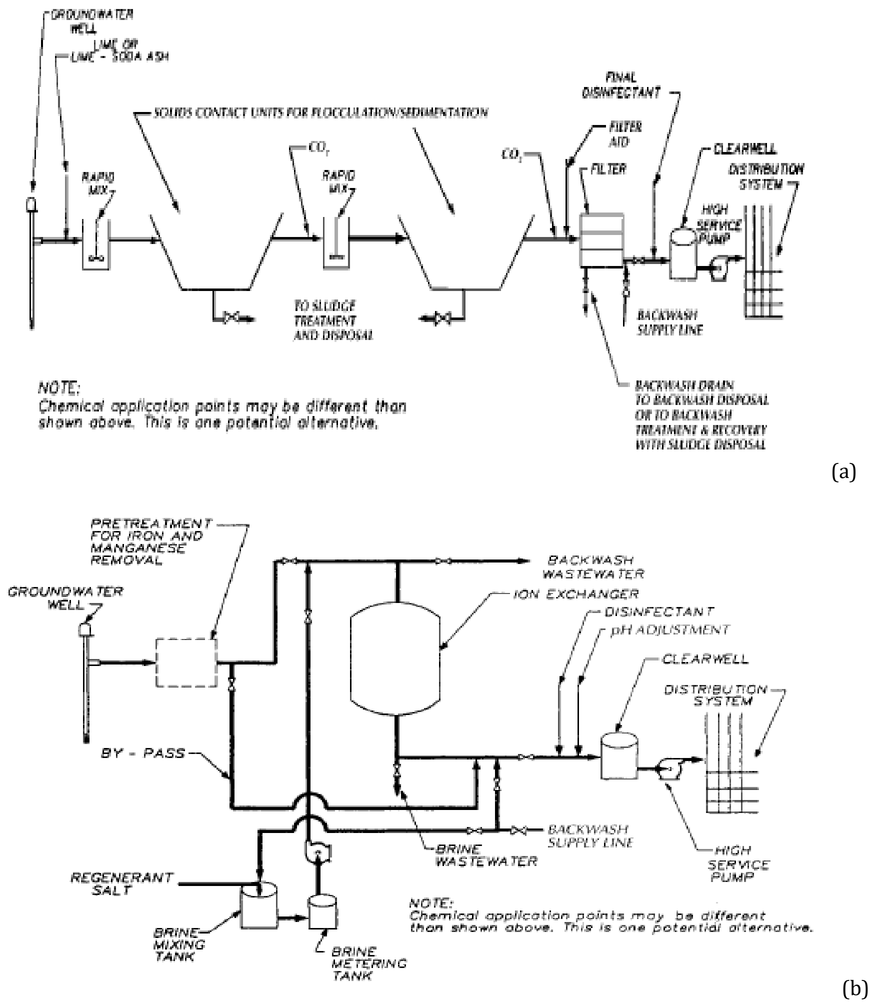


Fig 4. Two-stage excess lime softening treatment (a), ion exchange softening (b), groundwater [30]

6. RESULTS AND CONCLUSION

As the main part of the PURE-H2O Project that intends to amend the situation (a) supporting the exchange of good practices and promoting green competencies for sustainable engineering and water management (from cleaner production and technical procedures), (b) providing training materials in the attractive and practically enriched model, (c) providing new jobs for young population in the drinking water supply sector, (d) exploring water business sector and its opportunities for young entrepreneurs in the partner countries, which is comprised of Turkey, Bulgaria, and the Netherlands, this study focuses on the selection of the water source, unit operations for drinking water and choosing water treatment processes.

Many treatment processes (sometimes called unit processes/operations) are linked together to form a treatment plant for producing water of the desired quality. To achieve this goal, a variety of treatment procedures are used employing a variety of physical and chemical phenomena to remove or reduce the undesirable constituents from the water. Surface and groundwater treatment can be achieved by a variety of process trains, based on source water quality. The essential concept of attaining the high-quality of source water, which is economically feasible, is an important factor in making decisions on source selection and treatment. Selecting the suitable treatment process is a primary step in procuring safe, reliable, top-quality drinking water at a cost-effective price. The sources of raw water can be an attractive target for an adversary. Whether it is a lake, river, or well field, many sources are remote can offer an attacker numerous opportunities to attempt contamination or physical attack. Process reliability is crucial contemplation and in most cases could be a primary notion in deciding which process to choose. Site constraints may be crucial in a choice of process, especially in pre-treatment when optional clarification processes are accessible, some of which require merely a insignificant portion of the space needed for a conventional settling basin. Source water quality should be well established when a treatment facility is designed so that good decisions on treatment processes would be made. After treatment processes are chosen, designed, and on-line, the water utility must be able to operate them fruitfully to acquire the desired water quality. Cost considerations usually one of the key factors in process selection.

Treatment procedures should be chosen to enhance water stability. The basis for selecting treatment process alternatives is established by the properties of the raw water and finished water quality goals. Surface and groundwater treatment can be attained by a variety of process trains, based on source water quality. Environmental compatibility issues for drinking water involve a broader range of concerns that include residual waste management, the fraction of source water wasted in treatment processes, and energy requirements for treatment. "SHTEFIE (Social, Health, Technological, Economic, Financial, Institutional and Environmental)" criteria can be grouped as a tool to help development programmes for pure water. New approaches to siting and designing critical system components, including water treatment plants, are evolving to reduce its vulnerability.

The PURE-H2O partnership among many institutions and national authorities contributes to the process of regulation, transparency, and recognition of qualifications at the national and European level. By applying the PURE-H2O, the regional development benefits from (i) standardized user-centered VET learning paths, (ii) qualifications descriptions in the field of PURE-H2O to be introduced into the educational and industrial sectors in Bulgaria, the Netherlands and Turkey and (iii) cluster activity with identical initiative for further conduct of the PURE-H2O model.

In the fields of chemistry and eco-engineering, environmental protection, biotechnology, health and food industry, there is a need for a qualified staffs emerging in the PURE-H2O Project. This study is a theory and practice guide of drinking water and focuses on this unique Project that provides a tool encouraging environmental planning and training in the development of sustainable practices in the operation of drinking water treatment plants. Due to absence of mutual recognition of qualification, which is frequently weakened by national limitations, by applying EUROPASS, EQF and ECVET instruments through the PURE-H2O will (i) provide guidance through these qualifying instruments for not only to partner countries but also EU-wide and (ii) assist Turkey in the Adaption of Acquis and carrying out the Development Plan as part of Turkey's accession process.

ACKNOWLEDGEMENTS

This study was a part of the project "Implementation of ECVET for Qualification Design in Drinking Water Treatment Plants and Sanitation for Pure Drinkable Water-PUREH2O" supported by European Union. The authors are wishing to acknowledge special work by the team of this project.

REFERENCES

[1]. L.W. Mays, Water Distribution Systems Handbook, pp. 1.1-1.30, McGraw-Hill, USA. 1999.

[2]. A. Zyara, "Sustainability assessment for a large water treatment plant via life cycle approach," M.Sc. Thesis, Graduate School of Science Engineering and Technology, Istanbul Technical University, Istanbul, Turkey, 2017.

[3]. M.L. Davis and D.A. Cornwell, Introduction to Environmental Engineering, 3rd ed., McGraw-Hill Companies Inc., Singapore. 1998.

[4]. R.C. Valle, S. Normandeau and G.R. Gonzalez, "Education at a glance interim report: update of employment and educational attainment indicators," Paris, OCDE, 2015.

[5]. M. Lundin and G. Morrison, "A life cycle assessment based procedure for development of environmental sustainability indicators for urban water systems," Urban Water, Vol. 4 (2), pp. 145-152, 2002.

[6]. S. Ozyılmaz, "Drinking water treatment by a model water purification system with solar panels," M.Sc. Thesis, Institute of Graduate Studies in Pure and Applied Sciences, Marmara University, Istanbul, Turkey, 2006.

[7]. https://europass.cedefop.europa.eu/en/learning-and-working-in-europe/working, The EUROPASS website. [Online]. Available: (2019).

[8]. http://www.eqavet.eu/qc/tns/monitoring-your-system/evaluation/EQAVET_indicators.aspx, The EQUAVET website. [Online]. Available: (2019).

[9]. https://pure-h2o-learning.eu/book-al , The PUREH2O website. [Online]. Available: (2019).

[10]. F. Ciner, N. Dogan-Saglamtimur, A. Dizdar, G. Yucel Isildar, A. Soylemez, H.N. Ardor, M.N. Coskun, E. Dizdar, Ç. Dizdar, A. Kujumdzieva and C. Stracke, Qualification Design and Sanitation for Sustainable Drinking Water. Handbook of Research on Supply Chain Management for Sustainable Development. ISBN: 9781522557579, IGI Global Publishing, USA. 2018.

[11]. F. Çiner, and N. Dogan-Saglamtimur, Unit Operations for Providing Clean Drinking Water. Researches on Science and Art in 21st Century Turkey. ISBN: 978-605-180-771-3, Gece Publishing, Ankara, Turkey. 2017.

[12]. N. Dogan-Saglamtimur and F. Çiner, Selection of Drinking Water Treatment Processes. Researches on Science and Art in 21st Century Turkey. ISBN: 978-605-288-062-3. Gece Publishing, Ankara, Turkey. 2017.

[13]. W.P. Cunningham and M.A. Cunningham, Environmental Science A Global Concern, 17th ed., McGraw-Hill International Edition, New York, USA. 2010.

[14]. H.J. McGhee, Water Supply and Sewerage, McGraw-Hill International Editions Civil Engineering Series, New Jersey, USA. 1991.

[15]. D.A. Chin, 2006. Water-Resources Engineering, Second Edition, Pearson Education Inc., 962, New Jersey, USA.

[16]. D.J. Flynn, Raw water clarification and filtration. The Nalco Water Handbook. McGraw-Hill Publication, USA. 2009.

[17]. H.S. Peavy, D.R. Rowe and G. Tchobanoglous, Environmental Engineering. McGraw-Hill Book Co., Singapore. 1985.

[18]. M.J. Hammer and M.J. Hammer, Water and Wastewater Technology. 6th ed., Pearson International Edition, New Jersey, USA. 2008.

[19]. R.L. Droste, Theory and Practice of Water and Wastewater Treatment. John Wiley&Sons Inc., USA. 1997.

[20]. S. Kawamura, Integrated Design and Operation of Water Treatment Facilities. John Wiley&Sons, Inc., USA. 2000.

[21]. G. Kiely, Environmental Engineering. McGraw-Hill, USA. 2007.

[22]. T. Scherer, Iron and Manganese Removal. NDSU, USA. 2019.

[23]. E. Worch, Adsorption Technology in Water Treatment, de Gruyter, Berlin, Germany. 2012.

[24]. J.C. Hesby, Oxidation and disinfection. Water Treatment Plant Design, McGraw-Hill Publishing, USA. 2005.

[25]. https://www.lenntech.com/processes/softening/faq/water-softener-faq.htm, LENNTECH website. [Online]. Available: (2019)

[26]. W.M. Grayman, L.A. Rossman and E.E. Geldreich, Water Quality. Water Distribution Systems Handbook. USA. 1999.

[27]. F.G. Saber, Modeling Control and simulation of a drinking water treatment plant. M.Sc. Thesis, Graduate School of Natural and Applied Sciences, Çankaya University, Ankara, Turkey. 2012.

[28]. J.P. Chen, S.Y. Chang, J.Y.C. Huang, E.R. Bauman and Y.T. Hung, Gravity Filtration. Physicochemical Treatment Processes. Humana Press, Totowa, NJ. 2005.

[29]. M. Muntisov, "Guide to selection of water treatment processes," Water Encyclopedia, Vol. 1, pp. 439-444, 2005.

[30]. G. Logsdon, A. Hess and M. Horsley, Guide to Selection of Water Treatment Processes. Water Quality and Treatment, McGraw-Hill Publ., USA. 1999.

[31]. V.K.K. Upadhyayula, S. Deng, M.C. Mitchell and G.B. Smith, "Application of carbon nanotube technology for removal of contaminants in drinking water: A review,". Science of the Total Environment, Vol. 408 (1), pp. 1-13, 2009.

[32]. F.W. Pontius, "New horizons in federal regulation," Jour AWWA, Vol. 90, pp. 38-50, 1999.

[33]. J.W. Winslow, The Challenge of Water Treatment Plant Design. Water Treatment Plant Design. McGraw-Hill Publ., USA. 2005.

[34]. N.F. Gray, Drinking Water Quality. Cambridge University Press, London, England. 2008.

[35]. Technical Manual. Joint Departments of the Army and Air Force. TM 5-813-3/AFM 88-10, Vol. 3, Water Supply, Water Treatment, USA. 1985.

[36]. https://core.ac.uk/reader/34725270, The CORE website. [Online]. Available: (2019).

Environmental Research & Technology, Vol. 2 (3), pp. 141-157, 2019

Turkish JournalPark ACADEMIC

Environmental Research & Technology

http://dergipark.gov.tr/ert

RESEARCH ARTICLE

Public private partnerships for successful solid waste management and prospects for reducing public health risks in Kinondoni Municipality-Dar es Salaam, Tanzania

Proscovia Kamugisha[1,*], Julius Ludete[2], Sebastian Mhanga[3]

[1]Mzumbe University, Morogoro, TANZANIA
[2]Mufindi District Council, P.O.BOX 223, Mafinga, Iringa, TANZANIA
[3]Menonite Development Associates (MEDA), Box 3182, Morogoro, TANZANIA

ABSTRACT

In Tanzania only 40% of solid wastes in urbanized areas are collected and transported to the dumping sites. The remaining 60% are illegally disposed along road sides, sewage canals and reserved open spaces that contribute to floods and breeding of rodent vectors that eventually spread diseases such as intestinal schistosomiasis and soil transmitted helminths. Public Private Partnership (PPP) has been adopted to address Solid Waste Management (SWM) in various countries and yielded robust results. However the PPP model has not been effective for Tanzania since its initiation in 1995. Therefore this paper examined factors influencing performance of PPPs in SWM at Kinondoni municipality. A cross sectional survey was employed to collect data that was analyzed using descriptive and multiple regression model. Findings showed that poor monitoring and evaluation practices influenced poor performance of PPP in SWM. Moreover, low capacity of the contracted companies, limited accessibility of residential areas and weak enforcement of laws and regulations governing solid waste management had negative influence at 0.05 significant levels. The study recommends the system should establish regular plan in combination with imprompt monitoring to eliminate the effect of possible falsified compliance. Furthermore, the municipal council has to improve town settlements to access the households easily for SWM. Lastly research on end use products of the waste should look at the technical, economic viability of the waste markets for the products processed from the waste for mitigating public health risks associated with SWM.

Keywords: Solid waste management, Kinondoni, Tanzania, public-private partnership, public health, health risks

1. INTRODUCTION

Generation of solid waste is linked with urbanization and economic development. This is because as economies urbanize, people's incomes increase due to increased economic productivity. In turn the increased income rises consumption of goods and services that enlarges the amount of solid waste produced [1, 2] Tanzania's urbanization is accelerating at an annual rate of 5.2%, or more than twice the world average (at 2.1%) and higher than the average for Africa (3.5%). Dar es Salaam which is the metropolitan city of Tanzania is growing at 5.6%; and it is the fastest growing city in Africa [3, 4].

In Tanzania only 40% of wastes in urbanized areas are collected and transported to the dumping sites [5-7]. The remaining 60% are illegally disposed along road sides, sewage canals and reserved open spaces that contribute to floods and breeding of rodent vectors that eventually spread diseases [8, 9].

At global level UN- Habitat [10] estimated the incidence of diarrhoea and acute respiratory infections to be twice and six times higher respectively, for children living in the households where solid wastes are dumped at homesteads compared to children living in the households where wastes are dumped away. In Tanzania the situation is even worse because 50% of Tanzanians suffer from intestinal schistosomiasis and soil transmitted helminths resulting from haphazard solid waste dumping [11]. Sakijege et al [12] estimated the presence of total coliform in drinking water to stand at 70 and 23 counts/100 ml compared to WHO recommended rate of zero (0) coliform/100 ml (coliform free water) in the drinking water [13]. The results imply presence of pathogens causing

Corresponding Author: ppkamugisha@mzumbe.ac.tz (Proscovia Kamugisha)
Received 5 August 2019; Received in revised form 21 September 2019; Accepted 23 September 2019
Available Online September 2019
Doi: https://doi.org/10.35208/ert.601999

infectious waterborne diseases such as cholera, dysentery, typhoid fever and schistosomiasis. In fact Sakijege et al [12] determined the incidence of diarrhoea, schistosomiasis, and typhoid to stand at 53, 21 and 17 cases respectively at just one dispensary in Keko Machungwa, Dar es Salaam within three months of March, April and June 2009.

In response to this situation various efforts have been made by national governments and researchers in an attempt to address the issue of solid waste management in urban areas. The most common model for addressing the issue in various countries of the world has been Public Private Partnership (PPPs) [10, 14]. The PPPs model has proved useful for SWM in countries like India [15], South Africa [16], European countries [17] and Japan [18]. However, this model in Tanzania and Kinondoni in particular has not performed well since its initiation in 1995 when only handful (5.5%) of the SW was collected and disposed to the dumping site [19]. Since then a slight improvement in solid waste collection and disposal have been experienced with only two fifth of SW being collected and disposed in the country [5, 20].

Characterisation of solid waste in Tanzania is based on material composition and source or generator of the waste. Based on material composition solid waste is classified into five groups which include organic, recyclable, electrical, hazardous and toxic wastes. Organic waste is mainly generated from food, kitchen waste and green waste. Recyclable waste is generated from glass, bottles, plastic and metals. The electrical waste is created from used up electrical appliances and electronic appliances such as televisions and computers. Harzadous wastes are generated from corrosive materials such as paints and chemicals. The last category of waste is toxic waste which is waste generated from poisonous materials such as pesticides and herbicides (pesticides, herbicides) wastes [21]. Organic wastes form the major component (64%) of solid waste generated in Tanzania's urban centres; followed by plastics (11.9%), Hazardous (8%), papers (6.6%), leather & rubber (6%). The rest is composed of other other that include glass, textile wastes, electronics and other solid wastes not mentioned [22]. Alternatively, characterisation of solid waste from its origin is generated from households, institutions, market, industries and streets [23]. Households form major source of solid waste accounting for 56% of all solid waste generated from in the countries urban centers [24].

Numerous studies related to SWM have been done in Tanzania [5, 6, 7, 25, 26, 42]. The scope of these studies is limited to compliance on regulatory framework and economics of solid waste management. Based on the current research work there is limited empirical evidence showing the key drivers of inefficiency in Public Private Partnership. Therefore this paper examined factors influencing performance of PPPs for pro-health SWM in Kinondoni municipality. Specifically the paper analysed the policy, legal and regulatory environment, the operational capacity of contracted private companies for SWM, accessibility to the residential areas and the monitoring & evaluation practices in place.

2. METHODOLOGY

2.1. Study area

This study was conducted in Kinondoni municipal council located in Dar-es-Salaam city which is also the biggest commercial city in Tanzania as indicated in Figure 1 below.

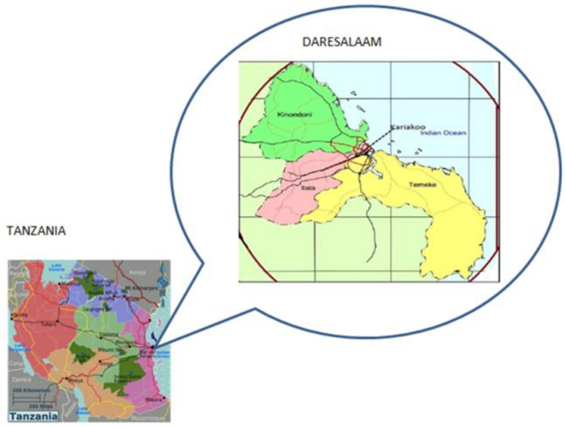


Fig 1. A map of Kinondoni municipal council

2.2. Analytical conceptual framework

The Agency Theory forms the foundation of this paper by looking at the relationship between public and private entities in solid waste management projects as principal and an agent respectively. The principal delegates an agent to perform the work on its behalf [16]. It is assumed that agent will represent the interests of the principal and not focusing on the self-interest. When the principal and the agent are motivated by inherent self-interest conflict may occur during implementation of the project. Therefore to minimize the individual inherent conflicts of the principal and the agent, there must be a sound legal and regulatory framework. Moreover, motivation for the agent to abide to the principal's interest have to be given so as they work as a union; meanwhile clear information on the performance of the agent to the principal must be in place.

Principally, the performance of PPP in SWM is influenced by several factors: well drafted output specification, robust business case, committed senior management, full consultation to end users, good political will, capacity of the garbage collection companies, monitoring and evaluation, transparent and competitive procurement, and public participation. However this paper investigates four main factors in the solid waste subsector which are more relevant in Tanzania context: Policy, legal and regulatory environment, monitoring and evaluation practices, capacity of the PPP contracted companies to implement the project successfully and accessibility of residential areas (Figure 2).

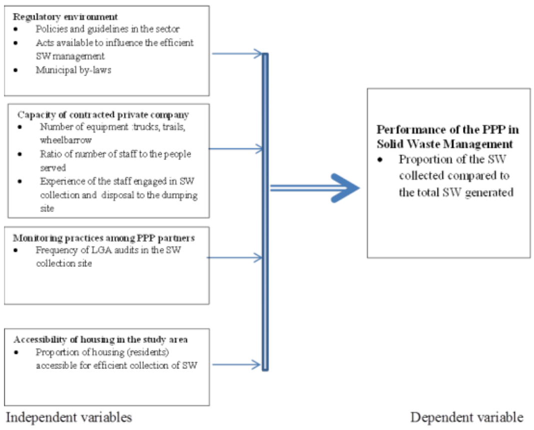


Fig 2. Conceptual framework

Policy, Legal and Regulatory framework

The policy, legal and regulatory framework encompasses national policies, Acts and regulations on environmental protection, municipal by-laws that govern issues of the solid waste management and tendering procedures in sub-contracting the companies to collect, transport and dispose the waste. It is acknowledged that Enabling legal, regulatory, and policy framework are key elements to a sustainable partnership project [27, 28, 29,]. A strong regulatory framework enhances the successes of the PPP project while a weak regulatory framework hinders the performance of PPP in various sectors and solid waste management in particular.

Monitoring and evaluation

Monitoring and evaluation entails routine tracking of information on a project and its intended outcomes based on the target set during planning process. When monitoring and evaluation is performed correctly informs the management to understand whether the project being implemented is going in the proper direction as planned or not. It gives early warning indicators in the performance of the project. In fact monitoring and evaluation have been acknowledged to influence the performance of PPPs on solid waste management [30, 31] and other sectors of the economy [32]. It can be generalized that a well framed monitoring and evaluation procedures enhances the performance of PPPs while a weak monitoring and evaluation structure hinders the performance of PPPs particularly in solid waste management. Therefore, monitoring and evaluation was assumed to have positive relationship with performance of PPPs in solid waste management in the study area. The monitoring and evaluation was measured in terms of frequency of auditing conducted by the entrusted bodies (LGAs and ward executives for making follow up to see whether the planned targets are attained.

Capacity of the PPP companies

The contracted companies whether Community Based Organisations or Private Company needs to have proper capacity to undertake the task of solid waste collection and disposal to the landfill or dumping site. The capacity referred here includes financial health, trained and experienced work force and equipment for the task at hand. Various authors acknowledge the influence of capacity for the contracted company to undertake the solid waste efficiently [27, 30, 33]. The proper capacity requirements are further made important by increasing urban population and changing socio – economic and demographic profile that necessitate quality services [30]. In this study, the capacity of the engaged company was thought to be measured in terms of number of staffs employed (refuse collectors), the work experience of the staff employed in contracted companies and equipment possessed by the company that can be used in solid waste collection and disposal. It is hypothesized that the number of refuse collectors employed has positive relationship with the performance of the PPP performance as the work will be distributed to the number of refuse collectors, hence less work per individual will enhance the collection and disposal of the waste. Moreover, longer experience improves skills to work efficiently; therefore it is assumed that the experience of the refuse collectors has a positive relationship to performance of the PPP in solid waste management. Furthermore, the equipment possessed used in SW collection and disposal is of paramount important for the efficient performance of the engaged company.

Accessibility to residential areas

Un-planned settlement is acknowledged to hinder the solid waste collection and disposal since some of settlements can-not be reached. Because in these kinds of settlement the roads tend to be narrow such that the motorcars can-not pass between houses. Therefore, this pose a serious challenge when comes to collection of solid waste from these locations. In fact, most of settlements (>70%) are located in unplanned settlements [4, 34, 35, 36]. The issue of unplanned settlements is prominent in Tanzanian urban cities and Kinondoni in particular. In this paper, accessibility of the homesteads was assumed to have positive association with performance of the PPPs.

The model was summarized using equation 1 below;

$$PPP_{pf} + \beta_0 + \beta_i X_i + \sigma \quad (1)$$

whereby

PPP_{pf} - Performance of the PPP contracted company to collect and dispose the solid waste measured by proportion of the solid waste collected and disposed to the dumping site

β_0 - Constant

χ_i – A vector of factors influencing performance of PPP contracted company

β_i – A vector of coefficients measuring the effect of independent variables on the performance of PPP contracted companies

σ – The error term measuring the effect of other variables not included in the model

Empirically the model can be expanded to read as;

$$PPP_{pf} + \beta_0 + \beta_1 Stfnn_1 + \beta_2 Stfexp + \frac{\beta_3 Stf}{ps} + \beta_4 hhaccess + \beta_5 Compcap + \beta_6 Monito + \sigma \quad (2)$$

whereby;

$Stfnn$ - Number of refuse collectors employed by companies engaged to collect and dispose the waste

$Stf\ exp$ - The experience of staff employed by companies engaged to collect and dispose the waste measured in years

Stf/ps – The ratio of refuse collectors per number of people served

$hhaccess$ – Accessibility of houses by motor vehicle in the study area

$Compcap$ – The capacity of the contracted company as measured in terms of equipment used in the collection and disposing of solid waste to the dumping site

$Monito$ – Monitoring and evaluation practiced among LGAs and ward officers responsible for solid waste management.

2.3. Data collection

Cross sectional survey research design was employed in the study. Multi-stage, stratified and random sampling techniques were used to select 91 respondents who were involved in the PPPs SWM (Table 1). All of respondents were involved in the PPPs solid waste management through their positions as they are entitled by the Environmental Impact Assessment (EMA) policy of 2004 and its subsequent solid waste management regulations of 2009. In practice the above mentioned respondents were chosen due to their decision making position for contracting companies to be involved in the SWM in their respective areas.

Structured questionnaire was used to interview ward councilors, municipal environment officer, members of Environment & health committee, ward executive officers, sub-wards executive officers, sub-wards chairpersons. Interview guides were used to solicit information from private companies' managers and refuse collectors during January – March 2016. The data collected included wards and sub-wards respondents' information on capacity of private company on solid waste collection and disposal and monitoring and evaluation practices on the part of participating companies and the municipal. Environmental policy, laws and regulations were solicited from the ministry of environment for review.

Table 1. Sample composition in the study area

Sample Type	Population	Sample	Percent (%)
Members of Ward Health Committees	59	15	25.0
Ward Executive officers	15	15	100.0
Members of Sub-wards Health Committees	59	15	25.4
Sub-wards Chairpersons	59	15	25.4
Sub-wards Executives Officers	59	15	25.4
Refusal Collectors	60	15	25.0
Ward councilors	15	15	100.0
Private companies managers	15	5	33.3
Environmental officer from KMC	1	1	100.0
Total	**342**	**96**	**32.5**

2.4. Data analysis

The study employed descriptive statistics and content analysis methods to analyse the policy, legal and regulatory environment. A multiple regression analysis was used to analyse factors influencing the performance of public private partnership (PPP) using Statistical Packages for Social Science (SPSS) software version 20.

Upon data analysis, various tests on the assumptions of regression in the model were performed to identify whether they were violated or not using SPSS software version 20. These tests included homoscedasticity test, autocorrelation test and collinearity test (Appendix IV, V and VI respectively).

3. RESULTS & DISCUSSION

3.1. Policy, legal and regulatory environment

Generally the study findings from content analysis show that, Tanzanian regulatory framework on solid waste management is well articulated with some minor defects. The major challenge is that it lacks enforcement procedures and levels of penalties for non-compliance. Moreover, the framework is entrusted to be implemented by diverse population (wards) with relatively less education on issues regulating the processes. Could the process of contracts be vested on experts at Local government authorities would, the situation would be harmonized.

The Tanzanian regulatory framework is composed of one policy, and four legislations that govern environmental issues and solid waste management in particular. The policy is the National Environmental Policy (NEP) [37] at one hand and Tanzania & Local Government (Urban Authorities) Act 1982, and the Environmental Management Act 2004 [38]. The Public Private Partnerships of 2010, The Public Private Partnerships Regulation 2011.

The National Environmental Policy (NEP) [37], addresses six (6) environmental problems land degradation; lack of accessible, good quality water; pollution of the environment; loss of wildlife habitats and biodiversity; deterioration of aquatic systems; and deforestation. In the case solid waste in towns is considered to affects health of people such that it raises concerns. In this regard NEP [37] addresses the issue of solid waste management through the issue of environmental pollution that is cited on its section 11 part (iii) that pollution in towns and countryside affects health of many people and lowers the productivity of the environment. Moreover, in its section 28 the policy highlights the need for technology which when used bears in the quality of a product in the type and amount of the resulting waste and emissions. It is emphasized that environmentally sound technologies in the context of pollution are "process and product technologies" that generate low or no waste for prevention of the pollution. Moreover, in its section 29 stipulates the emphasis for recycling of wastes and products and handle residues wastes in a more acceptable manner.

The main objective of the Environmental Management Act 2004 [38] is to promote the conservation and management of the environment. In this Act some aspects that are directly associated with solid waste management include (i) The legal framework for the overall management of the environment giving power and responsibilities for various organs and institution the enforcement mandate. (ii) Establishment of administrative and institutional framework for the management of the environment. In its Part IX Caption 114 -119, the Act stipulates roles and responsibilities of LGAs in managing the solid waste. It can be generalized that the role of the LGAs is to ensure minimization of the solid waste in their areas of jurisdiction. The Act gives mandate to the Local Government Authorities to involve the private sector and Non-governmental Organizations (NGOs) in solid waste management activities. Moreover, the Act requires the waste to be separated based on its type. However, separation of the solid waste practices did not exist during the data collection.

Institutionally, the NEP [37] stipulates advisory bodies in its sections 98 – 100 to protect the environment. In addition to the policy, the Environment Management Act 2009 provides the room for establishment of National Environmental Management Council (NEMC) that is charged with formation and evaluation of policies, acts, plans and guidelines on environmental based issues and advice the government appropriately. Moreover, NEMC is also charged with the responsibility of making environmental impact assessment on projects and advice appropriately.

In its section 97 – 101, Local Government Authorities (LGAs) has been entrusted to construct, operate, control and maintain economic, social and environmental infrastructure. The section 102 the LGAs has been empowered to oversee the planning processes and establish the local environmental policies and regulations. This policy is well articulated with regard to the Local government (Urban Authorities) Act 1982, the Act entrusts urban authorities the responsibility to ensure that their areas of jurisdiction and sanitary conditions are kept clean as stipulated in its section 55. Moreover, the Act delegates the urban authorities with the mandate to make their own by-laws to enable them to execute their responsibility of waste management in their respective areas of administration.

With regard to the Public Private partnerships, also the legislations are well articulated on the performance of the task at hand. The function for each part (public sector, private or other stakeholders are stipulated in Public Private Partnership Act 18 of 2010 and its subsequent Public Private Partnership Regulations 2011.

Hence legally, Dar es Salaam city council is entrusted to manage solid waste at the dumping site currently being disposed at Pugu dumping site for all three LGAs (Kinondoni, Ilala and Temeke) that has been expanded to (Kinondoni, Ilala and Temeke, Ubungo and Kigamboni). In Kinondoni Municipality there are 34 wards that are charged with mobilization of establishment of Community Based Organisations (CBOs) for offering the service of solid waste collection from the household homesteads and nearby waste collection points to the disposal dumping site. The wards are also entrusted to engage private companies in contracts to provide the service of solid waste to the dumping site. In fact the wards are responsible for the waste in the households and the collection points while LGAs are responsible with the collection of the solid waste from public centers like at schools, governments and in the market premises.

With the above regulatory environment, it was observed that solid waste collection and disposal in the study area was fairly poor during data collection, since only 42% of the generated solid waste was collected and disposed to the Pugu dumping site. The rest (58%) was left unmanaged to illegal sites and drainage systems that can lead to endemic diseases outbreak. The pandemic diseases such as cholera have been reported in Tanzania particularly Dar-es-Salaam (Sekijege et al., 2012; Outwater et al., 2013) that can be associated with the mismanaged solid waste. Moreover, the situation is worsened by the limited number of collection points (Table 2) that leads to improper disposal of the waste. In addition to that frequency of solid waste collection was reported to be low (Table 2) when compared to the daily generation of the waste. This finding is similar to the findings by Huisman et al (2016) who observed that in most cases the collection points in Dar-es-Salaam seemed as a dumping site since the garbage stays longer in the collection points.

Different agents were involved in solid waste collection and disposal in the study area. Table 3 shows that private companies participate in PPPs for street cleansing by 100% and participate in open space cleansing by 66.7%. Meanwhile, the private companies accounted for only 6.7% of household waste collection and disposal. The Community Based Organisations accounted for 93.3% of the solid waste management from the household sources in Kinondoni Municipal (Table 3). Engagement of the CBOs in household waste collection and disposal can define the inefficiency observed in the study area. This is defined in the moral hazards and free riding paradox whereby the CBOs lacks owner. Hence their commitment is questionable to afford the heavy task of the CBOs. Moreover, the distribution of the earnings from the service offered is not known. On the other hand, the private companies seem to prefer to offer services mainly in the open space and streets (Table 3). This associated with the fact that most homesteads (72%) were not accessible in the study area. This would add up to the cost of management since some people with trolleys or pushcarts would be necessitated to be hired to collect the waste to the nearby collection points. Coupled with inefficient collection waste fee collection observed in the study and other studies (Huisman et al., 2016) the profit margin would be minimized that demotivates private sector to get involved in the household waste collection and disposal.

Table 2. Attributes of the SWM in the study area

	Frequency	Percentage	Cumulative percentage
Presence of waste collection points			
Yes	10	13.3	13.7
No	65	86.7	100.0
	75	100.0	
Frequency of waste collection			
Once per month	29	38.7	38.7
Twice per month	9	12.0	50.7
Three times per month	20	26.7	77.3
Four times per month	17	22.7	100.0
		100.0	
The companies responsible for waste disposal			
Community Based Organisations (CBOs)	44	58.7	58.7
Private companies and CBOs	31	41.3	100.0

Table 3. Roles performed by different companies in Kinondoni Municipality

	Frequency	Percentage	Cumulative (%)
Street cleaning			
Community Based Organisations	0.0	0.0	0.0
Private companies	2.0	100.0	100.0
	75	100.0	
Open space cleaning			
Community Based Organisations (CBOs)	1.0	33.3	33.3
Private companies	2.0	66.7	100.0
		100.0	
Households			
Community Based Organisations (CBOs)	14.0	93.3	93.3
Private companies	1.0	6.7	100.0
		100.0	

3.2. Capacity of contracted companies in PPPs for SWM

The capacity of the privately contracted companies was sought in terms of equipment, human resources, experience, and financial resources owned by the contracted companies. Table 4 express the capacity of contracted companies for SWM in the study area.

Down to the details of descriptive statistics, findings of the study indicate that SWM contracted companies had 28 trucks, 6 tractors, 6 trails, 69 pushcarts and 127 wheelbarrows. However, the equipment had the average capacity of collecting only 42.2% of solid waste generated in the area under study. The effects of about two third of the generated wastes (equivalent to 1,216tons/day) being left without proper management regime cannot be overestimated. These wastes are really dumped in the illegal sites (Figure 3) that would lead to health hazards to the public. These findings are in line with finding by Breeze [5] who revealed that about 76% of the respondents were not served since they had no access to the door to door equipment for solid waste collection in Dar es Salaam city. This implies that PPP agents have a deficit of facilities and equipment for disposing garbage. In addition to that the trucks were not specialized for the waste collection to easing the task of waste disposal (Figure 4). The finding of illegal dumping of SW in the study area is more or less similar to the study findings by [39] who found that shortage of SW disposing bags in houses and long distance to waste containers caused illegal dumping in the street and in the water drainage canals.

Table 4. Equipment capacity of private contracted companies for SWM

Sub-ward	**Type of equipment**					**Average Collection (%)**
	TRU	**TRA**	**TRL**	**PU**	**WH**	
Kwatumbo	2	1	1	5	10	40
Kilungule	1	0	0	6	8	45
Kinzudi	1	0	0	4	8	44
Kumbukumbu	2	1	1	5	9	43
Azimio	1	0	0	5	8	38
Mkunguni B	2	0	0	6	10	46
Mbezi beach A	3	1	1	3	8	56
Bunju B	1	0	0	4	8	42
Hondogo	2	0	0	3	8	44
Tegeta	1	0	0	3	10	40
Idrisa	3	1	1	5	9	40
Kigogo mkwajuni	3	1	1	6	9	35
Mwenge	2	1	1	6	8	45
Kilungule A	2	0	0	5	6	30
Njeteni	2	0	0	3	8	30
Total	28	6	6	69	127	42.2

Key: TRU=Trucks; TRA= Tractors; TRL=Trails; PU=Pushcarts and WH = Wheelbarrow

Fig 3. Uncollected solid waste disposed along the water canals

Fig 4. Non specialized truck collecting Solid waste at Magomeni informal market

Moreover, for delivering efficient waste collection services, the contracted companies in PPPs require enough staff to manage the waste in their areas of operation. The finding indicates that average persons served per staff is 941 (Table 5) compared to the staff needed in Pakistan that ranged between 280 and 1613 persons per staff [40]. However, the extremes were noted in two sub wards (Azimio with 1750/staff and Kilungule A with 1759/staff). Moreover, the findings revealed lack of experience among human resources employed in the contracted SW collection companies. It was revealed that most staffs in contracted companies had an average working years of 1.71 as opposed to the reasonable minimum experience of 3 years. This implies that companies' employees have inadequate experience for performing their daily responsibilities. The low level of experience may lead to inefficiency in garbage collection as it is acknowledged that experience is a teacher. In fact; the contracted companies had no sence of permanence in employing their staff. This finding is different from the findings by [41] which revealed that limitation of labour force was the major constraint in SWM in Uganda cities.

Another factor related to capacity of contracted companies which contributes to influencing performance in SWM is the financial soundness of the companies. Financial strength of the PPP agent is important for delivering quality and sustainable SWM services. Five companies contracted for SWM were interviewed to find out the amount of money that is needed to be topped up on a weekly basis for a smooth running of their SWM activities. Findings showed that all (100%) of the company managers for the contracted companies acknowledged to suffer from financial deficits for meeting their financial operational costs. The deficit was maximum at 4,000,000Tsh/week and minimum at 1,000,000Tsh/week. On average the contracted companies were running short of TZS. 2,290,000 ± 903,033 Tsh/week for efficient solid waste collection in the study area. The finding indicates that agents were failed to meet SWM obligations and therefore poor performance of PPPs due to weak financial capability. The major reason for deficit was the fact that the refusal collection fee was not enough to cover 100% the refuse collection operational costs. This finding is in line with the study findings by [5] in Dar es Salaam City and Arusha which found that there is poor financing strategy by PPP agents. Moreover; the results is similar to the results by Maziku [36] in his study on Solid Waste Management in the Dar-es-Salaam Coastal Belt who pointed out that there was existence lack of financial motivation within waste collection agents. Lack enough Huisman et al, (2016) revealed that if the prevailing solid waste collection fee could be collected efficiently at 100%, it suffices to cover the operational costs and retain a reasonable gross margin for investors in the SWM.

The results from multiple regression analysis (Table 9) revealed that an increase of one refuse collector employed by contracted companies to manage the waste leads to an increase of 1.64% of the solid waste collected and disposed to the dumping site. This calls for increase of number of refuse collectors to the adequate available quantities of the waste in Kinondoni municipality. Coupled low experience of refuse collectors estimate at only 1.7 years and the fact that experience had positive association with performance of the PPPs contracted companies, there should be harmonised working should be retain them rather than just being employed as labourers. The results reveal that an increase of one year of experience for the refuse collector improves the solid waste management by 1.11%. (Table 9). The proportion of staff/people served ratio, experience and expatriates has been reported by other authors as an important factor influencing the PPP companies performance elsewhere in the globe (Lop et al., 2017; Minjire and Waiganjo, 2015).

Table 5. Staff in solid waste collection in private companies

No.	Sub-wards	Number of Staff	Average working	Population	Persons
1	Kwatumbo	14	1	10.066	719
2	Kilungule	9	1	11,068	1,230
3	Kinzudi	9	2	5,880	653
4	Kumbukumbu	13	2	5,854	450
5	Azimio	9	1	15,754	1,750
6	Mkunguni B	12	1	8,184	682
7	Mbezi beach A	13	3	18,499	1,423
8	Bunju B	9	2	5,614	624
9	Hondogo	10	2	6,369	637
10	Tegeta	11	2	13,784	1,253
11	Idrisa	14	2	5,380	384
12	Kigogo mkwajuni	14	3	21,173	1,512
13	Mwenge	12	1	9,156	763
14	Kilungule A	8	1	14,071	1,759
15	Njeteni	10	2	6,273	627
	Total	**167**	**1.71**	**157,125**	**941**

3.3. Monitoring and evaluation

Monitoring and evaluation is considered as an important component in the successfulness of the project. Hence monitoring and evaluation practices exercised in Kinondoni municipality were identified. These include 'imprompt audits', 'daily follow up' and 'after crisis follow up'. Findings from the regression analysis revealed that the proportion of SW collected by PPP contracted companies declined by 2.63% when using 'after crisis follow up' procedures compared to when using the imprompt follow up approach (Table 9). The imprompt follow up has its strength in the fact that the agent (contracted company) would not know exactly when the audit will be conducted and for that case; the agent would get prepared at any time such that the principal should come at any time and find things right. In addition to that, the imprompt audit's strength is based on its identification of the problem and resolves the problem before things get worse. The solid waste collection fee from households was associated with a positive increase in solid waste collection and disposal. Hence improved efficiency in user fee for solid waste collection will lead to improved performance of the PPPs in solid waste collection and disposal. In fact Huisman et al, (2016) established that the current solid waste collection fees structure can meet the costs of operation and normal profit margin if it is collected efficiently.

Results from descriptive statistics revealed that 100% of respondents had reported that there were no any documented monitoring schedules in their authority. Moreover, the auditing frequency from the Principal (LGAs and ward executive officers) to the waste source was limited (Table 6). More than 45% of respondents acknowledged the audit exercised was 'after crisis follow up'. This portrays the fact that SWM is poorly exercised in the study area.

Table 6. Monitoring and evaluation practices Kinondoni Municipality

	Frequency	Percent	Cumulative Percent
Occasional Audits	20	26.7	26.7
Daily follow up	21	28.0	54.7
After crisis follow up	34	45.3	100.0
Total	**75**	**100.0**	

3.4. Accessibility of residential areas

Unplanned settlements pose difficulties in solid waste management. Congested houses and informal pathways are among the major challenges towards management of the solid waste. Findings from the multiple regression analysis revealed that a one per cent increase in accessibility of the houses was associated with a 0.63% increase of the solid waste management though not significant. In fact it was established that the proportion of SW collected by PPP contracted companies increased by 2.99% where there was SW collection centers compared to collection of SW without solid waste collection centers (Table 9). In this case, the insignificancy of the factor might be attributed with the fact that there were solid waste collection centers nearby homes where accessibility was a problem. However, the collection centers were not properly managed since the waste took long on the site such that, they were seen as dumping sites. This was also observed by Huisman et al, [26] in Dar-es-Salaam, Tanzania. The interviewed respondents estimated the proportion of accessible houses in Kindondoni to range between 20 and 40% with average accessible households of 28 ± 7.5% using trucks, trailers and wheel barrows. This justifies the reason of private companies to avoid tendering in unplanned settlements. The finding suggests that establishment of refuse collection points within accessible household premises in the unplanned settlements is inevitable.

Factors influencing PPPs performance using regression model

The regression model fit was found to be good fit to the data with an adjusted R square of 0.804 (Table 7) and significant F statistic at significance level of P<0.05 (Table 8). The model is well fitted to the collected data such that it accounts for 82% of variations in the solid waste performance in the study area. The remaining 18% can be explained by other factors not included in the model. The same model applies to the capacity of the contracted companies, accessibility to the residential areas for solid waste collection and monitoring and evaluation of the PPP for solid waste management which constitute the independent variables of the model.

Table 7. Model summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	0.905[a]	0.820	0.804	2.71173

a. Predictors: (Constant), Average person served by one staff, average working years for the staff engaged companies, Proportion of houses accessible in the locality, After crisis follow up vs occasional follow up, presence of waste collection centers vs no waste collection centers, Number of staff for the engaged private company in SW collection

Table 8. ANOVAa

Model		Sum of Squares	Df	Mean Square	F	Sig.
	Regression	2271.750	6	378.625	51.489	0.000[b]
	Residual	500.036	68	7.353		
	Total	2771.787	74			

a. Dependent Variable: Proportion of SW collected in your sub-ward
b. Predictors: (Constant), Average person served by one staff, average working years for the staff engaged companies, Proportion of houses accessible in the locality, After crisis follow up vs occassional follow up, presence of waste collection centers vs no waste collection centers, Number of staff for the engaged private company in SW collection

Table 9. Factors influencing performance of PPP contracted companies in SWM

	Unstandardized Coefficients		Std Coefc.	t	Sig.
	B	Std. Error	Beta		
(Constant)	14.858	1.931		7.696	0.000
Capacity of the contracted companies					
Staff numbers employed in SW collection	1.637	0.139	0.790	11.804	0.000
Experience of staffs in SW collection (years)	1.109	0.547	0.123	2.028	0.047
Ratio of staff/people served	0.003	0.001	0.225	3.441	0.001
Household accessibility					
Households' accessibility in the locality (%)	0.063	0.045	0.077	1.408	0.164
Solid waste fee collected from households (Tsh)	4.76E-008	0.000	0.124	2.037	0.046
Solid waste collection centres vs no waste collection centres	2.990	0.986	0.167	3.032	0.003
Monitoring and evaluation					
After crisis follow up vs occasional follow up monitoring	-2.627	0.653	-0.215	-4.023	0.000

4. CONCLUSIONS & RECOMMENDATION

Just to reiterate that about 60% of solid waste in Kinondoni municipality are left uncollected and disposed in illegal sites that poses health risks to the general public in the area to be vulnerable to endemic disease outbreaks such as cholera. Findings of the study showed that poor monitoring and evaluation system of the PPP initiatives for solid wastes collection was the main factor influencing poor performance of solid waste management in Kinondoni municipal. Other factors included low capacity of the contracted companies in terms of manpower and financial stability, limited accessibility of unplanned settlement areas and weak enforcement of laws and regulations governing solid waste management. The main conclusions of the study were that contracted companies have low capacity to perform, laws and regulations governing solid waste management are not effectively enforced, the unplanned settlements are not easily accessible and the monitoring and evaluation system in place is ad hoc where there is no regular plan that warrants learning and accountability check. The study recommends that the monitoring and evaluation system should be the primary target for improvement by establishing a clear regular plan in combination with imprompt monitoring in order to eliminate the effect of possible falsified compliance. As a long term solution the study recommends to the municipal council to improve towns and settlements planning for easy access to the households to improve garbage collection. Lastly but not least further research on end use products of the waste should look at the technical and economic viability of such end use products. Key aspects in the research that need to be clear is whether there is potential market for the end use products and whether the products can generate a reasonable profit margin that makes a business sense as a sustainable business. Positive outcome of the research will help to inform potential investors to make informed decisions on the business options available for converting waste into wealth. A study such as costs and benefits analysis of compositing organic fertilizers that accounts for a major portion of the solid waste is a potential research topic. Both short term and long-term solutions are expected to highly contribute in mitigating health risks associated with the solid waste mismanagement.

ACKNOWLEDGEMENTS

The author would like to thank Kinondoni municipal director on behalf of other municipal staff for their heart fully cooperation and more specific ward and sub-wards executives of whom their cooperation is very valuable.

REFERENCES

[1]. S. Countreau, "Occupational and environmental health issues of solid waste management: Special emphasis on middle and lower countries", Urban Sector Board and the World Bank, Washington, D.C. 48 pp, 2006.

[2]. IFC [International Finance Corporation, World Bank Group], "Handshake IFC's Quarterly Journal on Public – Private Partnerships", Issue 12, 84 pp., 2014.

[3]. IGC [International Growth Center], "Urbanisation in Tanzania. An internation growth center", Number 2, 55 pp., 2014.

[4]. L. Worrall, S. Colenbrander, I. Palmer, F. Makene, D. Mushi, J. Mwijage, M. Martine and N. Godfrey, "Better urban growth in Tanzania: Preliminary exploration of the opportunities and challenges", *Coalition for Urban Transitions, London and Washington, DC.* Available at: http://newclimateeconomy.net/content/cities-working-papers. 90 pp., Accessed on 16.11.2018 2017.

[5]. R. Breezes, "Municipal solid waste management in Dar-es-Salaam", A report prepared for the World Bank Washington, DC. 23 pp, 2012.

[6]. N.B. Mnyanyi, Assessment of solid waste management in Kinondoni Municipality", *A Dissertation Submitted in Partial Fulfilment for the Requirements for the Degree of Master of Environmental Studies (Science) of the Open University of Tanzania*, 2014.

[7]. E.L. Mollel, "Economic analysis of the solid waste management options in Morogoro Municipality", *A Dissertation Submitted in Partial Fulfilment of the Requirements for the Award of Degree for Master of Science in Environmental and Natural*

Resource Economics of Sokoine University of Agriculture, Morogoro, Tanzania, 67 pp., 2016.

[8]. C. Zurbrugg, "Urban solid waste management in low- income countries of Asia, How to cope with the garbage crisis", *A paper presented for: Scientific Committee on Problems of the Environment (SCOPE). Urban Solid Waste Management* Review Session, Durban, South Africa, November, 2002. 13 pp., 2002.

[9]. P. Mgaya and L. Nondek, "Disposal frequencies of selected recyclable wastes in Dar es Salaam", *Waste Management*, Vol. 24, pp. 927–933, 2004.

[10]. UN-HABITAT, [United Nations Human Settlements Programme], "Solid waste management in the World's cities", 228 pp., 2010.

[11]. A.H. Outwater, S. Pamba and A.B. Outwater, "Water–related diseases of people using municipal wasterwater: Risks, exposure, effects on health and control approaches in Tanzania", *A Report Prepared for Dissemination of Sustainable Wastewater Technology of Constructed Wetlands in Tanzania*, 119 pp., 2013.

[12]. T. Sakijege, J. Lupala and S. Sheuya, "Flooding, flood risks and coping strategies in urban informal residential areas: The case of Keko Machungwa, Dar es Salaam, Tanzania", *Jamba: Journal of Disaster Risk Studies,* Vol. 4 (1), 10 pages, 2012.

[13]. WHO [World Health Organization], "Guidelines for drinking-water quality", *Fourth Edition Incorporating the First Addendum*. World Health Organization, Geneva, 541 pp., 2017.

[14]. UNEP [United Nations Environmental Program], "Summary report: Waste management in ASEAN countries", 64 pp., 2017.

[15]. K.P. Sigh, "Issues and prospects of public-private partnership in India", *International Journal of Multidisciplinary Research*, Vol. 1 (5), pp. 244 – 256, 2011.

[16]. C.J. Liebenberg, "Public private partnership solutions to waste management in developing countries in Africa, Menlo Park, South Africa", *Proceedings Sardinia 2007, Eleventh International Waste Management and Landfill Symposium*, S. Margherita di Pula, Cagliari, Italy; 1 - 5 October 2007 by CISA, Environmental Sanitary Engineering Centre, 2007.

[17]. G. Bel and X. Fageda, "Empirical analysis of solid management waste costs: Some evidence from Galicia, Spain", *Resources, Conservation and Recycling*, 54 (3), pp.187-193, 2010.

[18]. JETRO [Japan External Trade Organisation], "Public private partnerships in Australia and Japan facilitating private sector participation", 2010.

[19]. J. Palfreman, "Waste management and recycling in Dar es Salaam, Tanzania", DOI: 10.13140/2.1.3196.4482 Retrieved 02/05/2016 https://www.researchgate.net/publication/271441207, 2014.

[20]. J.H. Ludete, "Factors influencing public private partnerships in solid waste management for local government authorities: A case of Kinondoni Municipality-Dar es Salaam", *A Dissertation Submitted in Partial Fulfilment of the Requirements for the Degree of Master in Project Planning and Management of Mzumbe University*, Morogoro, Tanzania, 2016.

[21]. M.K. Karija, Q.I. Shiua and Y.S. Lukaw, "The impact of poor municipal solid waste management practices and sanitation status on water quality and public health in cities of the least developed countries: The case of Juba, South Sudan", *International Journal of Applied Science and Technology,* Vol. 3 (4), pp. 87–99, 2013.

[22]. J.P. Senzige, Y. Nkansah-Gyeke, D.O. Makinde, and K.N. Njau, "The potential for solid waste recycling in urban area of Tanzania: The case of Dar Es Salaam", *International Journal of Environmental Protection and Policy*, Vol. 2 (5), pp. 147-152, 2016.

[23]. C. Mgimba, and A. Sanga, "Municipal solid waste composition characterization for sustainable management systems in Mbeya City, Tanzania", *International Journal of Science, Environment and Technology*, Vol. 5(1), pp. 47–58, 2016.

[24]. A.O. Solomon, "The role of households in solid waste management in East Africa capital cities", (*Unpublished Doctoral Dissertation). Wageningen University. Netherland,* 2011.

[25]. J.D. Maziku, "Improving solid waste management in the Dar-Es-Salaam coastal belt, Tanzania", *A Thesis Submitted for Partial Fulfilment of Natural Resource Management of Novia University of Applied Sciences*, Finland, 140 pp., 2014.

[26]. H. Huisman, H. Breukelman and B. Keesman, "Expert mission on integrated solid waste management (ISWM) to Dar es Salaam, MAT16TZ01 Report of findings, 31pp. 2016.

[27]. F. Contreras, T. Aramaki, S. Ishii and S. Connors, "Drivers in current and future municipal solid waste management systems: Cases in Yokohama and Boston, Doi 10.1177/0734X09349417, 2009.

[28]. ADB [Asian Development Bank], Government of Mongolia, "Public-Private Partnership Development (Financed by the ADP's Technical Assistance Special Funds – IV)", Visited from https://www.adb.org/sites/default/files/project-document/156500/41203-022-tacr.pdf on 03.01.2019. 2013.

[29]. E. Minjire and E. Waiganjo, "Factors affecting the performance of public-private partnerships in healthcare projects in Kenya: A case study of the Ministry of Health, Nairobi", *The Strategic Journal of Business & Change Management*, Vol. 2 (36), pp. 717 – 746, 2015.

[30]. A.Z. Ndumbu, "Factors affecting public-private partnerships projects in solid waste management in Mombasa County", *A Research Project Report Submitted in Partial Fulfillment of the Requirements for the Award of Master of Arts Degree in Project Planning and Management of the University of Nairobi*, 75 pp., 2013.

[31]. K.L. Thyberg and D.J. Tonjes, “A management framework for municipal solid waste systems and its application to food waste prevention”, *Systems 2015*, Vol. 3, pp. 133-151; doi:10.3390/systems3030133, 2015.

[32]. S.O. Babatunde, A. Opawole and O.E. Akinsiku, "Critical success factors in public-private partnership (PPP) on infrastructure delivery in Nigeria", *Journal of Facilities Management*, Vol. 10 (3), pp. 212-225, 2012.

[33]. N.S.B. Lop, K. Ismail, H.M. Isa and N. Khalil, “Factors affecting the operational performance of public private partnership (PPP) projects: Cases in Malaysia”, *International Journal of Academic Research in Business and Social Sciences*, Vol. 7 (11), pp. 1394-1409, 2017.

[34]. A.G. Kyesi, “Formalization of unplanned settlements and its implications on poverty reduction: The case study of Dar-es-Salaam city”, *The Tanzania Journal of Development Studies*, Vol. 8(2), pp. 421-427, 2008.

[35]. M.I. Rasmussen, “The power of informal settlements, the case of Dar-es-Salaam, Tanzania”, *Platinum Journal of Urbanisation*, Vol. 26, pp. 1-11, 2013.

[36]. J.D. Maziku, “Improving solid waste management in the Dar-es-Salaam Coastal belt, Tanzania”, *Degree Thesis for a Bachelor of Natural Resources*, Degree Programme in Integrated Coastal Zone Management, 2014.

[37]. NEP [National Environmental Policy], 32 pp., 1997.

[38]. The Environmental Management Act. 158 pp., 2004.

[39]. I.A. Al-Khatib, M. Monou, A.S.F.A. Zahra, H.Q. Shaheen and D. Kassinos, “Solid waste characterization, quantification and management practices in developing countries. A case study: Nablus district–Palestine”. *Journal of Environmental Management*, 91(5), pp. 1131-1138, 2010.

[40]. PEPA [Pakistan Environmental Protection Agency], “Guideline for solid waste management”, 142 pp., 2005.

[41]. O.J. Okumu and R. Nyenje, “Municipal solid waste management under decentralisation in Uganda”, *Habitat International*, Vol. 35(4), pp. 537-543, 2011.

[42]. Mungure M. J. (2008). Governance and community participation in Municipal Solid Waste management, case of Arusha and Dar es Salaam Tanzania. M.Sc. In Environmental Management. Aalborg University; 2008.

APPENDICES

Appendix 1. Sampling Frame Kinondoni Ward-Random Sampling

No	Wards	Randomization
1.	Tandale	0.146654
2.	Bunju	0.921422
3.	Goba	0.9274
4.	Hananasif	0.254062
5.	Kawe	0.021533
6.	Kibamba	0.963947
7.	Kigogo	0.435602
8.	Kijitonyama	0.269693
9.	Kimara	0.40483
10.	Kinondoni	0.303324
11.	Kunduchi	0.751684
12.	Kwembe	0.047996
13.	Mabibo	0.749994
14.	Mabwepande	0.45121
15.	Magomeni	0.137539
16.	Makongo	0.784137
17.	Makuburi	0.28642
18.	Makumbusho	0.584824
19.	Makurumla	0.185209
20.	Manzese	0.664696
21.	Mbezi	0.446709
22.	Mbezi juu	0.566404
23.	Mburahati	0.885115
24.	Mbweni	0.23154
25.	Mikocheni	0.296323
26.	Msasani	0.456265
27.	Msigani	0.551432
28.	Mwananyamala	0.974451
29.	Mzimuni	0.002684
30.	Ndugumbi	0.440836
31.	Saranga	0.824436
32.	Sinza	0.3376
33.	Ubungo	0.000604
34.	Wazo	0.900414

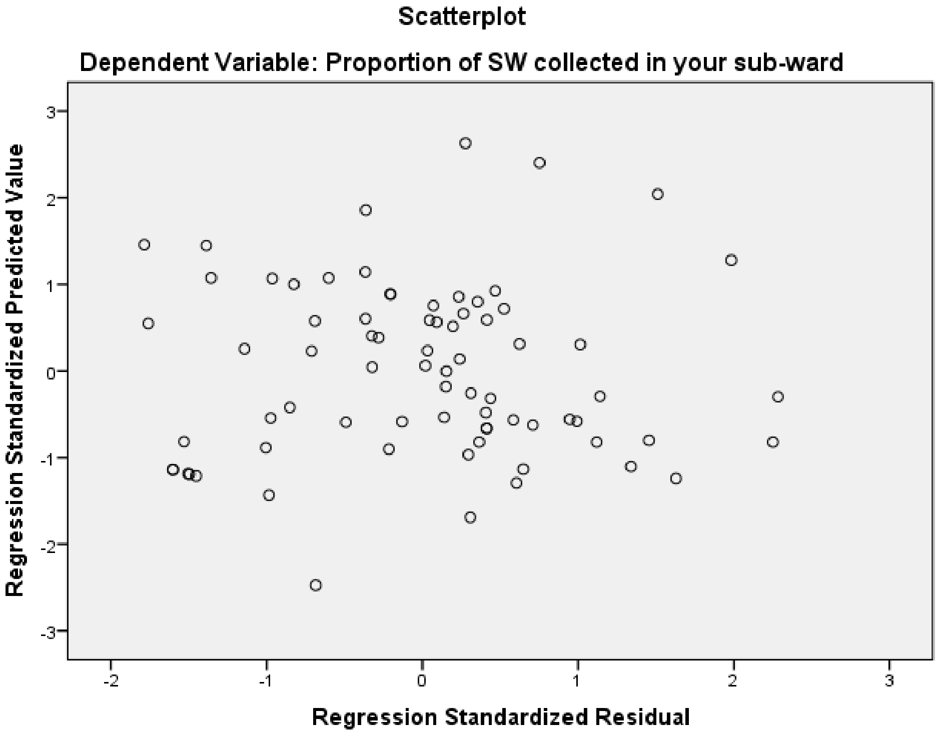
Appendix 2: Kinondoni sub wards sample randomisation

Tandale	**SAMPLE**		**Magomeni**	**SAMPLE**
Kwa Tumbo	0.075071		Idrisa	0.167576
Muharitani	0.176397		Suna	0.275869
Pakacha	0.157774		Makuti 'A'	0.711817
Mkunduge	0.240282		Dossi	0.829765
Mtogole	0.21575		Makuti 'B'	0.842808
Bunju	**SAMPLE**		**Kigogo**	**SAMPLE**
Kilungule	0.317763		Kigogo Mkwajuni	0.390857
Mkoani	0.857956		Kigogo Mbuyuni	0.401399
Dovya	0.303795		Kigogo Kati	0.470745
Bunju 'A'	0.448043		**Kijitonyama**	**SAMPLE**
Boko	0.59702		Mwenge	0.019171
Basihaya	0.639859		Mpakani 'B'	0.221142
Goba	**SAMPLE**		Bwawani	0.323158
Kinzudi	0.076682		Alimaua 'A'	0.335052
Goba	0.168094		Mpakani 'A'	0.370354
Kibululu	0.212996		Nzasa	0.659541
Kulangwa	0.346676		Kijitonyama	0.791616
Tegeta A	0.501734		**Kimara**	**SAMPLE**
Muungano	0.579218		Kilungule 'A'	0.431577
Kunguru	0.604377		Kimara Baruti	0.647166
Matosa	0.675902		Baruti	0.712707
Kinondoni	**SAMPLE**		Kilungule 'B'	0.815839
Kumbukumbu	0.337883		Golani	0.977632
Ada Estate	0.406938		Mavurunza	0.984488
Kinondoni Mjini	0.796189		**Kwembe**	**SAMPLE**
Kinondoni Shamba	0.915387		Njeteni	0.065044
Mabibo	**SAMPLE**		Kisopwa	0.108169
Azimio	0.069893		Mjimpya	0.158615
Matokeo	0.172786		Mpakani	0.34381
Mabibo	0.442699		Mlongazila	0.366894
Jitegemee	0.660802		King'azi	0.464077
Mabibo Farasi	0.904298		King'azi B	0.870209
Kanuni	0.967078		Msakuzi	0.919394
Hananasif	**SAMPLE**		Luguruni	0.925365
Mkunguni 'B'	0.129536		Kwembe	0.946006
Kawawa	0.752135		**Mabwepande**	**SAMPLE**
Hananasif	0.194384		Bunju 'B'	0.025515
Mkunguni 'A'	0.795273		Mjimpya	0.14652
Kisutu	0.606761		Mabwepande	0.293288
Kawe	**SAMPLE**		Kihonzile	0.700156
Mbezi Beach 'A'	0.078782		Mbopo	0.917578
Mzimuni	0.169442			
Mbezi Beach 'B'	0.640253			
Ukwamani	0.697305			
Kibamba	**SAMPLE**			
Hondogo	0.006939			
Gogoni	0.047898			
Kibwegere	0.37248			
Kibamba	0.444402			
Kiluvya	0.555327			
Kunduchi	**SAMPLE**			
Tegeta	0.278271			
Kondo	0.358668			
Kilongawima	0.643346			
Pwani	0.851544			
Ununio	0.96956			
Mtongani	0.970093			

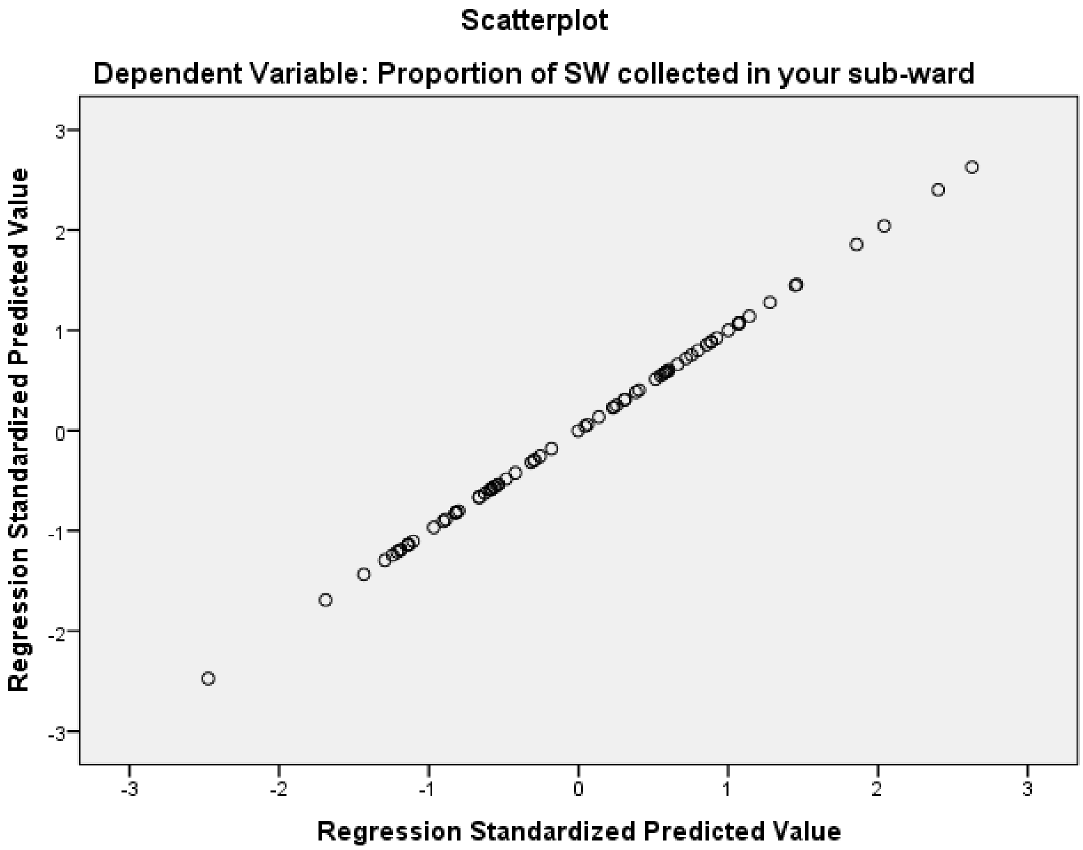
Appendix III. List of Cleansing Contractors at Kinondoni Municipal Council

No	Name of the company
1.	A. J. M COMPANY LTD
2.	BAM WASTE MANAGEMENT
3.	ENEA GROUP
4.	KURO ENVIRONMENTAL CARE LTD
5.	GORDIAN Z. KIKARUGA
6.	JUHUDI COOPORATION CO. LTD
7.	KIFUNA HERSHODAN INTER.CO LTD
8.	KINONDONI ENVIRONMENTALIST
9.	KIWODET
10.	UUGAI NENGA CO. LTD
11.	LYCAM INVESTMENT
12.	LUGOLI ENTERPRISEE
13.	MNEMVU TRADERS CO. LTD
14.	QUALITY SYSTEMS (T) LTD
15.	SKY MARS SERVICES CO. LTD
16.	T.T.M. GROUP
17.	ZUBISH ENTERPRISES

Appendix IV: Testing of homoscedasticity in the residuals



Appendix V: Test of normality in the error term (autocorrelation test)



Appendix VI: Collinearity tests

Model	Unstandardized Coefficients		Std Coeft	t	Sig.	Collinearity Statistics	
	B	Std. Error	Beta			Tolerance	VIF
(Constant)	14.858	1.931		7.696	0.000		
Staff numbers employed in SW collection	1.637	0.139	0.790	11.804	0.000	0.566	1.767
Experience of staffs in SW collection (years)	1.109	0.547	0.123	2.028	0.047	0.687	1.455
Ratio of staff/people served	0.003	0.001	0.225	3.441	0.001	0.595	1.682
Households' accessibility in the locality (%)	0.063	0.045	0.077	1.408	0.164	0.844	1.185
Solid waste fee collected from households (Tsh)	4.763E-008	0.000	0.124	2.037	0.046	0.682	1.466
Solid waste collection centres vs no waste collection centres	2.990	0.986	0.167	3.032	0.003	0.833	1.200
After crisis follow up vs occasional follow up monitoring	-2.627	0.653	-0.215	-4.023	0.000	0.887	1.128

a. Dependent Variable: Proportion of SW collected in your sub-ward

Environmental Research & Technology, Vol. 2 (3), pp. 158-170, 2019

Turkish JournalPark ACADEMIC

Environmental Research & Technology

http://dergipark.gov.tr/ert

REVIEW

The impact of nitrogen starvation on the dynamics of lipid and biomass production in *Scenedesmus sp.*

Gamze Dogdu Okcu[1,*]

[1]Bolu Abant Izzet Baysal University, Environ. Eng. Dept., Golkoy Campus, 14030 Bolu, TURKEY

ABSTRACT

Microalgal lipid is a major natural feedstock for biodiesel production. However, microalgae-based biofuel technology comes with obstacles to production, such as high investment and operating costs. To overcome these problems, nowadays some strategies have been used during cultivation stage of the microalgae for enhancing biomass and accumulate lipids and carbohydrates which could be used for biofuel production. The most common methods applied to microalgae are classified as nutrient stress and changes in growth conditions that lead to increase the lipid content in the species without decreasing the growth rate of their potential strains or by simultaneously increasing both of these. *Scenedesmus sp.* are considered to be the most appropriate microalgae to culture commercially due to their high biomass, lipid and carbohydrate yield. The purpose of this review was to describe nutrient stress strategy to develop biofuels as a sustainable alternative to fossil fuels and, in particular, with respect to nitrogen nutrient limitations, the lipid yield and biomass development in *Scenedesmus sp.* microalgae. The nitrogen starvation/limitation strategy that will increase the general economic feasibility of microalgal lipid production and affect the fatty acid composition was presented.

Keywords: Biofuel, lipid productivity, microalgae, nitrogen starvation, *Scenedesmus sp.*, triacylglycerol (TAG)

1. INTRODUCTION

Biofuels have been considered to be a clean alternative to fossil fuels in recent years because of their sustainability, nontoxicity, biodegradability, and low greenhouse gas emissions [1-3]. Microalgae have a 30% lipid content, which is higher than that in either palm oil or soybean oil, which are currently used in biodiesel production (<5% of dry biomass) [4, 5]. The lipid content in microalgae varies from 20 to 40% on a dry-weight basis; whereas, some microalgae have lipid contents as high as 85% [6, 7]. Microalgae offer many advantages over traditional oil crop biofuels and chemicals of high value because of their properties of high lipid productivity and photosynthetic efficiency, robust environmental adaptation, failure to compete with nutrients or arable lands, rapid fixation of environmental carbon, and ease of cultivation in media similar to wastewater and other media [8]; however, the biggest obstacle to obtaining biofuels from algae is the high cost of biodiesel production from oleaginous microalgae and the need for and cost of pilot-scale studies [9, 10]. Optimizing the conditions under which microalgae strains can be cultivated is crucial to creating enough lipid production to enable biofuel production on an economically significant scale [11]. Stimulating stress responses by limiting nutrients and controlling cultivation is one of the methods by which the lipid content in microalgae can be improved [12-14].

Microalgae are rich in tri- and diglycerides, phospho- and glycolipids, hydrocarbons, and other lipids [6], [15]. Under suitable environmental conditions, microalgae synthesize fatty acids to produce membrane glycerolipids, mainly glycolipids and phospholipids; however, several microalgae alter their lipid biosynthetic pathways to produce a large amount of neutral lipids in the form of triglycerides (TAGs), stored mostly in cytosolic lipid bodies under stress conditions [16]. Under these conditions, microalgae cell division will stop, and TAGs will be stored in their cells as a survival approach to withstand these adverse conditions [17]. These TAGs, which are generally found in a cell as storage lipids,

Corresponding Author: gamzedogdu@ibu.edu.tr (Gamze Dogdu Okcu)
Received 14 April 2019; Received in revised form 18 July 2019; Accepted 29 July 2019
Available Online September 2019
Doi: https://doi.org/10.35208/ert.553536

can be converted into biodiesel [18]. Lipids are stored in microalgae cells when accessible nutrients are consumed and depleted from a culture medium and become growth-limiting factors [19]. In addition, the amount and type of lipids are different in different species; therefore, the growth and cultivation conditions of the microalgae species are altered to affect their fatty acids [20]. *Scenedesmus sp.* is considered to be one of the most important microalgae for producing biofuel raw material because of their high biomass, high lipid and carbohydrate content, and ability to grow under various wastewater conditions [21].

Fatty acid ratios and lipid contents in microalgae differ according to environmental and cultural parameters, such as nitrogen and phosphorus concentrations, light intensity, growth phase, light-receiving period, temperature, salinity, and carbon dioxide (CO_2) concentration [22, 23]. Among these, nitrogen starvation is the most important technique reported in the literature that increases microalgae biomass and biochemical components, such as lipids and carbohydrates [24]. The purpose of this review was to investigate biomass productivity in the *Scenedesmus sp.*, a species with a high lipid content, to enable improvement of the economic feasibility of microalgae-based biofuels and to examine the methods by which nitrogen starvation or limitation increase the lipid yield and carbohydrate production; and also to guide researchers in understanding the reaction of *Scenedesmus sp.* against its cultivation in nitrogen-limited nutrient media.

2. MICROALGAE CULTURE CONDITIONS

The growth characteristics and composition of microalgae depend largely on four fundamental cultivation conditions—photoautotrophic, heterotrophic, mixotrophic, and photoheterotrophic [25]-[26]. Table 1 provides the characteristics of these different conditions.

Table 1. Characteristics of the different microalgae culture conditions [27]

Culture conditions	Energy source	Carbon source
Photoautotrophy	Light	Inorganic
Heterotrophy	Organic carbon	Organic
Photoheterotrophy	Light	Organic
Mixotrophy	Light and organic carbon	Inorganic and organic

Microalgae are divided into two groups—autotrophic and heterotrophic. Autotrophic microalgae use sunlight to convert CO_2 into lipids without the need for carbon; however, cultivation requires a large area, and lipid accumulation is slow [28]. On the contrary, heterotrophic microalgae have a high lipid content and rapid growth rate and lipid accumulation; therefore, they have a high capacity for lipid production. Photoautotrophic cultivation, in which microalgae utilize inorganic carbon (such as CO_2) and solar energy to generate chemical energy, is the most widespread technique [29]. In heterotrophic cultivation, microalgae can grow in the absence of light by utilizing glucose and other similar organic carbon sources [30]. Although the heterotrophic system provides higher lipid output than the autotrophic system, the need for organic substrates and their cost prevent its industrial-scale production and commercialization [31].

Mixotrophic cultivation combines both autotrophic and heterotrophic systems because both CO_2 and organic carbon are simultaneously absorbed [32]. In photoheterotrophic cultivation, microalgae need both organic carbon and light. The difference between the two is that photoheterotrophs use light and mixotrophs use organic carbon as an energy source.

When comparing different microalgae species with different carbon sources, autotrophs generally have satisfactory lipid content, but because their growth rate is low, subsequent lipid production efficiency is also low. The opposite is true for heterotrophs, in which lipid content is low but the growth rate is very high, resulting in higher biomass and lipid production. Mixotrophs utilize both inorganic and organic carbon sources; these conditions result in the highest biomass and lipid yield among all cultivation methods [14].

3. MICROALGAL LIPID CLASSIFICATION AND ACCUMULATION STRATEGIES

Microalgae-based biodiesel technologies contain the conditions that determine optimum microalgae growth, define economically feasible and efficient culturing media, harvest and separate microalgae biomass, and produce biodiesel (Fig 1). Biodiesel production from microalgae comprise the following four basic steps: isolating and characterizing the microalgae, producing microalgae biomass, harvesting, and processing [33].

Lipids are not only the energy sources in microalgae cells but also a promising raw material for biodiesel production [37]. When energy input (photosynthesis rate) exceeds energy output (cell growth and division), microalgae synthesize lipids [38]. These microalgae contain refined lipids that can be extracted to create fuel oils [39]. There are more than 300,000 known microalgae species, of which 70% have a high lipid content and a fuel yield of 9500–35000 liters per 1000 m^2 [40]. Microalgae have advantages over other microorganisms in biofuel production because of their greater biomass productivity and ability to accumulate high amounts of lipids [42].

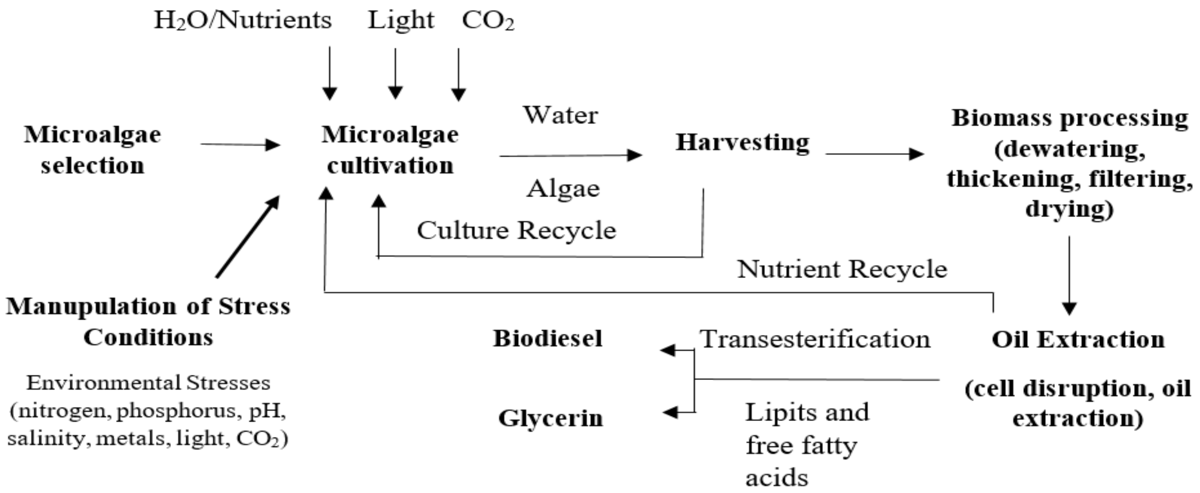


Fig 1. Overall process of biodiesel production from microalgae [34-36]

The biochemical composition of microalgae comprises four main components—proteins, carbohydrates, nucleic acids in varying ratios among species, and lipids. Lipids are the highest energy source at 37.6 kJ g-1, which can be either polar or nonpolar, followed by proteins at 16.7 kJ g-1 and carbohydrates at 15.7 kJ g-1. Depending on the metabolic rate, the ratio of these lipids changes during different microalgae growth periods [43]. Neutral lipids are composed of glycerol and free fatty acids (FFAs) and because of their low degree of unsaturation, they are more suited for producing biodiesel [44]. Polar lipids, such as phospholipids (PL) and glycolipids (GL), are structural [45] and are important components of the outer membranes of chloroplasts. Nonpolar (neutral) lipids, such as TAGs, diglycerides (DAGs), monoglycerides (MAGs), FFAs, pigments (e.g., chlorophylls), and hydrocarbons, are stored. Algae store lipids differently depending on the species, their growth periods, and environmental conditions. FFA components also vary with different microalgae strains. In most cases, polyunsaturated fatty acids (PUFAs) are located in the structural lipids, while monounsaturated fatty acids (MUFAs) and saturated fatty acids (SFAs) are located in the stored lipids [46]-[48]. Table 2 presents the lipid classifications in microalgae.

Table 2. Lipid classifications in microalgae [49]

Neutral Lipids	Polar Lipids	
	Glycolipids	Phospholipids
Triglycerides	Phosphatidylcholine	Polymerized triglyceride
Wax esters	Phosphatidylethanolamine	Monogalactosyl diglyceride
Hydrocarbons	Phosphatidylserine	Digalactosyl diglyceride
Free fatty acids	Phosphatidylglycerol	
Sterols	Phosphatidylinositol	

Algae growth has five different phases [50] as follows: 1) lag or acclimation, 2) logarithmic, 3) decreasing, 4) stationary, and 5) death. To obtain the highest biomass yield, the growth rate in the media should always be within the logarithmic growth phase. The highest lipid synthesis takes place during the transition between the lag and the stationary growth phases (i.e., stages 2 and 3) [51].

Microalgae harvested during the stationary phase have less polar lipids and more neutral lipids (e.g., TAGs) than those harvested during the logarithmic growth phase, so harvesting at the stationary phase is more suitable for biodiesel production [47].

The most well-known lipids are TAGs formed by one glycerol and three fatty acids, and PLs (and GLs), formed by two fatty acids and one phosphate (and carbohydrate). The natural lipids produced by microalgae are TAGs, which makes them the main focal point because of having the necessary molecular structure for biodiesel production [52]. TAG molecules function as electron pools when the electron supply of energy and carbon storage compounds and photosynthesis cannot meet the demand of growing cells [47]. The common methyl esters used in biodiesels are methyl palmitate (C16:0), methyl stearate (C18:0), methyl oleate (C18:1), methyl linoleate (C18:2), and methyl linolenate (C18:3). In other words, microalgae lipids are generally composed of neutral lipids with a lower amount of unsaturation [43], which is the natural fatty acid profile of microalgae [53]. The optimum fatty acid ratio from microalgae for producing biodiesel is 5:4:1 for C16:1, C18:1, and C18:2, respectively, which gives biodiesel its distinguishing properties, such as high cetane number (CN), low iodine value (IV), and low cold filter plugging point (CFPP) [11].

The reaction of fatty acids in 1 mole of triglycerides and 3 moles of alcohol during biodiesel production yields fatty acid methyl esters (FAME) and glycerol (side product) (Fig 2). The glycerol can be separated from the biodiesel using phase separation techniques or "transesterification", in which glycerol is displaced by methanol in the presence of a catalyst [6].

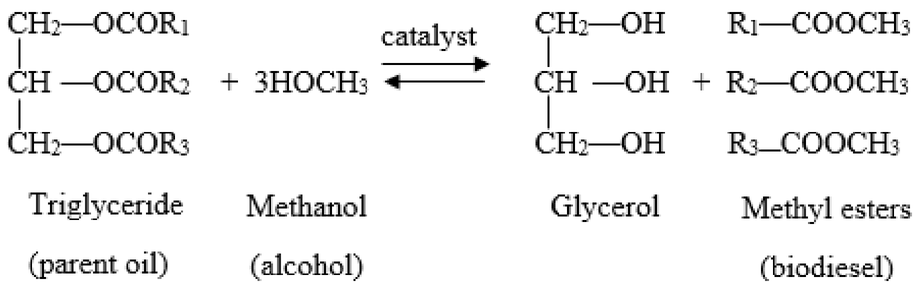


Fig 2. Algae biodiesel production using transesterification [54]

The efficiency of lipid production is related to overall lipid composition (i.e. percentage of dry cell weight [DCW] and biomass yield [daily dry mass growth L^{-1}]), which are the two crucial parameters to be considered for optimizing overall microalgae lipid yield [37]. Without these, reporting lipid content, the basic indicator both in terms of yield in unit volume and time, would be misleading. For example, a rapidly growing species might yield more lipids over a given period of time compared to a more lipid-containing species [55].

Because they contain a high fraction of PUFAs, microbial lipids have a large potential as a transportation fuel [56]; therefore, to realize higher economic performance, the lipid content in the microalgae must be higher [57]. Under stressful conditions, microalgae tend to accumulate more neutral lipids to protect themselves from photooxidation [58, 59]. These neutral lipids, especially TAGs, are used the most for biodiesel production [47].

There are two main stress types—nutritional and physical—exerted on microalgae. Nutritional stresses include restrictions on nitrogen and phosphorus or an altered source of carbon. Physical stresses are related to the processing conditions, such as high light intensity, salinity, electromagnetic fields, metals, CO_2 levels, and oxidative stresses [32, 60, 61]. The key factors in lipid metabolism in microalgae that increase biodiesel yield are as follows: (1) stress can increase lipid content; (2) manipulation of the growth media can increase biomass yield; (3) some microalgae can survive marginal environmental conditions in which managing production and preventing contamination are easier; (4) lipid metabolism is completely known; and (5) some microalgae can also produce valuable chemicals, such as astaxanthin, lutein, and β-carotene [62].

Under specific conditions after inducing stresses and depending on the species, the lipid content in the microalgae can change to between 1 and 90% of their dry weight [6]. Table 3 lists the parameters to which changes can induce lipid accumulation.

Table 3. Parameters that affect lipid production in microalgae [37]

Physicochemical Properties	Species-Dependent Factors	Culture System Improvement
***Light**	***Lipid productivity**	***Photosynthetic efficiency**
–Intensity	–Biomass productivity	–Light penetration
–Spectral quality	–Lipid contents	–Light distribution
***Temperature**	***Fatty acid profiles**	*Mass transfer rate
–Reactive oxygen species level	–Optimal fatty acid ratio	–Aeration rate
–Fatty acid composition	*Harvesting method	***Nutrient control**
***Carbon dioxide (CO2) and pH**	–Cell size	–Semipermeable membrane
–CO2 concentration	–Cell density	
– Bicarbonate ion (HCO3-) concentration	–Surface property	
***Nutrient starvation**	–Medium condition	
–Nitrogen starvation (two-stage or continuous nitrogen limitation)		

The cost of the microalgae-based biodiesel is comparable to that of petroleum diesel, and this has driven many researchers to study how to increase lipid production in microalgae to further decrease the cost of producing biodiesel [63-66]. Put simply, by following new methods by which high biomass yields, the desired lipid content, and the desired lipid composition can be generated, the overall efficiency of lipid production and other valuable chemicals produced by microalgae can increase [16, 43].

Because most microalgae accumulate a considerable amount of lipids under stress, lipid production can be highly efficient under specific conditions leading stresses. On the other hand, under these stress conditions in which lipids and TAGs are biosynthesized, cell growth and biomass yield are jeopardized, which also leads to protein decomposition and can affect the overall lipid yield differently depending on the species [36].

General properties of Scenedesmus sp.

The success of mass cultivation of microalgae, especially considering a low-value product, such as biodiesel, depends on selecting the correct species [55]. Even though there are many ways suggested in the literature by which to improve lipid production in microalgae, if the appropriate species is not used, several limitations can arise [37]. Nannochloropsis sp., Chlorella sp., Chlamydomonas sp., Scenedesmus sp., Dunaliella sp., Isochrysis sp., and Botryococcus braunii are multifunctional microalgae that accumulate lipids between 10 and 75% of their dry weights [21]. Among these, *Scenedesmus sp.* are considered to be the most appropriate microalgae for producing biodiesel because of their high biomass, lipid and carbohydrate yield and ability to grow in various wastewater environments, and short doubling time [21, 67, 68].

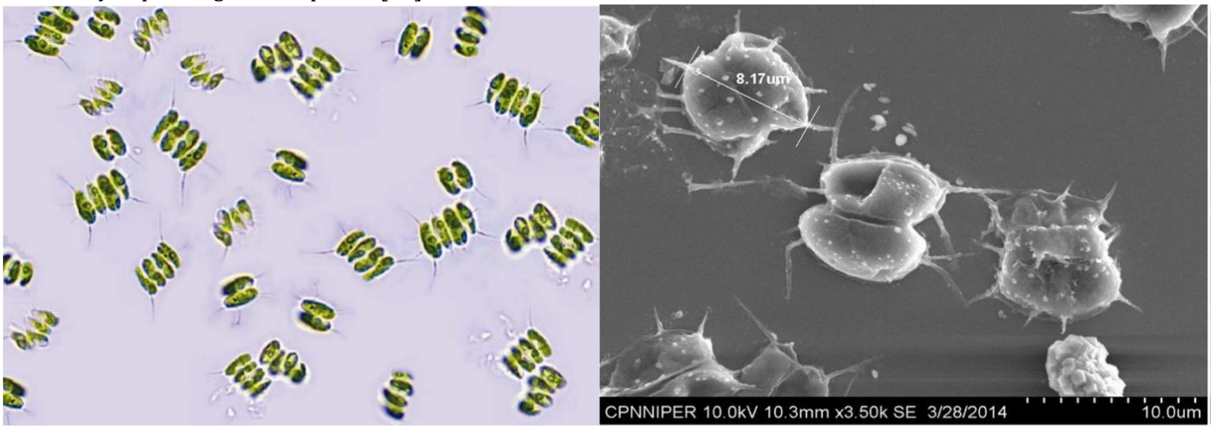


Fig 3. *Scenedesmus sp.* (a) Freshwater green microalgae *Scenedesmus sp.*[1], (b) Scanning electron micrographs of *S. quadricauda*[2]
[1][69]; [2][70]

Different *Scenedesmus* species show differences in the number of cell spikes and the texture of their cell walls. Morphologic changes in *Scenedesmus* species result from changes in nutrient concentrations, pH, and/or allelochemicals [71, 72].

Nutrient stress

Nitrogen, iron, phosphorus, magnesium, sulfur, and silicon are important for photosynthesis, cell division, respiration, intercellular transport, and protein synthesis in microalgae [73]. In particular, nitrogen and phosphorus are the two basic macronutrients for microalgae growth. Nitrogen is required for the synthesis of growth metabolites and protein, which are limiting factors on the overall growth rate, and is part of the chemical structure of nucleic acids, proteins, and other biomolecules [74]. Theoretically, these elements in the microalgae growth media should be within a stoichiometric ratio of $C_{106}H_{181}O_{45}N_{16}P$ for optimum growth (C for carbon, H for hydrogen, O for oxygen, N for nitrogen, P for phosphorus). When the nitrogen: phosphorous ratio is 5:1, the environment is classified as nitrogen limiting, and when the ratio is 30:1, the environment is phosphorus limiting [43].

Rapid growth rate increases the biomass yield of microalgae, and stress conditions increase their lipid contents [75, 76]. Microalgae have a tendency to accumulate polysaccharides and/or neutral lipids under stress. This defense mechanism is exploited in the production of various metabolites; such as neutral lipids, carotenoids, and polysaccharides [77]. Fig 4 illustrates the increase in the lipid content in microalgae under different stress conditions.

While a nutrient efficiency ceases cell growth, it helps in channeling metabolic fluxes towards fatty acid biosynthesis. It is resulted in accumulation of storage lipid in the form of triacylglycerols (TAGs). Under the nutrient starvation-driven lipid accumulation concept, the activation of diacylglycerol acyltransferase enzyme is thought to convert acyl-CoA to triglyceride (TAG) that results in lipid accumulation [78].

A large amount of lipids can be accumulated in microalgae under nitrogen-limiting conditions [79]; however, the challenge is to find the balance between increased lipid production and biomass yield. Nitrogen has a huge impact on both processes and is directly proportional to biomass yield and negatively proportional to lipid content [80]. As a result, both high biomass yield and high lipid content cannot be attained at concurrently [81]. Stresses adversely affect microalgae growth and, in the end, reduce output of the desired product; however, doubling the biomass yield can reduce biodiesel prices by 41–42% [82]. Under nutrient-limiting conditions, microalgae relocate their carbon resources into energy-rich lipid and starch compounds [79]. The proportion of polar and nonpolar lipids can be controlled by changing the ratio of nitrogen, phosphorus, and inorganic carbon in the growth media [83].

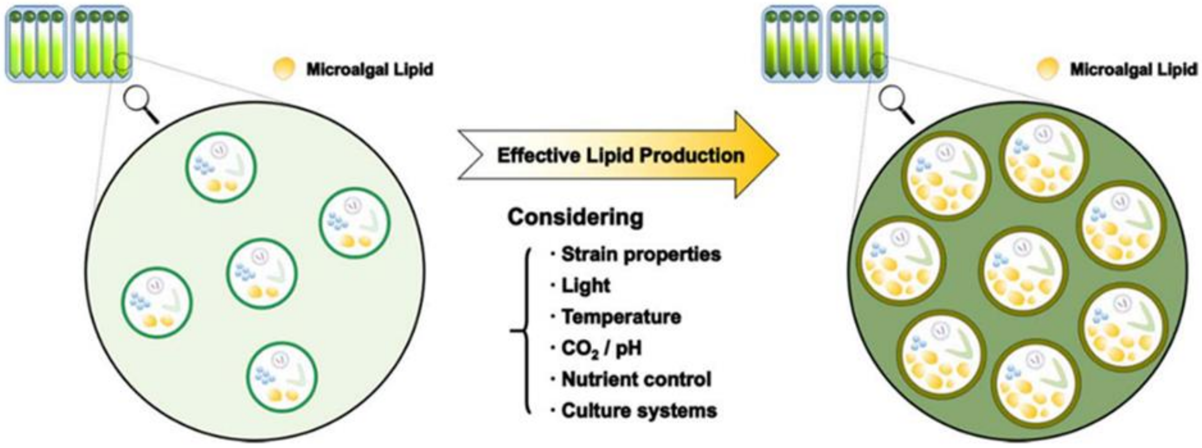


Fig 4. Effective lipid production in microalgae under various stress conditions [37]

There are three degrees of microalgae sensitivity to the manipulation of nutrient concentration—starvation, limitation, and depletion. Khozin-Goldberg and Cohen [84] presented three possible reasons for lipid accumulation under nitrogen starved conditions: (1) decreased in cellular content of thylakoid membrane, (2) activation of acyl hydrolase and (3) stimulation of phospholipids hydrolysis [78, 85, 86]. Conventional process biochemistry approaches involving nutrient limitation/deprivation or physiological stress conditions might be useful for enhancing lipid content on dry weight basis. However, the increment in lipid content happens at the cost of biomass. So, it fails to enhance lipid productivity significantly. Therefore, the proportion of lipid productivity versus biomass formation remains same [78]. In Fig 5, the effects of physico-chemical parameters on lipid accumulations was given in a microalgal cell factory. As a nitrogen stress condition, nitrate starvation was defined in the algal cell. Other physico-chemical stress conditions also affect lipid accumulation in the algal cell but the probable mechanism for lipid accumulation is not known. Therefore, the knowledge of the biochemical mechanisms and molecular insights for lipid accumulation influenced by the environmental conditions might be improved by metabolic and molecular engineering.

During starvation, the microalgae are first grown in a nutrient-rich environment and then transferred into a nutrient-depleted environment. This nutrient deficiency results in the generation of high-energy compounds and their accumulation. In nutrient-limited media, one nutrient that limits maximum biomass production and induces a physiological reaction is limited while the others are abundant. The fundamental idea behind this condition is called "the law of the minimum", which assumes that there is usually one nutrient lacking in a media and that limits biomass growth while all other nutrients are in excess. This method is sequentially conducted in a culture medium. First, the cells are cultivated in a nutrient-rich environment and cell density and growth rate increase until the nutrients are depleted. Then, with changes in some metabolic processes, energy-rich compounds increase and growth rate and photosynthesis decrease [43].

Nitrogen starvation

Nitrogen is not only a significant element found in the structure of proteins and genetic material, but also one of the most prevalent elements in the entire structures, after carbon, hydrogen and oxygen; therefore, cells require nitrogen to grow and multiply [87]. Nitrogen deficiency in the microalgae growth media is applied as either nitrogen depletion or limitation (Fig 6). In nitrogen depletion, microalgae grow in a media without a nitrogen source; in nitrogen limitation, there is a specific nitrogen source but it is limited compared to that of other nutrients [88]. When nitrogen is limited more than other nutrients, photosynthesis will continue, but the chemicals produced in microalgae will have less nitrogen and be more energy rich (e.g., will contain more lipids and carbohydrates). Moreover, when the nitrogen in the cell is depleted, microalgae begin to decompose nitrogen-containing nonlipid cellular chemicals and free the nitrogen [89]. Nitrogen deficiency is the cheapest and easiest method by which to enhance lipid production; therefore, utilization of this method is widespread and is trustworthy and effective for many species [83].

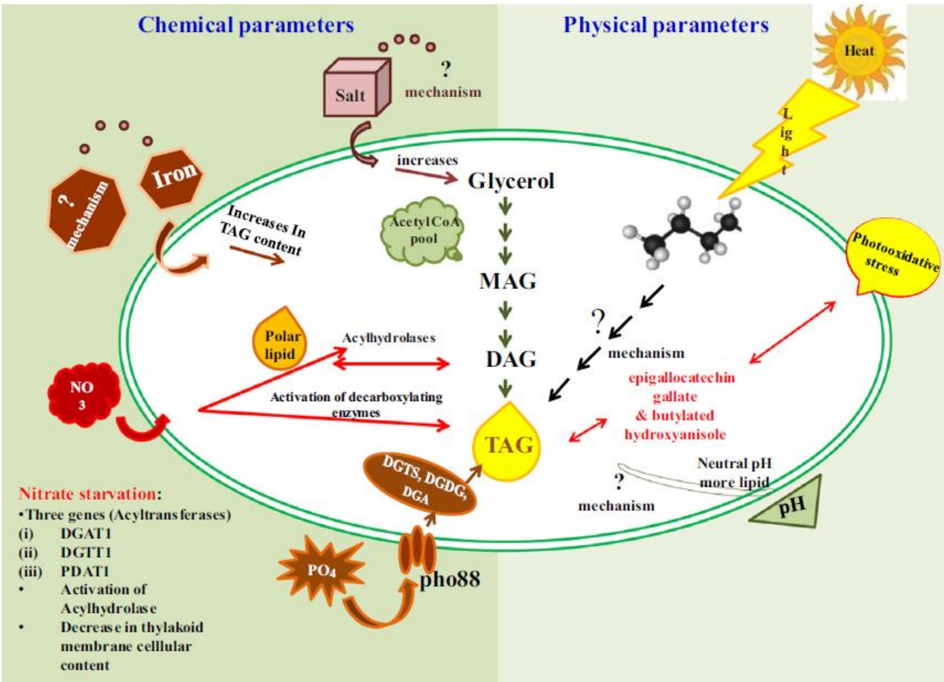


Fig 5. Description of physico-chemical parameters leading towards lipid accumulations in a microalgal cell factory. (Probable reasons for lipid accumulation: i) Nitrate starvation results in activation of acyltransferases, acylhydrolases and decrease in thylakoid membrane cellular content; (ii) Phosphate starvation results in storage lipid accumulation by activation of enzymes namely DGTS and DGDG and alteration in phosphate transporter may also lead to TAG synthesis; (iii) Increase in salt and iron content results in TAG formation but the exact mechanism is unknown) [78]

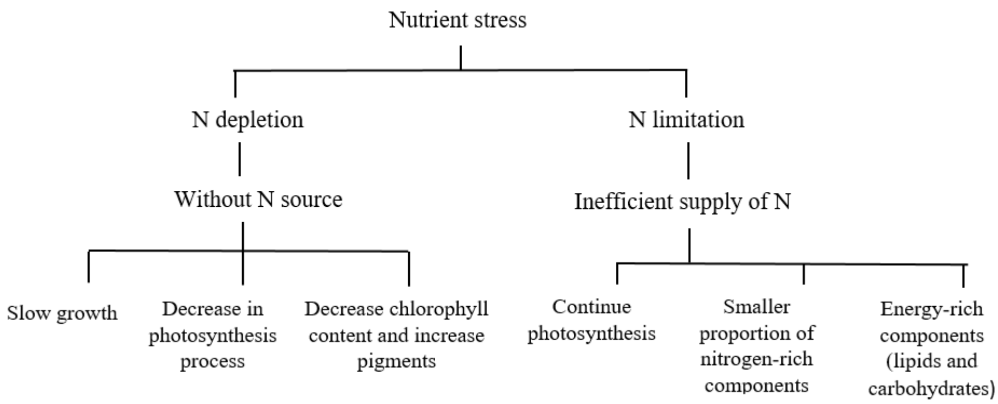


Fig 6. General overview of nitrogen stress in microalgae culture (Notes: N, nitrogen) [32]

Nitrogen is quantitatively important in growth media and its limitation, depending on the species, inhibits microalgae growth [90]. Declining cell multiplication changes the route through which lipids are synthesized from membrane lipids to neutral lipids [91].

Nitrogen limitation or starvation causes an increase in lipid and carbohydrate content while decreasing growth rate, protein synthesis, photosynthesis, and cell size [92]. Some examples for nitrogen starvation effect on lipid production of *Scenedesmus sp.* were shown in Table 4. Schnurr et al. [93] have researched the possibility of increasing the neutral lipid content in a nutrient-deficient algae biofilm using *S. obliquus* and *Nitzschia palea*. Although the neutral lipid content in suspensions of the same species was doubled, there was no concentration increase observed in their biofilms.

Many researchers have reported that nitrogen starvation decreases photosynthesis and protein synthesis but increases lipid and carbohydrate synthesis [92]. In addition, environmental conditions, especially nitrogen-rich nutrients, play a significant role in the amount and quality of the lipids produced in the microalgae [47, 93].

Lipid production in microalgae increases with nitrogen deficiency [95]-[96], and changes in the fatty acid chain length and unsaturation results in more suitable TAG production for biodiesel. Many microalgae species can similarly adapt their metabolism under nitrogen deficiency [47, 97]. During the stationary growth phase, nutrient starvation is the most well-known method by which to improve lipid content. In addition, temperature, salinity, light, and changes during the growth phase also impact microalgae metabolism [98]. Breuer et al. [99] have found that the highest lipid content, independent of light intensity, was observed in S. obliquus and changed from 18 to 40% of dry weight with changes in pH and temperature. This lipid accumulation stores the energy to be allocated for growth to prevent a decline in growth rate and, subsequently, in biomass and lipid production [100]. Toledo-Cervantes et al. [101] have evaluated CO_2, aeration, and light intensity impacts on the growth of and lipid production in S. obstusiusculus under nitrogen-limiting conditions. Without any nutrient limitations, in 20% nonpolar algae–containing culture with 5% CO_2 and 134 µmole m^{-2} s^{-1} light intensity, biomass productivity was 500 g m^{-3} d^{-1} and maximum biomass concentration was 6000 g m^{-3}. Under nitrogen-limiting conditions with 5% CO_2, lipid accumulation was 55.7% of the dry weight.

Table 4. Effect of nitrogen limitation/deprivation on lipid production of *Scenedesmus sp.*

Strain of *Scenedesmus sp.*	Lipid productivity	References
S. obliquus	0.18 g m^{-2} d^{-1} lipid productivity	[93]
S. obliquus	322 mg L^{-1} d^{-1} lipid productivity	[99]
S. obstusiusculus	For the inlet CO2 concentrations of 0.04% and 5% CO2, the maximum lipid productivities were 51 and 200 g m^{-3} d^{-1} respectively.	[101]
S.obliquus CNW-N	45.48 mg L^{-1} d^{-1} lipid productivity	[103]
S. acutus	The amount of lipid in the 50% nitrogen-limited media was 19.48% higher than that in the control group	[104]
S. dimorphus	0.17 g L^{-1} d^{-1} lipid productivity	[106]
S. abundans	5.999 g L^{-1} d^{-1} lipid productivity	[107]
S. quadricauda	25.13 mg L^{-1} d^{-1} lipid productivity	[108]
S. obtusiusculus	0.34 g L^{-1} d^{-1} lipid productivity	[109]
Scenedesmus sp. LX1	204 mg L^{-1} d^{-1} lipid productivity	[85]

Although these nutrient-starvation conditions are generally considered for systems with long turnover periods, in recent studies, there have also been satisfactory results for systems with short-turnover periods [102]. The lipid content of *Scenedesmus sp.* changes with three different phases. The biomass on day 2 during the nitrogen-consuming logarithmic phase is dark green with 20% lipid content. During the early stress phase (5–7 d), the biomass is greenish yellow with ~35% lipid content. During the late stress period (10–14 d), the biomass is brownish with ~45% lipid content. Ho et al. [103] have applied nitrogen starvation to Scenedesmus obliquus and observed that the highest lipid content was 22.4% on day 5. Agirman and Cetin [104] have investigated the development of Scenedesmus acutus and changes in its protein and lipid contents under nitrogen stress. According to their results, at <50% nitrogen limitation, the lipid content was 19.48% higher than that of the control group. In addition, an inverse correlation was observed among cell development, lipid content, and nitrogen concentration.

Nitrogen starvation triggers several reactions in microalgae from the decomposition of nitrogen-containing compounds, such as proteins, chlorophyll, and DNA, to the accumulation of energy-rich compounds, such as carbohydrates [72]. The critical point here is that nitrogen-rich chlorophyll supports biomass growth and cellular development. Microalgae synthesize chlorophyll in huge amounts when nitrogen is plentiful and within their reach; however, when the opposite is true, they begin to use chlorophyll to obtain free nitrogen [101]. Because chlorophyll is green in microalgae, its decomposition results in microalgae becoming first greenish yellow and then brown when nearly all chlorophyll has been decomposed [32]. Wu et al. [105] have reported that in Scenedesmus sp., the concentration of nitrogen and phosphorus is highest during the exponential growth phase and lower during the stationary phase. Similarly, Wang et al. [106] have set up a photobioreactor that is open to the atmosphere, and under nitrogen starvation, observed that over a 10-d period, the protein content in *Scenedesmus sp.* decreased from 33 to 10% and the total lipid content increased from 8 to 37%.

4. CONCLUSIONS

Microalgae are promising candidates for replacing fossil fuels because of their rapid growth, uniquely highly efficient solar energy conversion, sustainability and renewability, high lipid content, and high potential for biofuel production. Microalgae use has been increasing as feedstock for biofuel in response to the energy crisis. In particular, the energy stores in microalgae are the raw materials for the biodiesel used in the transportation sector, and enhancement of microalgae's lipid content and its subsequent production have gained considerable attention among researchers. This review has illustrated that limiting nitrogen in the culture of high lipid-accumulating *Scenedesmus sp.* is a feasible strategy by which to increase lipid production.

ACKNOWLEDGEMENT

The author would like to thank The Scientific and Technological Research Council of Turkey (TUBITAK) Science Fellowships and Grant Programmes Department for the Post-Doctoral Research given to the author within "2219-Post-Doctoral Post-Fellowship Scholarship Program". Also, the author would like to thank Prof Bruce E. Rittmann and the laboratory group from the Arizona State University-The Biodesign Institute Swette Center for Environmental Biotechnology, who granted the author with training in "Increasing Microalgae Productivity" in their research centers.

REFERENCES

[1]. R.A. Voloshin, M.V. Rodionova, S.K. Zharmukhamedov, T. Nejat Veziroglu, and S.I. Allakhverdiev, "Review: biofuel production from plant and algal biomass," *International Journal of Hydrogen Energy*, Vol. 41(39), pp. 17257-17273, 2016.

[2]. K.L. Man, and K.T. Lee, "Microalgae biofuels: a critical review of issues, problems and the way forward," *Biotechnology Advances*, Vol. 30(3), pp. 673-690, 2012.

[3]. D. Song, J. Fu, and D. Shi, "Exploitation of oil-bearing microalgae for biodiesel," *Chinese Journal of Biotechnology*, Vol. 24(3), pp. 341-348, 2008.

[4]. M.K. Lam, and K.T. Lee, "Microalgae biofuels: a critical review of issues, problems and the way forward," *Biotechnology Advances*, Vol. 30(3), pp. 673-690, 2012.

[5]. Y. Chisti, "Biodiesel from microalgae beats bioethanol*," Trends in Biotechnology*, Vol. 26(3), pp. 126-131, 2008.

[6]. Y. Chisti, "Biodiesel from microalgae," *Biotechnology Advances*, Vol. 25(3), pp. 294-306, 2007.

[7]. A. Banerjee, R. Sharma, and Y. Chisti, "Botryococcus braunii: a renewable source of hydrocarbons and other chemicals," *Critical Reviews in Biotechnology*, Vol. 22(3), pp. 245-279, 2002.

[8]. S.H. Ho, X. Ye, T. Hasunuma, J.S. Chang, and A. Kondo, "Perspectives on engineering strategies for improving biofuel production from microalgae – a critical review," *Biotechnology Advances*, Vol. 32(8), pp. 1448-1459, 2014.

[9]. V. Amanor-Boadu, P.H. Pfromm, and R. Nelson, "Economic feasibility of algal biodiesel under alternative public policies," *Renewable Energy*, Vol. 67, pp. 136-142, 2014.

[10]. C. Santander, P.A. Robles, L.A. Cisternas, and M. Rivas, "Technical–economic feasibility study of the installation of biodiesel from microalgae crops in the Atacama Desert of Chile," *Fuel Processing Technology*, Vol. 125, pp. 267-276, 2002.

[11]. H.S. Kwak, J.Y.H. Kim, H.M. Woo, E. Jin, B.K. Min, and S.J. Sim, "Synergistic effect of multiple stress conditions for improving microalgal lipid production," *Algal Research*, Vol. 19, pp. 215-224, 2016.

[12]. B. Singh, A. Guldhe, I. Rawat, and F. Bux, "Towards a sustainable approach for development of biodiesel from plant and microalgae," *Reneweble and Sustainable Energy Reviews*, Vol. 29, pp. 216–245, 2014.

[13]. A.J. Klok, D.E. Martens, R.H. Wijffels, and P.P. Lamers, "Simultaneous growth and neutral lipid accumulation in microalgae," *Bioresource Technology*, Vol. 134, pp. 233–243, 2013.

[14]. W.H. Leong, J.W. Lim, M.K. Lam, Y. Uemura, Y.C. Ho, "Third generation biofuels: A nutritional perspective in enhancing microbial lipid production," *Renewable and Sustainable Energy Reviews*, Vol. 91, pp. 950-961, 2018.

[15]. P. Spolaore, C. Joannis-Cassan, E. Duran, and A. Isambert, "Commercial applications of microalgae," *Journal of Bioscience and Bioengineering*, Vol. 101(2), pp. 87–96, 2006.

[16]. G. Sibi, V. Shetty, and K. Mokashi, "Enhanced lipid productivity approaches in microalgae as an alternative for fossil fuels-A review," *Journal of Energy Institute*, Vol. 89(3), pp. 330-334, 2016.

[17]. R.R. Narala, S. Garg, K.K. Sharma, S.R. Thomas-Hall, M. Deme, Y. Li, and P.M. Schenk, "Comparison of microalgae cultivation in photobioreactor, open raceway pond, and a two-stage hybrid system," *Frontiers in Energy Research*, Vol. 4(29), pp. 1-10, 2016.

[18]. L. Barsanti, P. Gualtieri, Algae: Anatomy, Biochemistry, and Biotechnology, CRC Press, United States, 2014.

[19]. C.C. Fu, T.C. Hung, J.Y. Chen, C.H. Su, and W.T. Wu, "Hydrolysis of microalgae cell walls for production of reducing sugar and lipid

extraction," *Bioresource Technology*, Vol. 101(22), pp. 8750–8754, 2010.

[20]. G. Petkov, and G. Garcia, "Which are fatty acids of the green alga Chlorella?" Biochemical Systematics and Ecology, Vol. 35(5), pp. 281–285, 2007.

[21]. T.M. Mata, A.C. Melo, M. Simões, and N.S. Caetano, "Parametric study of a brewery effluent treatment by microalgae Scenedesmus obliquus," *Bioresource Technology*, Vol. 107, pp. 151–158, 2012.

[22]. C.J. Zhu, Y.K. Lee, and T.M. Chao, "Effects of temperature and growth phase on lipid and biochemical composition of Isochrysis galbana TK1," *Journal of Applied Phycology*, Vol. 9(5), pp. 451–457, 1997.

[23]. X. Wu, E.M. Joyce, and T.J. Mason, "The effects of ultrasound on cyanobacteria," *Harmful Algae*, Vol. 10(6), pp. 738-743, 2011.

[24]. V. Ördög, W.A. Stirk, P. Bálint, J. van Staden, and C. Lovász, "Changes in lipid, protein and pigment concentrations in nitrogen-stressed Chlorella minutissima cultures," *Journal of Applied Phycology*, Vol. 24(4), pp. 907–914, 2012.

[25]. K. Chojnacka, and F.J. Marquez-Rocha, "Kinetic and stoichiometric relationships of the energy and carbon metabolism in the culture of microalgae," *Biotechnology*, Vol. 3(1), pp. 21–34, 2004.

[26]. N. Rashid, M.S. Ur Rehman, M. Sadiq, T. Mahmood, and J.I. Han, "Current status, issues and developments in microalgae derived biodiesel production," *Reneweble and Sustainable Energy Reviews*, Vol. 40, pp. 760–78, 2014.

[27]. G.Q. Chen, and F. Chen, "Growing phototrophic cells without light," *Biotechnology Letters*, Vol. 28(9), pp. 607–616, 2006.

[28]. S. Bellou, M.N. Baeshen, A.M. Elazzazy, D. Aggeli, F. Sayegh, and G. Aggelis, "Microalgal lipids biochemistry and biotechnological perspectives," *Biotechnology Advances*, Vol. 32(8), pp. 1476–1493, 2014.

[29]. G.H. Huang, F. Chen, D. Wei, X.W. Zhang, and G. Chen, "Biodiesel production by microalgal biotechnology," *Applied Energy*, Vol. 87(1), pp. 38–46, 2010.

[30]. M. Chen, H. Tang, H. Ma, T.C. Holland, K.Y.S. Ng, and S.O. Salley, "Effect of nutrients on growth and lipid accumulation in the green algae Dunaliella tertiolecta," *Bioresource Technology*, Vol. 102(2), pp. 1649–1655, 2011.

[31]. Y. Liang, N. Sarkany, and Y. Cui, "Biomass and lipid productivities of Chlorella vulgaris under autotrophic, heterotrophic and mixotrophic growth conditions," *Biotechnology Letters*, Vol. 31(7), pp. 1043–1049, 2009.

[32]. J.R. Benavente-Valdés, C. Aguilar, J.C. Contreras-Esquivel, A. Méndez-Zavala, and J. Montañez, "Strategies to enhance the production of photosynthetic pigments and lipids in chlorophycae species," *Biotechnology Reports*, Vol. 10, pp. 117-125, 2016.

[33]. L. Zhu, Z. Wang, Q. Shu, J. Takala, E. Hiltunen, P. Feng, and Z. Yuan, "Nutrient removal and biodiesel production by integration of freshwater algae cultivation with piggery wastewater treatment," *Water Research*, Vol. 47(13), pp. 4294–4302, 2013.

[34]. Y. Ma, X. Gao, Q. Wang, and Y. Liu, "Biodiesels from microbial oils: Opportunity and challenges," *Bioresource Technology*, Vol. 263, pp. 631-641, 2018.

[35]. K. Singh, D. Kaloni, S. Gaur, S. Kushwaha, and G. Mathur, "Current research and perspectives on microalgae- derived biodiesel," *Biofuels*, DOI: 10.1080/17597269.2017.1278932, 2017.

[36]. B. Chen, C. Wan, M.A. Mehmood, J.S. Chang, and F. Bai, "Manipulating environmental stresses and stress tolerance of microalgae for enhanced production of lipids and value-added products–A review," *Bioresource Technology*, Vol. 244(Pt 2), pp. 1198-1206, 2017.

[37]. Y.S. Shin, H.I. Choi, J.W. Choi, J.S. Lee, Y.J. Sung, and S.J. Sim, "Multilateral approach on enhancing economic viability of lipid production from microalgae: A review," *Bioresource Technology*, Vol. 258, pp. 335-344, 2018.

[38]. P.G. Roessler, "Purification and characterization of acetyl-CoA carboxylase from the diatom Cyclotella cryptica," *Plant Physiology*, Vol. 92, pp. 73–78, 1990.

[39]. K. Tsukahara, and S. Sawayama, "Liquid Fuel Production using Microalgae," *Journal of the Japan Petroleum Institute*, Vol. 48(5), pp. 251-259, 2005.

[40]. KEMA Inc, Algae-to-energy opportunities in Louisiana: a market potential report. (Louisiana Economic Development, 2009.

[41]. P.S. Nigam, and A. Singh, "Production of liquid biofuels from renewable resources," *Progress in Energy and Combustion Science*, Vol. 37(1), pp. 52-68, 2011.

[42]. M.K. Lam, and K.T. Lee, "Microalgae biofuels: a critical review of issues, problems and the way forward," *Biotechnology Advances*, Vol. 30(3), pp. 673–90, 2012.

[43]. B. Sajjadi, W.Y. Chen, A.A.A. Raman, and S. Ibrahim, "Microalgae lipid and biomass for biofuel production: A comprehensive review on lipid enhancement strategies and their effects on fatty acid composition," *Renewable and Sustainable Energy Reviews*, Vol. 97, pp. 200-232, 2018.

[44]. P.J.I.B. Williams, and L.M.L. Laurens, "Microalgae as biodiesel & biomass feedstocks: review and analysis of the biochemistry, energetics & economics," *Energy & Environmental Science*, Vol. 3(5), pp. 554–590, 2010.

[45]. A. Sukenik, Y. Yamaguchi, and A. Livne, "Alterations in lipid molecular species of the marine eustigma tophyte Nannochloropsis sp.," *Journal of Phycology*, Vol. 29(5), pp. 620–626, 1993.

[46]. C.M. Torres, S.D. Ríos, C. Torras, J. Salvadó, J.M. Mateo-Sanz, and L. Jiménez, "Microalgae- based

biodiesel: a multicriteria analysis of the production process using realistic scenarios," *Bioresource Technology*, Vol. 147, pp. 7–16, 2013.

[47]. Q. Hu, M. Sommerfeld, E. Jarvis, M. Ghirardi, M. Posewitz, M. Seibert, and A. Darzins, "Microalgal triacylglycerols as feedstocks for biofuel production: perspectives and advances," *The Plant Journal*, Vol. 54(4), pp. 621–639, 2008.

[48]. M. Olofsson, T. Lamela, E. Nilsson, J.P. Bergé, V. del Pino, P. Uronen, and C. Legrand, "Seasonal variation of lipids and fatty acids of the microalgae nannochloropsis oculata grown in outdoor large-scale photobioreactors," *Energies*, Vol. 5(12), pp.1577–1592, 2012.

[49]. G. Soydemir, "Characterization and evaluation of lipids of microalgae grown in wastewater," D. Eng. thesis, Gebze Technical University, Istanbul, Turkey, Ap. 2016.

[50]. N. Moazami, A. Ashori, R. Ranjbar, M. Tangestani, R. Eghtesadi, and A.S. Nejad, "Large-scale biodiesel production using microalgae biomass of Nannochloropsis," *Biomass Bioenergy*, Vol. 39, pp. 449–453, 2012.

[51]. M. Çelikkol Türkmani, "Chlorella protothecoides mikroalg türünün yetiştirilmesinde baca gazının etkisi," M. Eng. thesis, Yıldız Technical University, Istanbul, Turkey, Feb. 2016.

[52]. Z. Wen, and M.B. Johnson, "Microalgae as a feedstock for biofuel production," Communications and Marketing, College of Agriculture and Life Sciences, Virginia Polytechnic Institute and State University, Publication 442-886, Blacksburg, VA; 2009.

[53]. S. Mishra, K. Anand, and P.S. Mehta, "Predicting the cetane number of biodiesel fuels from their fatty acid methyl ester composition," *Energy Fuels*, Vol. 30(12), pp. 10425–10434, 2016.

[54]. B. Kuepker, Commission E, editor. European renewable energy policy. Brussels: European Commission, p. 1–10, 2015.

[55]. M.J. Griffiths, and S.T.L. Harrison, "Lipid productivity as a key characteristic for choosing algal species for biodiesel production," *Journal of Applied Phycology*, Vol. 21(5), pp. 493-507, 2009.

[56]. B. Liam, and P. Owende, "Biofuels from microalgae. A review of technologies for production, processing, and extractions of biofuels and co-products," *Renewable and Sustainable Energy Reviews*, Vol. 14(2), pp. 557-577, 2010.

[57]. Q. Hu, C.W. Zhang, and M. Sommerfeld, "Biodiesel from Algae: Lessons Learned Over the Past 60 Years and Future Perspectives," Juneau, Alaska: Annual Meeting of the Phycological Society of America, Journal of Phsicology, Vol. 42(1), pp. 40–41, 2006.

[58]. Y. Jiang, T. Yoshida, and A. Quigg, "Photosynthetic performance, lipid production and biomass composition in response to nitrogen limitation in marine microalgae," *Plant Physiology and Biochemistry*, Vol. 54, pp. 70–77, 2012.

[59]. C. Adams, V. Godfrey, B. Wahlen, L. Seefeldt, and B. Bugbee, "Understanding precision nitrogen stress to optimize the growth and lipid content tradeoff in oleaginous green microalgae," *Bioresource Technology*, Vol. 131, pp. 188–194, 2013.

[60]. Z. Liu, G. Wang, and B. Zhou, "Effect of iron on growth and lipid accumulation in Chlorella vulgaris," *Bioresource Technology*, Vol. 99(11), pp. 4717–4722, 2008.

[61]. L. Wang, Y. Li, M. Sommerfeld, Q. Hu, "A flexible culture process for production of the green microalga Scenedesmus dimorphus rich in protein, carbohydrate or lipid," *Bioresource Technology*, Vol. 129, pp. 289–295, 2008.

[62]. E.B. D'Alessandro, and N.R. Antoniosi Filho, "Concepts and studies on lipid and pigments of microalgae: A review," *Renewable and Sustainable Energy Reviews*, Vol. 58, pp. 832-841, 2016.

[63]. E.W. Becker, Microalgae: Biotechnology and Microbiology. Cambridge University Press, 1994.

[64]. G. Zhao, J. Yu, F. Jiang, X. Zhang, and T.W. Tan, "The effect of different trophic modes on lipid accumulation of Scenedesmus quadricauda," *Bioresource Technology*, Vol. 114, pp. 466-471,2012.

[65]. X. Li, H. Hu, K. Gan, and Y. Sun, "Effects of different nitrogen and phosphorus concentrations on the growth, nutrient uptake, and lipid accumulation of a freshwater microalga Scenedesmus sp.," *Bioresource Technology*, Vol. 101(14), pp. 5494-5500, 2010.

[66]. L.F. Rios, B.C. Klein, L.F. Luz, R.M. Filho, and M.R.W. Maciel, "Nitrogen starvation for lipid accumulation in the microalga species Desmodesmus sp.," *Applied Biochemistry and Biotechnology*, Vol. 175(1), pp. 469-476, 2014.

[67]. S.S. Ho, C.Y. Chen, and J.S. Chang, "Effect of light intensity and nitrogen starvation on CO2 fixation and lipid/carbohydrate production of an indigenous microalga Scenedesmus obliquus CNW-N," *Bioresource Technology*, Vol. 113, pp. 244–252, 2012.

[68]. Y. Li, D. Han, M. Sommerfeld, and Q. Hu, "Photosynthetic carbon partitioning and lipid production in the oleaginous microalga Pseudochlorococcum sp. (Chlorophyceae) under nitrogen-limited conditions," *Bioresource Technology*, Vol. 102(1), pp. 123–129, 2011.

[69]. T. Řezenka and M. Temina, "Natural Microbial UV Radiation Filters – Mycosporine-like Amino Acids," *Folia Microbiology*, Vol. 49(4), pp. 1-14, 2004.

[70]. R.S. Gour, A. Chawla, H. Singh, R.S. Chauhan, and A. Kant, "Characterization and Screening of Native *Scenedesmus sp.* Isolates Suitable for Biofuel Feedstock," *PLoS ONE*, 11(5): e0155321. doi:10.1371/journal.pone.0155321.

[71]. M. Lürling, "Effect of grazing-associated infochemicals on growth and morphological development in Scenedesmus acutus

(chlorophyceae)," *Journal of Phycology*, Vol. 34, pp. 578–586, 1998.

[72]. I. Pancha, K. Chokshi, B. George, T. Ghosh, C. Paliwal, R. Maurya, and S. Mishra, "Nitrogen stress triggered biochemical and morphological changes in the microalgae *Scenedesmus sp.* CCNM 1077," *Bioresource Technology*, Vol. 156, pp. 146-154, 2014.

[73]. X. Zhang, S. Yan, R.D. Tyagi, R.Y. Surampalli, and J.R. Vale´ro, "Wastewater sludge as raw material for microbial oils production," *Applied Energy*, Vol. 135, pp. 192–201, 2014.

[74]. M.T. Madigan, J.M. Martinko, P.V. Dunlap, and D.P. Clark, Brock: Biology of Microorganisms. Pearson Benjamin Cummings Inc, 2009.

[75]. R. Yadavalli, R.S. Ramogapol, and C.S. Rao, "Lipid Accumilation Studies in Chlorella pyreniodosa Using Customized Photobioreactor-Effect of Nitrogen Source, Light Intensity and Mode of Operation," *International Journal of Engineering Research and Application*, Vol. 2(3), pp. 2446-2453, 2012.

[76]. H. Wu, and X. Miau, "Biodiesel quality and biochemical changes of microalgae Chlorella pyrenoidosa and Scenedesmus obliquus in response to nitrate levels," *Bioresource Technology*, Vol. 170, pp. 421-427, 2014.

[77]. N. Yu, L.T.J. Dieu, S. Harvey, and D.-Y. Lee, "Optimization of process configuration and strain selection for microalgae-based biodiesel production," *Bioresource Technology*, Vol. 193, pp. 25–34, 2015.

[78]. G.D. Bhowmick, L. Koduru, and R. Sen, "Metabolic pathway engineering towards enhancing microalgal lipid biosynthesis for biofuel application—A review," *Renewable and Sustainable Energy Reviews*, Vol. 50, pp. 1239-1253, 2015.

[79]. R. Praveenkumar, K. Shameera, G. Mahalakshmi, M.A. Akbarsha, and N. Thajuddin, "Influence of nutrient deprivations on lipid accumulation in a dominant indigenous microalga Chlorella sp., BUM11008: evaluation for biodiesel production," *Biomass Bioenergy*, Vol. 37 (Supplement C), pp. 60–66, 2012.

[80]. C. Adams, V. Godfrey, B. Wahlen, L. Seefeldt, and B. Bugbee, "Understanding precision nitrogen stress to optimize the growth and lipid content tradeoff in oleaginous green microalgae," *Bioresource Technology*, Vol. 131, pp. 188–194, 2013.

[81]. X. Li, H.Y. Hu, K. Gan, S. Ying-xue, "Effects of different nitrogen and phosphorus concentrations on the growth, nutrient uptake, and lipid accumulation of a freshwater microalgae Scenedesmus sp.," *Bioresource Technology*, Vol. 101(14), pp. 5494–5500, 2010.

[82]. S. Nagarajan, S.K. Chou, S. Cao, C. Wu, and Z. Zhou, "An updated comprehensive techno-economic analysis of algae biodiesel," *Bioresource Technology*, Vol. 145, pp. 150–156, 2013.

[83]. L. Rodolfi, G.C. Zittelli, N. Bassi, G. Padovani, N. Biondi, G. Bonini, and M.R. Tredici, "Microalgae for Oil: Strain Selection, Induction of Lipid Synthesis and Outdoor Mass Cultivation in a Low-Cost Photobioreactor," *Biotechnology and Bioengineering*, Vol. 102(1), pp. 100-112, 2009.

[84]. I. Khozin-Goldberg and Z. Cohen, "The effect of phosphate starvationon the lipid and fatty acid composition of the fresh water eustigmatophyte Monodus subterraneus," *Phytochemistry*, Vol. 7, pp. 696–701, 2006.

[85]. L. Xin, H. Hon-ying, G. Ke, and S. Ying-xue, "Effects of different nitrogen and phosphorus concentrations on the growth, nutrient uptake, and lipid accumulation of a freshwater microalga Scenedesmus sp.," *Bioresource Technology*, Vol. 101, pp. 5494-5500, 2010.

[86]. S.K. Lenka, N. Carbonaro, R. Park, S.M. Miller, I. Thorpe, and Y. Li, "Current advances in molecular, biochemical, and computational modeling analysis of microalgal triacylglycerol biosynthesis," *Biotechnology Advances*, Vol. 34, pp. 1046-1063, 2016.

[87]. J. Vymazal, Algae and Element Cycling in Wetlands, Lewis Publishers, Boca Raton, FL, 1995 (689 pp.).

[88]. F. Bona, A. Capuzzo, M. Franchino, and M.E. Maffei, "Semicontinuous nitrogen limitation as convenient operation strategy to maximize fatty acid production in Neochloris oleoabundans," *Algal Research*, Vol. 5, pp. 1–6, 2014.

[89]. J. Sheehan, T. Dunahay, J. Benemann, and P. Roessler, A Look Back at the U.S. Department of Energy's Aquatic Species Program: Biodiesel from Algae. Close-Out report. National Renewable Energy Lab, Department of Energy, Golden, Colorado, U.S.A. Report number NREL/TP-580-24190, 1998.

[90]. M. Arumugam, A. Agarwal, C.A. Arya, and A. Ahmed, "Influence of nitrogen sources on biomass productivity of microalgae Scenedesmus bijugatus," *Bioresource Technology*, Vol. 131, pp. 246–249, 2013.

[91]. A. Converti, A.A. Casazza, E.Y. Ortiz, P. Perego, and M.D. Borghi, "Effect of temperature and nitrogen concentration on the growth and lipid content of Nannochloropsis oculata and Chlorella vulgaris for biodiesel production," *Chemical Engineering and Processing*, Vol. 48(6), pp. 1146–1151, 2009.

[92]. D. Simionata, M.A. Block, N.L. Rocca, J. Jouhet, E. Marechal, and G. Finazzi, "The Response of Nannochloropsis gaditana to Nitrogen Starvation Includes De Novo Biosynthesis of Triacylgylcerols, a Decrease of Chloroplast Galactolipids, and Reorganization of the Photosynthetic Apparatus," *E.C Journal ASMorg*, Vol. 12(5), pp. 665-676, 2013.

[93]. P.J. Schnurr, G.S. Espie, and D.G. Alleni "Algae biofilm growth and the potential to stimulate lipid accumulation through nutrient starvation" *Bioresource Technology*, Vol. 136, pp. 337-344, 2013.

[94]. P.G. Roessler, "Environmental-control of glycerolipid metabolism in microalgae-commercial implications and future-research directions," *Journal of Phycology*, Vol. 26, pp. 393–399, 1990.

[95]. Y. Li, J. Mu, D. Chen, F. Han, H. Xu, F. Kong, F. Xie, and B. Feng, "Production of biomass and lipid by the microalgae Chlorella protothecoides with heterotrophic-Cu(II) stressed (HCuS) coupling cultivation," *Bioresource Technology*, Vol. 148, pp. 283–92, 2013.

[96]. G.Q. Chen, Y. Jiang, and F. Chen, "Salt-induced alterations in lipid composition of diatom Nitzschia Laevis (Bacillariophyceae) under heterotrophic culture condition(1)," *Journal of Phycology*, Vol. 44, pp. 1309–1314, 2008.

[97]. G. Breuer, P.P. Lamers, D.E. Martens, R.B. Draaisma, and R.H. Wijffels, "The impact of nitrogen starvation on the dynamics of triacylglycerol accumulation in nine microalgae strains," *Bioresource Technology*, Vol. 124, pp. 217-226, 2012.

[98]. N.R. Boyle, and J.A. Morgan, "Flux balance analysis of pri- mary metabolism in Chlamydomonas reinhardtii," *BMC Systems Biology*, Vol. 3 (4), pp. 1-14, 2009.

[99]. G. Breuer, P.P. Lamers, D.E. Martens, R.B. Draaisma, and R.H. Wijffels, "Effect of light in-tensity, pH, and temperature on triacylglycerol (TAG) accumulation induced by nitrogen starvation in Scenedesmus obliquus," *Bioresource Technology*, Vol. 143, pp. 1–9, 2013.

[100]. R.H. Wijffels, and M.J. Barbosa, "An outlook on microalgal biofuels," *Science*, Vol. 329(5993), pp. 796–799, 2010.

[101]. A. Toledo-Cervantes, M. Morales, E. Novelo, and S. Revah, "Carbon dioxide fixation and lipid storage by Scenedesmus obtusiusculus," *Bioresource Technology*, Vol. 130, pp. 652–658, 2013.

[102]. E. Eustance, S. Badvipour, J.T. Wray, and M.R. Sommerfeld, "Biomass productivity of two Scenedesmus strains cultivated semi-continuously in outdoor raceway ponds and flat-panel photobioreactors," *Journal of Applied Phycology*, Vol. 28, pp. 1471–1483, 2016.

[103]. S.H. Ho, C.Y. Chen, and J.S. Chang, "Effect of light intensity and nitrogen starvation CO2 fixation and lipid/carbonhydrate production of an indigenous microalgae Scenedesmus obliquus CNW-N," *Bioresource Technology*, Vol. 113, pp. 244-252, 2012.

[104]. N. Agirman, and A.K. Cetin, "Effect of nitrogen limitation on growth, total lipid accumulation and protein amount in Scenedesmus acutus as biofuel reactor candidate," *Natural Science and Discovery*, Vol. 3(3), pp. 33-38, 2017.

[105]. Y.H. Wu, Y. Yu, X. Li, H.Y. Hu, Z.F. Su, "Biomass production of a *Scenedesmus sp.* under phosphorous-starvation cultivation condition," *Bioresource Technology*, 112 (2012) 193–198.

[106]. L. Wang, Y. Li, M. Sommerfeld, and Q. Hu, "A flexible culture process for production of the green microalga Scenedesmus dimorphus rich in protein, carbohydrate or lipid," *Bioresource Technology*, Vol. 129, pp. 289–295, 2013.

[107]. M. P. Rai and S. Gupta, "Effect of media composition and sunlight supply on biomass, lipid content and FAME profile for quality biofuel production from Scenedesmus abundans," *Energy Conversion and Management*, Vol. 141, pp. 85-92, 2017.

[108]. J. Anand and M. Arumugam, "Enhanced lipid accumulation and biomass yield of Scenedesmus quadricauda under nitrogen starved condition," *Bioresource Technology*, Vol. 34, pp. 1046-1063, 2016.

[109]. J. Cabello, A. Toledo-Cervantes, L. Sánchez, S. Revah, and M. Morales, "Effect of the temperature, pH and irradiance on the photosynthetic activity by Scenedesmus obtusiusculus under nitrogen replete and deplete conditions," *Bioresource Technology*, Vol. 181, pp. 128-135, 2015.