

Comparative Study of Leachate Treatment by Combined System

Hanane El Fadel*, Mohammed Merzouki, Mohamed Benlemlih

Biotechnology Laboratory, Science Faculty of Dhar El Mahraz, University of Sidi Mohamed Ben Abdellah, Fez, Morocco

Email address:

elfadelha@gamil.com (Hanane El Fadel)

*Corresponding author

To cite this article:

Hanane El Fadel, Mohammed Merzouki, Mohamed Benlemlih. Comparative Study of Leachate Treatment by Combined System. *American Journal of Chemical Engineering*. Vol. 11, No. 3, 2023, pp. 46-51. doi: 10.11648/j.ajche.20231103.11

Received: June 15, 2023; **Accepted:** June 29, 2023; **Published:** September 14, 2023

Abstract: Leachate from landfill requires treatment before discharge into the environment to avoid surface and underground water contamination. In this paper, the treatment performance of combined system by physico-chemical and biological techniques for landfill leachate are studied, the biological treatment by Sequencing Batch Reactor (SBR), the coagulation-flocculation and the filtration-fly ash. Both coagulation-flocculation and treatment biologique by Sequencing Bach Reactor are effective for over 98,07% COD removal, 99,16% BOD₅, a removal rate of 96,14% for NH₄, 79,82% for NO₃⁻, 97,32% for NO₂⁻, 89,09% for suspended solids (SS) and 87,71% for PO₄. A combination of physical and biological treatments has demonstrated its effectiveness for the treatment of intermediate leachate. Almost complete removal of COD and nitrogenous forms has been accomplished by a combination of biological treatment by SBR and physical treatment by filtration with COD concentration of 5200 mg/L and BOD₅ concentration of 1375,12 mg/L. It is important to note that the selection of the most suitable treatment method for landfill leachate depends on the characteristics of landfill leachate, technical applicability and constraints, effluent discharge alternatives, cost-effectiveness, regulatory requirements and environmental impact. As a whole, a combination of two treatments proves to be more efficient and effective than individual treatment. This could be because a two-step treatment has the ability to synergize the advantages of individual treatments, while overcoming their respective limitations. A combined treatment is indeed capable of improving the effluent quality and minimizing the residue generated than an individual treatment.

Keywords: Combined Treatment, Landfill Leachate, SBR, Coagulation-Flocculation, Filtration

1. Introduction

Water has always been inseparable from human activity, and the depletion of water resources and the degradation of their quality is a major challenge. Indeed, one of the factors governing the development of human societies is the concern to obtain and maintain an adequate supply of water. As the possibilities for increasing the supply of water are increasingly costly, both economically and environmentally, scarcity situations develop and reinforce the need for sound water management. Water use creates a new product called effluent or wastewater. Indeed, the polluting loads contained in these waters have various origins, their discharge into the natural environment is the main pollution that affects our streams and more generally the entire natural environment. The stakes are now high because at the same time it will be

necessary to resolve the issues relating to the collection of water and its treatment, and to consider its safe reuse in order to cope with the scarcity of water resources.

In Morocco, the growing production of household waste and industrial waste leads to critical pollution problems. The increasingly complex and heterogeneous nature of these wastes implies difficulties in their treatment and management. A large part of it is landfilled without precautions, which is a real and permanent threat to the environment. In addition, several studies, both at the laboratory scale and at the pilot scale or in full scale have been performed to select the most reliable method for treating these particular waters [1]. The first research, dating from the 1970 [2], was based on the treatment of both domestic wastewater and landfill leachate. The inefficiency of this process prompted researchers to treat the two types of water separately through aerated lagoons

and activated sludge. However, these processes have low yields for temperatures below 10°C and poor denitrification [3, 4]. In order to overcome these drawbacks, several processes have been proposed such as treatment with submerged aerobic biological filters developed by Pedersen and Jansen, 1992 [5] and biological reactors [6]. Although the characteristics of landfill leachate depend on the degree of solid waste stabilization, site hydrology, moisture content, seasonal weather variations, age of the landfill and stage of the decomposition in the landfill [6]. The common feature of stabilized leachate are moderately high strength of COD (5000-20000), as well as a low ratio of BOD/COD (less than 0,1) [7]. If not properly treated, leachate that seeps from a landfill can enter the underlying groundwater, thus posing potentially serious hazards to the surrounding environment, thus posing potentially serious hazards to the surrounding environment and to public health.

As the treatability of landfill leachate depends on its composition and characteristics (Table 1) [8], the nature of the organic matter present as well as the age and structure of the landfill.

Table 1. Characteristics of different types of landfill leachate [8].

Type of leachate	Young	Intermediate	Stabilized
Age of landfill (years)	<1	1-5	>5
pH	<6.5	6.5-7.5	>7.5
BOD ₅ /COD	0.5-1	0.1-0.5	<0.1
COD (g/L)	>15	3-15	<3
NTK (g/L)	0.1-2	NA	NA
Heavy metals (mg/L)	>2	<2	<2

Due to its reliability, simplicity and high cost-effectiveness, biological treatment (suspended / attached growth) is commonly used for the removal of the leachate containing high concentrations of BOD [9]. When treating young (biodegradable) leachate, biological techniques can yield a reasonable treatment performance with respect to COD, TKN and heavy metals. However, when treating stabilized (less biodegradable) leachate, biological treatment may not be able to achieve the permitted maximum COD levels for direct or indirect discharge due to the recalcitrant characteristics of organic carbon in the leachate. As a result, the search for other effective and efficient technologies for the treatment of stabilized landfill leachate has intensified in recent years. Physico-chemical treatments have been found to be suitable not only for the removal of refractory substances from intermediate and stabilized leachates, but also as a refining step for biologically treated leachate.

In this article, we are carrying out a comparative study of leachate treatment by combined systems using the biological treatment by Sequencing Batch Reactor (SBR), the coagulation-flocculation and the filtration-fly ash.

2. Materials and Methods

2.1. Biological Treatment by Sequencing Batch Reactor

The sequencing batch reactor (SBR) is an activated sludge

system for wastewater treatment. Its particularity lies in the fact that aeration, decantation and clarification take place in the same tank. The SBR system was effective in treatment but required constant monitoring. Following the development of reliable and inexpensive automatic control devices. The evolution and popularization of this equipment have made the SBR process very competitive in many respects: economy, performance and reliability [10]. The SBR process is based on the principle of aerobic biological treatment of effluents in cycles. The advantages of this process are:

- 1) Compact process;
- 2) Lower installation and running costs;
- 3) High purification efficiency;
- 4) No sludge recirculation;
- 5) Elimination of nitrogen because in the SBR process, there is an aerobic phase allowing the oxidation of ammoniacal nitrogen into nitrite and then into nitrate (nitrification), possibly followed by an anaerobic phase allowing denitrification;
- 6) Elimination of phosphorus by modifying the operating sequences, but without adding additional structures;
- 7) Good technical reliability.
- 8) Limited labor requirement.
- 9) Possibility of direct discharge of treated effluents into the natural environment [10].

2.2. Chemical Treatment by Coagulation-Flocculation

The main purpose of coagulation is to destabilize the suspended solids, which is to say to facilitate their agglomeration. This process is characterized by the injection and dispersion of chemicals (coagulants). It consists of adding an electrolyte to the water to neutralize the negative charges that are responsible for keeping it in stable suspension. Salts of a trivalent metal, Fe³⁺ or Al³⁺ are generally used [11]. The purpose of flocculation is to promote contact between the destabilized particles by slow mixing, these particles clump together to form a floc that can be eliminated by settling.

Coagulation-flocculation can be successfully used in the treatment of intermediate or old leachate [12]. It is widely used as a pre-treatment [13] before reverse osmosis or before biological processes to protect the biomass from the aggression of toxic elements from discharges (case of activated sludge) [14] or even as the last treatment step to eliminate bio-recalcitrant organic matter. Aluminum sulphate, ferrous sulphate, ferric chloride and ferric chloro-sulphate have been commonly used as coagulants [15]. The general approach for this technique includes pH adjustment and involves the addition of ferric/alum salts at the coagulant to overcome the repulsive forces between the particles [16].

2.3. Physical Treatment by Filtration

A coupling of the SBR treatment system with filtration using a natural support was performed in this study. The raw leachates treated in the aeration tank (SBR) were conveyed to the filtration column with 6 cm in diameter and 50 cm in

height. The effective height of the filter bed is 36 cm (H_s), 14 cm is used for the leachate to be filtered (H_E), which is kept constant along the experiments in order to keep the same leachate load on the filter bed

2.4. Analytical Methods

Different analysis techniques have been used to follow the evolution of organic and mineral compounds concentrations, the analytical methods used are those described by Rodier [17]. These analyses were carried out three times for each sample.

3. Results and Discussion

3.1. Effect of pH on Coagulation-Flocculation Efficiency

In the coagulation–flocculation process, it is very important to adjust the pH since coagulation occurs within a specific pH range for each coagulant and according to the type and characteristic of the raw effluent to be treated.

The results are obtained following a variation of the pH from 6.0 to 7.5 of the leaching water. The concentration of $FeCl_3$ used as a coagulant is 140 mg/L. The maximum pH of 7.35 was selected so as not to generate too large a quantity of suspended solids by raising the pH, while seeking to minimize the quantity of NaOH added. The optimal pH is located at a value close to 7.35 with a COD reduction rate of 33,34%.

Given the results obtained, the coagulation-flocculation tests must be carried out at a constant pH of 7,35. These results were in agreement with the previous study undertaken by Diamadopoulou [18].

3.2. Effect of Coagulant Concentration on Coagulation-Flocculation Efficiency

The figure 1 shows the results obtained following a variation in the concentration of two coagulants usually used in the field of wastewater treatment: ferric chloride ($FeCl_3$) and aluminum sulphate [$Al_2(SO_4)_3 \cdot 14H_2O$]. During the tests, the concentrations of each of the two coagulants vary from 0 to 500 mg/L and from 0 to 600 mg/L respectively for ferric chloride and aluminum sulphate.

The pH is kept constant at 7,35. A somewhat lower threshold of COD is reached when the concentration of aluminum sulphate exceeds 300 mg/L, while better performance is observed when low concentrations of ferric chloride are used., these two coagulants offer fairly satisfactory treatment performance in terms of COD reduction. Ferric chloride offers an abatement rate of 81,67% while at a higher concentration of aluminum sulphate, the abatement rate is 85%. Based on these results, respective concentrations of ferric chloride and aluminum sulphate of 200 mg/L and 386 mg/L are recommended for the treatment of this leachate.

The choice of ferric chloride and its concentration is based on the fact that this coagulant agent allows, at very low concentrations, a satisfactory reduction of the COD. This low

concentration employed contributes to a reduction in the volume of sludge produced and in the cost price of the treatment process.

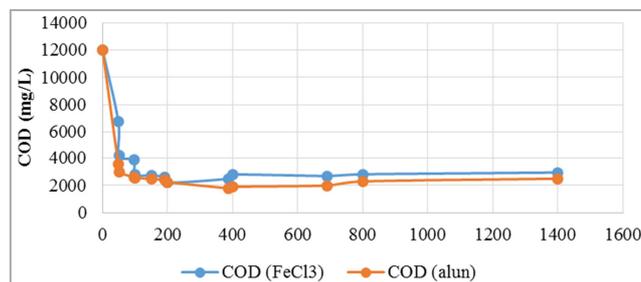


Figure 1. Effect of coagulant concentration on coagulation-flocculation efficiency.

3.3. Physico-Chemical and Microbiological Characterization of the Sludge Used

The results of the microbiological and physicochemical analyses of the sludge used in our SBR process show a composition essentially of heterotrophic microorganisms, which degrade organic matter: total germs with $30 \cdot 10^6$ UFC/mL, total coliforms with $43 \cdot 10^4$ UFC/mL, Fecal coliforms with $72 \cdot 10^3$ UFC/mL, streptococci with $90 \cdot 10^3$ UFC/mL, staphylococques with $22 \cdot 10^5$ UFC/mL, yeasts with 10^7 UFC/mL and fungi with 10^5 UFC/mL. There are also degradation products, of which ammonium (NH_4^+) with 16 mg/L is degraded into nitrites (NO_2^-) with a concentration of 54,9 mg/L.

The calculated Mohlman index varies between a minimum value of 110 ml/g and a maximum value of 140 ml/g independently of the duration of the aeration phase. However, it should be emphasized that the values we recorded are far from causing a malfunction in our process such as sludge expansion, since the standards require that this index be between 50 and 150 ml/g. These results clearly show that the sludge from our SBR process underwent good settling given the values of the Mohlman index.

These results shows the great diversity and abundance of the microbial populations contained in the sludge. This count also makes it possible to deduce that bacteria dominate yeasts and fungi. Among these bacterial populations, we note the large presence of staphylococci and total coliforms, but also the test germs of fecal contamination.

3.4. Coupling of SBR Treatment System and Coagulation-Flocculation

Table 2 shows the results of the physicochemical analyses before and after SBR and coagulation-flocculation treatment, which are compared with the raw leachate to determine the abatement rate. The results are presented as mean values of the raw leachates and the mean value after SBR treatment coupled with the coagulation-flocculation treatment over the study period.

The BOD_5 abatement rate is greater than that of the COD, it takes the value of 99,16%. The average value at the outlet

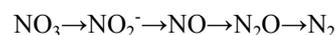
of the SBR is 166,6 mg/L, this concentration is much lower than that of the standard for indirect discharges (500 mg/L). The value of the COD obtained is 1026,6 mg/L, slightly higher than the standard (1000 mg/L). The high BOD₅ reduction rate can be explained by the performance of the mud used in the SBR which degrades the biodegradable organic matter present in the leachate.

The concentration of orthophosphates is reduced from 3,22 mg/L to 2,04 mg/L at the outlet of the SBR with a reduction rate that does not exceed 36,64%. This low rate of reduction of orthophosphates can be explained by the absence of the phase anaerobic. During the aeration phase of our bioreactor, which lasted 22 hours, the phosphate-depleting bacteria accumulate orthophosphates. However, to promote the accumulation of the latter, it is better to precede the aerobic phase by an anaerobic treatment phase to release the orthophosphates in order to facilitate their accumulation during the aerobic phase. The alternation of the two anaerobic and aerobic phases promotes the growth and selective enrichment of phosphate accumulating bacteria [19].

The nitrogen pollution, essentially in soluble form, is found in the form of organic nitrogen and ammoniacal nitrogen. These two forms of nitrogen are involved in the phenomenon of eutrophication. Based on the results presented in table 2, the ammonium concentration at the SBR inlet of 2,41 mg/L decreases to a concentration of 0,093 mg/L. The reduction rate takes the value of 92,5%. The decrease in the concentration of ammonium after treatment with SBR can be explained by the phenomenon of nitrification. The average concentration of nitrates present in the leachate at the entrance to the SBR is 4,84 mg/L, after treatment, this concentration drops to 2,28 mg/L with an abatement rate of

52,89%. Monitoring of the nitrite concentration shows a treatment rate in the bioreactor of 85,96%. The value found at the outlet of the bioreactor is 0,08 mg/L. This reduction in NO₂⁻ and NO₃⁻ levels is explained by the process of aerobic denitrification reducing nitrate and nitrite to N₂O or molecular nitrogen by common facultative anaerobic heterotrophic bacteria, such as *Paracoccus denitrificans*, *Thiobacillus denitrificans*, *Pseudomonas* and *Alcaligenes* [20-22].

During denitrification, a nitrogen oxide serves as an electron acceptor in order to generate an electrochemical potential on either side of the cytoplasmic membrane of the microorganism. The electrons, usually coming from an organic carbon source, but can also derive from an inorganic molecule, travel to different oxidoreductases, each specific to a particular nitrogen oxide [23]. The concerted action of all these enzymes therefore leads to the formation of N₂ from nitrate, according to the following chain of transformations [23, 24]:



The concentration of SS in the bioreactor was recorded at the threshold of 5 g/L due to the sludge present in the bioreactor. On leaving the SBR, the concentration of SS has become 0,6 g/L. This decrease is explained by the calculated Mohlman index, which is between 50 and 150 mL/g. This further prevents the phenomenon of bulking or swelling of the sludge. In this case, the settling characteristics of the sludge are satisfactory, which is attributable to a biological balance in the community of microorganisms present in the mixed liquor.

Table 2. Results of physico-chemical analyzes before and after treatment with the combined system.

	Average values raw leachates	Average values of leachates treated with coagulation-floculation	Entrance SBR	Exit SBR	Average values of leachates treated with SBR	% abatement with treatment by SBR	% abatement with treatment by combined system	Limit values of discharges into surface and underground waters
Dissoved oxygen (mg/L)	0.86	0.86	-	5.23	1	-	-	-
COD (mg/L)	53199.6	9751	81.67	7886.6	1026.6	86.99	98.07	500
BOD ₅ (mg/L)	20000	14166	29.17	5166	166.6	96.77	99.16	100
PO ₄ (mg/L)	16.61	14.6	12.1	3.22	2.04	36.64	87.71	2
NH ₄ ⁺ (mg/L)	2.41	1.35	43.98	1.24	0.093	92.5	96.14	-
NO ₃ ⁻ (mg/L)	11.3	9.8	13.27	4.84	2.28	52.89	79.82	-
NO ₂ ⁻ (mg/L)	2.99	2.07	30.76	0.57	0.08	85.96	97.32	-
SS (mg/L)	5500	2866.66	47.88	4833.33	600	87.85	89.09	100

3.5. Coupling of SBR Treatment System and Filtration

Table 3 shows the results of the physico-chemical analyses before and after SBR and filtration-fly ash treatment, which are compared with the raw leachate to determine the abatement rate. The results are presented as mean value of the raw leachate and the mean value after SBR treatment coupled with the filtration treatment over the study period. After leachate treatment by sequential aeration in the SBR, there is a decrease in the concentration of the parameters.

Regarding the COD after the SBR treatment, the concentration for the COD is 1632,26 mg/l, and there is a decrease in the concentration up to 112,32mg/l. The following points can explain this strong elimination:

The performance of the sludge used in the SBR, which degrades the biodegradable organic matter present in the leachate, as well as by the presence of purifying biomass;

- 1) The high content of SiO₂ (silico-aluminous structure) of the fly ash [25]. It is an important adsorbent with a strong electrical polarity and mineral elements in

particular ferric ions (Fe^{3+}), the latter contribute to the neutralization of the negative charges of the organic matter contained in the leachates;

- 2) The small particle size of the fly ash, which does not exceed 200 μm , which allows better leachate treatment performance by increasing the adsorption surface thanks to the reduction in the size of the adsorbent grains [26].

- 3) The latter contributes to the neutralization of the negative charges of nitrites, nitrates, orthophosphate, and sulfates, which traps them by chemical bonds. We can also explain this increase in abatement rates by the formation of biofilms inside the column. The pollutants of the effluent either can adsorb on the cell membrane of the organisms forming the biofilms or be assimilated by the biofilms [27].

Table 3. Leachate analysis results after SBR treatment coupled with the filtration column.

	Average values raw leachates	Average values of leachates treated with SBR	Average values of leachates treated by filtration	% abatement	Limit values of discharges into surface and underground waters
pH	8,13	7,54	8,17	-	5,5-9,5
COD (mg/L)	5200	1632,26	112,32	93%	500
BOD ₅ (mg/L)	1357,12	84	26	69%	100
TP (mg/L)	0,65	1,12	$9,5 \times 10^{-3}$	99%	2
Electrical conductivity (ms/cm)	37,9	27,7	8,99	67%	-
NH_4^+ (mg/L)	1185	123,56	0,4	99%	-
NO_3^- (mg/L)	2,20	85,55	1,55	98%	-
NO_2^- (mg/L)	3,60	1,02	0,39	61%	-
SS (mg/L)	430	80	0	100%	100

4. Conclusion

The combination of chemical and biological treatment or physical and biological treatment is required for optimum treatment of intermediate or stabilized leachate. Overall, it is found that a combination of chemical and biological treatment can maximize the removal of recalcitrant organic compounds from intermediate leachate, as reflected by a significant decrease of the COD and BOD₅ values after treatment, while this combined treatment is required to achieve effective removal of nitrogenous forms and COD with a substantial amount of biodegradable organic matter.

It is important to note that the selection of the most suitable treatment for intermediate landfill leachate depends on the characteristics of the wastewater, the legal requirements of the residual concentrations of nitrogenous forms and COD, the overall treatment performance compared to other techniques, age of a landfill, plant flexibility and reliability as well as environmental impact. Due to seasonal weather variations, it is also necessary to consider temporal fluctuations in the quantity and composition of leachate. Finally, economic parameters such as investment and operational costs (energy consumption, residual deposition and maintenance) also play major roles in this decision-making process. All the factors mentioned above should be considered to select the most effective and inexpensive treatment in order to protect the environment.

References

- [1] Khattabi H., Aleya L and Mania J. Natural lagooning of landfill leachate. *Revue des sciences de l'eau, Rev. Sci. Eau*, 15 (2002) 411-419.

[2] Boyle W. C and Ham R. K. Biological treatability of landfill leachate. *Wat. Res. Poll. Cont. Fed*, 46 (1974) 860-872.

[3] Knox K. Treatability studies on leachate from a co-disposal landfill. *Environ. Poll., (series B)*, 5 (1983) 157-174.

[4] Knox K. Leachate treatment with nitrification of ammonia. *Wat. Res.*, 19 (1983) 595-904.

[5] Pedersen B. M., Jansen J. I. A. C. Treatment of leachate-polluted ground water in an aerobic biological filter. *Euro. Water. poll. control.*, 2 (1992) 40-45.

[6] Spengel D. B and Dzombak D. A. Treatment of landfill leachate with rotating biological contractors. *Res. J. WPFC*, 63 (1991) 971-981.

[7] X. Z. Li, Q. L. Zhao, MAP precipitation from landfill leachate and seawater bitter waste, *Environ, Technol.* 23 (2002) 989-1000.

[8] H. Alvarez-Vazquez, B. Jefferson, S. J. Judd, Membrane bioreactors vs conventional biological treatment of landfill leachate: a brief review, *J. Chem. Technol, Biotechnol*, 79 (2004) 1043-1049.

[9] A. Uygur, F. Karg. Biological nutrient removal from pretreated landfill leachate in a sequencing batch reactor, *J. Environ. Manage.* 71 (2004) 9-14.

[10] Génie et modélisation des bioprocédés de l'environnement I. Séminaire: Sequencing batch reactor. Ecole polytechnique fédérale de Lausanne. CT. 2004.

[11] Mouchet P. B. Traitement des eaux avant utilisation. *Matières particulière; Techniques de l'Ingénieur, traité Environnement.* (2004).

[12] Silva A. C., Dezotti M and Sant'Anna Jr G. L. Treatment and detoxication of a sanitary landfill leachate, *Chemosphere.* 55 (2004) 207-214.

[13] Amokrane A., Comel C and Veron J. Landfill leachates pretreatment by coagulation-flocculation, *Water Res.* 31 (1997) 2775-2782.

- [14] Laconi C. D., Lopez A., Ramadori R., Di pinto A. C and Passino R. Combined chemical and biological degradation of tannery wastewater by a periodic submerged filter (SBBR) (2002).
- [15] Ehrig H. J. Treatment of sanitary landfill leachate: Biological treatment, *Waste. Manage. Res.* 2 (1984) 131-152.
- [16] G. M. Ayoub, L. Semerjian, A. Acra, M. El Fadel, B. Koopman, Heavy metal removal by coagulation with seawater liquid bittern, *J. Environ. Eng.* 127 (2001) 196-202.
- [17] J. Rodier, L'analyse de l'eau, *Contrôle et interprétation* (2016).
- [18] E. Diamadopoulos, Characterization and treatment of recirculation stabikized leachate, *Water Res.* 28 (1994) 2439-2445.
- [19] Merzouki M. Thèse de doctorat d'Etat « Déphosphoration anoxique d'effluents par voie biologique: Optimisation et mise en œuvre d'un procédé intégré de dépollution azotée et phosphorée. (2001).
- [20] Roberston L. A., Cornelisse R., De Vos P., Hadioetomo R and Kuenen J. G. Aérobie denitrification in various heterotrophic nitrifiers. *Antonie van Leeuwenhoek*, 56 (1989) 289-299.
- [21] Colliver B. B and Stephenson T. Production of nitrogen oxide and dinitrogen oxide by autotrophic nitrifiers. *Biotechnology Advances*, 18 (2000) 219-232.
- [22] Hu T. L and Kung K. T. Study of heterotrophic nitrifying bacteria from wastewater treatment Systems treating acrylonitrile, butadiene and styrene resin wastewater. *Water Science and Technology*, 42 (2000) 315-321.
- [23] Zumft W. G. Cell biology and molecular basis of denitrification. *Microbiology and Molecular Biology Reviews*, 61 (4) (1997) 533-616.
- [24] Bothe H., Jost G., Schloter M., Ward B. B and Witzel K. P. Molecular analysis of ammonia oxidation and denitnfication in natural environments. *FEMS Microbiology Reviews*, 24 (2000) 673-690.
- [25] Xu G., Shi X. Characteristics and applications of fly ash as a sustainable construction material: A state of the art review, *Resources, conservation and recycling*, 136 (2018) 95-109.
- [26] EL Fadel H, Merzouki M, Laamayem A, Benlemlih M. Comparative study of the metal pollution treatment from leachates by physical and biological methods. *J. Mater. Environ. Sci.*, volume 13, Issue 04 (2022) 391-408.
- [27] Backhouse, T. C., Bolliger, A. Australian marsupial trichosurus, 41 (1987) 435-464.