Management residues of chlorpyrifos insecticides on shallot cropping through remediations technology

Poniman, Indratin, A N Ardiwinata and S Rianto

Indonesian Agricultural Environment Research Institute, Pati, Indonesia

E-mail: poniman63ir@gmail.com

Abstract. Chlorpyrifos is a broad-spectrum insecticide and is widely used to Organism Pests Management (OPM). The remediation technology for polluted land is needed to reduce the risk of continuous impacts. The research aimed to reduce chlorpyrifos insecticide residues in shallot agriculture through remediation technology. The research was carried out in Naru Village, Sape Sub-District, Bima Regency (NTB) in June-August 2018. The experiment was designed in a randomized block design (RBD), three replications, and six treatments: (T1) farmers method, (T2) urea fertilizer-coated biochar, (T3) urea fertilizer-coated biochar enriched with consortia microbes, (T4) consortium microbes 2 L ha⁻¹, (T5) urea fertilizer-coated nanobiochar, and (T6) urea fertilizer-coated nanobiochar enriched with consortia microbes. Remediation agents containing carbon, such as biochar and manure and some microbes can help accelerate the degradation of insecticides in the environment. Decreased chlorpyrifos residue from highest to low, respectively: urea fertilizer coated nanobiochar>urea fertilizer coated nano biochar with enriched consortium microbes>urea fertilizer coated biochar>urea fertilizer coated biochar with enriched consortium microbes>consortium microbes 2 L ha⁻¹. Treatment of urea fertilizer coated nanobiochar and urea fertilizer coated nano biochar with enriched consortium microbes can be applied as a chlorpyrifos remediation technology in the shallot agriculture in silt texture soils.

1. Introduction

In modern agriculture, the intensive and excessive agrochemicals will increase their accumulation in soils, so land remediation should be mandatory as part of land management. The management of crop cultivation, especially vegetable crops, is almost impossible without using chemical insecticides. The use of insecticides caused unsanitary soil indicating to levelling off, symptoms of decreased yield, and increased attack by plant pests.

This condition needs to find a mitigation solution from the further impact of chemical insecticide residues through land remediation. Land remediation is an effective method because it can accelerate the degradation process of insecticide residues in the soils [1–4]. Meanwhile, the need for shallots as a kitchen spice and medicines continues to increase, causing the use of inorganic inputs to increase at the field level. Shallots are capital-intensive and solid tech, therefore the slight test disturbance to the plants will be responded to by farmers protectively. This demand then forces farmers to use insecticides above the average needs of other crops. Attack of plant pests organisms at each stage of shallot planted growth has an important significance for the success harvesting. Silkworm (Agrotis ipsilon) and Armyworms (Spodoptera litura) are pests that are greatly feared for the successful harvest of shallots [5]. The caterpillar attack on shallot crops could be causing total crop failure. Chlorpyrifos is one of the famous insecticides in controlling the worm attack on shallot crops.

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Chlorpyrifos is one of the wide-spectrum of organophosphate insecticides group that is most widely used in the agricultural sector [6, 7] and be used in 90 countries around the world [8, 9]. In the environment chlorpyrifos has a half-life between 10 to 120 days [10], even in humid soil, the degradation can reach 251 days [11]. Chlorpyrifos \( (\text{C}_6\text{H}_{12}\text{Cl}_3\text{NO}_3\text{PS}) \) is used worldwide to control a variety of chewers and suckers pests [7]. Chlorpyrifos is widely used to control pests in shallot agriculture, and is one of the five active ingredients selected by farmers [5, 12]. Chlorpyrifos has neurotoxic and immunotoxins properties and has proven to be harmful to animals, humans, and the environment. Overuse causing to reduced microbial populations (bacteria and fungi), and can inhibit nitrogen mineralization in the soil.

All applied chemical materials to soil agriculture will become pollutants in the soil and the environment. The chemical metabolite of chlorpyrifos could soluble by naturally water entry soil particles [13]. According to Akbar and Sultan [14], the detections of chlorpyrifos residue requires the seriousness of all parties.

To decrease the risk of further chlorpyrifos residues in the soils, mitigations efforts needed, i.e. through remediation technology. Remediation is a way to reduces chemical pollutions in soil agriculture, so that is created environmentally friendly agriculture. This study aims to obtain remediations technology to reduce chlorpyrifos insecticide residue in shallot agriculture.

2. Materials and methods

2.1. Time and place

The research was conducted in May-July 2018 in Naru Village, Sape Sub-District, Bima Regency (NTB). Bima Regency is the largest producer of shallots after Java Island. The experiment was designed in a randomized block (RBD), three replications, and six treatments. The treatments consisted of: (T1) farmers method, (T2) urea fertilizer-coated biochar, (T3) urea fertilizer-coated biochar enriched with consortia microbes, (T4) consortium microbes 2 L ha\(^{-1}\), (T5) urea fertilizer-coated nano biochar, and (T6) urea fertilizer-coated nano biochar enriched with consortia microbes.

2.2. Research implementation

As a basis for determining the needs for urea fertilizer, the doses of urea fertilization used by local farmers which is 400 kg ha\(^{-1}\) [15]. Urea fertilizer-coated biochar is made with a ratio of 80:20, while urea fertilizer-coated nano biochar is made with a ratio of 90:10 (m\(^{-3}\)) with adhesive of molasses dose 4 L every 100 kg of finished fertilizer-coated. The microbial consortia used include \( \text{Bacillus aryabhattai} \), \( \text{Bacillus thuringiensis} \), \( \text{Bacillus subtilis} \), \( \text{Achromobacter puhulans} \), \( \text{Achromobacter sp.} \), \( \text{Catenococcus thiocy} \), \( \text{Stenotrophomonas maltophilia} \). The application times of fertilizer for the plants were 10, 20, 30, and 40 days after planting (DAP), as well as with SP36 and KCl fertilizers. During the experimental progress, pest control was remained to be done with chemical insecticides with active ingredients of non-chlorpyrifics.

Seedsbeds the experimental are made with a width of 1.5 m and a length of 6 m. Between seedsbeds are made galleries with a width of 0.2 m to reduce water runoff to other plots. In the middle of the seedsbed, a small, 0.25 m created trench is made which services as a walkway for people to doing watering time. The shallot of Philippine variety is planted with a distance of 20 x 10 cm, one tuber/planting hole, and are located on the left and right of the seedsbeds.

For analysis of chlorpyrilfos residue, soil sample was taken diagonally randomly on each plot [16]. Soil samples were taken at a depth of 0 to 20 cm using soil auger. Chlorpyrifos residues analysis was carried out at the Integrated Laboratory of the Indonesian Agricultural Environment Research Institute, by using the QuEChERS method [17]. Meanwhile, to calculating the residual amount of chlorpyrifos using a formula [18] as follows:
Residue $= \frac{A_c \times V_{is} \times K_s \times V_{fc}}{A_s \times V_{ic} \times B \times R}$

Note:
- $A_c$ = sample area
- $A_s$ = standard area
- $V_{ic}$ = volume sample injection (µL)
- $V_{is}$ = volume standard injection (µL)
- $K_s$ = standard concentration (mg kg$^{-1}$)

3. Results and discussion

3.1. Soils properties of the research location

The soil characteristics of the research location are presented in Table 1. The soil texture is dominated by silt, with pH of 5.6 (slightly acidic), low C-organic (1.45%), high cation exchange capacity (CEC) (37.84 cmol kg$^{-1}$), very high P-available (209.54 mg 100 g$^{-1}$), and low K-available (21.10 mg 100 g$^{-1}$). The soil type in the research location was Inceptisols [19].

| Parameters     | Unit       | Value  | Criteria |
|----------------|------------|--------|----------|
| Texture        |            |        |          |
| - Sand         | %          | 7      | Silt     |
| - Silt         | %          | 86     |          |
| - Clay         | %          | 7      |          |
| P-Potential    | mg 100 g$^{-1}$ | 102.61 | Very high|
| P-Available    | ppm        | 209.54 |          |
| K-Potential    | mg 100 g$^{-1}$ | 12.80  | Low      |
| K-Available    | mg 100 g$^{-1}$ | 21.10  | High     |
| CEC            | cmol(+)$kg^{-1}$ | 37.84  |          |
| Exchangeable cations: | | | |
| K              | cmol(+)$kg^{-1}$ | ND     |          |
| Na             | cmol(+)$kg^{-1}$ | ND     |          |
| Ca             | cmol(+)$kg^{-1}$ | ND     |          |
| Mg             | cmol(+)$kg^{-1}$ | ND     |          |
| C-organic      | %          | 1.45   | Low      |
| N-total        | %          | 0.59   | High     |

Note: ND = No Data

Endoaquepts is a developing soil that comes from clay sediment materials, has a slightly light color (yellowish), chroma 2, value 3, and usually has quite a lot of brown spots. Generally, have reactions a slightly acidic (pH 5.5 to 6.0), with medium-high organic matter content, medium alkaline saturations, medium cation exchange capacity, and lower aluminum saturations [21].

3.2. Chlorpyrifos residue in the soil

The residual content of chlorpyrifos insecticide in the soil before applying treatment ranged from 0.0173 to 0.2483 mg kg$^{-1}$. The residues of chlorpyrifos insecticides at 1 day after application of treatment ranges from 0.0121 to 0.1288 mg kg$^{-1}$, increasing at 7 Day After Treatment Application (DATA) to ranges from 0.0240 to 0.0383 mg kg$^{-1}$, and decline at harvesting times (ranges of 0, 0165 to 0.0828 mg kg$^{-1}$). The residual values of chlorpyrifos in various treatments and various observation times are presented in figure 1. Degradations of chlorpyrifos insecticide residues depending on environmental conditions [2]. Degradations of chlorpyrifos in dry soil is more quickly about 1.6 days because chlorpyrifos degradation...
in moist soil conditions takes about 251 days [11]. Moist soil conditions due to watering the crops on this experiment are thought to slow down the process degradation of insecticide residues.

The pattern of decreasing chlorpyrifos residue during plant growth forms a polynomial pattern (Figure 2). The pattern of decreasing chlorpyrifos residue from planting time until harvesting time is showed by the regressions following: Farmers method \( y = 0.0196x^2 - 0.128x + 0.2692 \), urea fertilizer coated biochar \( y = 0.0176x^2 - 0.093x + 0.145 \), urea fertilizer coated biochar with enriched consortium microbes \( y = 0.0151x^2 - 0.1081x + 0.2236 \), microbes consortia 2 L ha\(^{-1} \) \( y = 0.0128x^2 - 0.0665x + 0.1575 \), and urea fertilizer coated nano biochar with enriched consortium microbes \( y = 0.0223x^2 - 0.111x + 0.1653 \).

From the regression above, it can be seen that the treatment of farmers method and urea, fertilizer-coated biochar enriched with consortium microbes reached the maximum remediation after 1-week treatment application. Meanwhile, the treatment of urea fertilizer-coated biochar, consortium microbes 2 L ha\(^{-1} \), urea fertilizer coated nano biochar, and urea fertilizer coated nano biochar with enriched consortium microbes, the maximum remediation was achieved before 1 week after the treatment application. Carbonated matter [22–25] and several microbes [24–27] can help accelerate the degradation of insecticides in the environment.

Insecticides contain positively charged functional groups and increase soil adsorption capacity. In certain conditions, the functional groups of insecticides are adsorbed on the clay surface and soil organic matter [28]. Both of them have a role together or individually in adsorbancy insecticide groups. The lower soil organic matter content of 1.45% at the research locations, causes the pesticide groups to be strongly bound by clay minerals, and causes the residues to remain firmly bound until harvesting times. The accumulations of insecticides in the soil are influenced by the type and nature of the soils, clay type, and soil organic matter content [29]. The residual chlorpyrifos can be decreased due to the result of the degradation process be harmless materials [3, 24, 30] and become 3,5,6-trichloro-2-pyridinyl (TCP) through the hydrolysis process [31, 32]. TCP is more dangerous to the environment than chlorpyrifos compound.
Figure 2. The pattern of degradations of chlorpyrifos insecticide residues in various remediation treatment on shallot agriculture, Bima 2018.

Note: BTA= Before Treatment Application; DATA = Day After Treatment Application; WATA = Week After Treatment Application; HT= Harvesting Time
The reductions in chlorpyrifos residue at harvesting time is presented in Table 2. The farmer practices could decrease the chlorpyrifos residue by 21.5% compared to the initial concentration. All treatments can increase the degradations of chlorpyrifos insecticide residues in the soil after the end of the shallot growth period. The number of reductions in chlorpyrifos insecticide residues in each treatment was from the highest respectively is urea fertilizer coated biochar with enriched consortium microbes (74.9%), urea fertilizer coated nano biochar with enriched consortium microbes (67.1%), urea fertilizer coated biochar (57.2%), urea fertilizer coated nano biochar (29.4%), and microbes consortium 2 L ha⁻¹ (26.5%).

Table 2. Chlorpyrifos residue before treatment applications and at harvesting time, as well as decreasing in its residue, Bima 2018

| Treatment | Before treatment application | Harvesting time | Value of residual reduction on the before treatment application | Value of residual reduction on the farmer method treatment |
|-----------|------------------------------|-----------------|---------------------------------------------------------------|----------------------------------------------------------|
|           | mg kg⁻¹                      | mg kg⁻¹         | %                                                             | %                                                        |
| T1        | 0.0413±0.0032                | 0.0324±0.0071   | 0.0089                                                        | 21.5                                                     |
| T2        | 0.0628±0.0011                | 0.0269±0.0039   | 0.0359                                                        | 57.2                                                     |
| T3        | 0.1184±0.0045                | 0.0297±0.0078   | 0.0887                                                        | 74.9                                                     |
| T4        | 0.0417±0.0008                | 0.0306±0.0017   | 0.0111                                                        | 26.5                                                     |
| T5        | 0.0175±0.0023                | 0.0124±0.0019   | 0.0052                                                        | 29.4                                                     |
| T6        | 0.0761±0.0056                | 0.0250±0.0013   | 0.0511                                                        | 67.1                                                     |
| CV (%)    | 19.7                         | 21.3            |

The chlorpyrifos residue between harvesting time and the before treatment application showed a decrease. The treatment based on microbial consortia (both biochar and nano biochar) showed a higher percentage of reduction. Some insecticides trigger the growth of soil microorganisms and partly bad influence [33, 34]. Organisms have a strategic and important role in degrading insecticide residues in the soil [35, 36]. The activity of several organisms in soils contaminated with chlorpyrifos residue is an important indicator of the degradation process [37].

The nanobiochar material was effective in lower chlorpyrifos residue in this study. The nanomaterials are reported to be able to accelerate the degradation rate of pesticide residues in soil and water environments [38]. The small size of the nanomaterial increases the surface area thereby increasing the chemical activity and adsorption ability of the nanoparticles in adsorbing pollutants on each surface [39].

4. Conclusions

The decreasing of chlorpyrifos residue from each treatment is as follows: urea fertilizer coated nano biochar>urea fertilizer coated nano biochar with enriched consortium microbes>urea fertilizer coated biochar>urea fertilizer coated biochar with enriched consortium microbes>consortium microbes 2 L ha⁻¹. Treatment of urea fertilizer coated nano biochar and urea fertilizer coated nano biochar with enriched consortium microbes can be applied as a chlorpyrifos remediation technology in the shallot agriculture in silt texture soils.

References

[1] Diez M C 2010 Capacidades físicas básicas en la educación secundaria obligatoria. J. Soil.Sci..Plant.Nutr. 10 (3): 244-267  http://dx.doi.org/10.4067/S0718-95162010000100004
[2] Chai L K, Wong M H and Hansen H C B 2013 Degradation of chlorpyrifos in humid tropical soils. *Journal of environmental management, 125*, pp.28-32. https://doi.org/10.1016/j.jenvman.2013.04.005

[3] Sirisha S, Mohan V and Readdy S J 2006 Effect of repeated applications of chlorpyrifos on its degradation in surface and subsurface soil *J. Tox. and Env.Chem.* Volume 88-Isuu.3. https://doi.org/10.1080/0277224060058834

[4] Gonzales-Condori E G, Celia Choquehuanca-Quispe and Stumber Álvaro Ramírez-Revilla 2020 study of the degradation of chlorpyrifos in contaminated soils in the presence of the red california earthworm *Rev. Int. Contam. Ambie.* 36 (1) 73-80 http://dx.doi.org/10.20937/RICA.2020.36.53201

[5] Basuki R S 2009 Farmers knowledge and effectiveness of insecticide use by farmers in controlling Spodoptera exigua Hubn on shallot plants in Brebes and Cirebon *J. Hort.* 19 (4): 459-74. http://ojs.unik-kediri.ac.id

[6] Cao Li, Wenhong Shi, Rundong Shu, Jian Pang, Yuetao Liu, Xiaohua Zhang and Yuming Lei 2017 Isolation and characterization of a bacterium able to degrade high concentrations of iprodione *Can.J.Micro.* vol.64 (1) pp:49-56. https://doi.org/10.1139/cjm-2017-0185

[7] Chen S, Liu C, Peng C, Liu H, Hu M and Zhong G 2012 Biodegradation of chlorpyrifos and its hydrolysis product 3, 5, 6-trichloro-2-pyridinol by a new fungal strain Cladosporium cladosporoides Hu-01 *PLoS ONE 7* (10): e47205. https://doi.org/10.1371/journal.pone.0047205

[8] Saunders M, Magnanti B L, Carreira S C, Yang A, Alamo-Hernández U, Riojas-Rodriguez H and Bartonova A 2012 Chlorpyrifos and neurodevelopmental effects: a literature review and expert elicitation on research and policy. *Environmental Health, 11* (S1), S5. https://doi.org/10.1186/1476-069X-11-S1-S5

[9] Raszewski G, Lemieszek M K, Łukawski K, Juszczak M and Rzeski W 2015 Chlorpyrifos and Cypermethrin Induce Apoptosis in Human Neuroblastoma Cell Line SH-SY 5Y. *Basic and clinical pharmacology and toxicology,* 116 (2), 158-167. https://doi.org/10.1111/bcpt.12285.

[10] Li X, Jiang J, Gu L, Ali SW, He J and Li S 2008 Diversity of chlorpyrifos-degrading bacteria isolated from chlorpyrifos-contaminated samples *International Biodeterioration and Biodegradation, 62* (4), 331-335 https://doi.org/10.1016/j.ibiod.2008.03.001

[11] Awasthi MD and Prakash NB 1997 Persistence of chlorpyrifos in soils under different moisture regimes. *Pesticide Science, 50* (1), 1-4. https://doi.org/10.1002/(SICI)1096-9063(199705)50:1<1::AID-PS549>3.0.CO;2-X

[12] Markesan TK and Murtiningsih R 2010 Effect of insecticide mixtures on shallot caterpillars Spodoptera exigua Hubn *J. Hortikultura, 20* (1), pp.67-79. http://hortikultura.litbang.pertanian.go.id/jurnal_pdf/201/moekasan_ulatbawang.pdf

[13] Lu P, Li Q, Liu H, Feng Z, Yan X, Hong Q and Li S 2013 Biodegradation of chlorpyrifos and 3, 5, 6-trichloro-2-pyridinol by Cupriavidus sp. DT-1. *Bioresource technology, 127*, 337-342. https://doi.org/10.1016/j.biortech.2012.09.116 .

[14] Akbar S and Sultan S 2016 Soil bacteria showing a potential of chlorpyrifos degradation and plant growth enhancement. *brazilian journal of microbiology, 47* (3), 563-570 https://doi.org/10.1016/j.bjm.2016.04.009

[15] Centre of Agricultural Extension Sape district Kecamatan Sape 2018 Report of fertilizer use in Sape District. *Bima Regency, 2017* 19 pages

[16] Suganda H, A Rachman and S Sotono 2006 *Soil Sampling Instructrctions* Eds: U. Kurnia, F. Agus, A. Adimihardja, and A. Dariah. Indonesian Center for Agricultural Land Resources Research and Development Pp:3-24

[17] Anastassiadis, SJ Lehotay, D Stajnbaher and FJ Schenck 2003 Fast and easy multiresidue method employing acetonitrile extraction/partitioning and “dispersive solid-phase extraction” for the determination of pesticide residues in produce *JAOAC Int 86* (2) 412-31. DOI: 10.1093/jaoac/86.2.412
[18] Centre of Licensing and Investment, Ministry of Agriculture 2006 Registered Pesticides for Agriculture and Forestry

[19] Centre for Soils and Agroclimate Research and Development Soils classification 1998, atlas of land resources scale 1:1.000.000 Centre for Soils and Agroclimate Research and Development Indonesian Agency for Agricultural Research and Development. Department of Agriculture

[20] Indonesian Soil Research Institute 2009 Technical Guidelines for Chemical Analysis of Soil, Plants, Water, and Fertilizers. Edition 2. Indonesian Soil Research Institute. Bogor

[21] Kaihatu S, Waas ED and Ayal Y. 2016 Jurnal Pertanian Agros, 18 (2), 170-180. e-journal.janabadra.ac.id

[22] Kookana R S 2010 The role of biochar in modifying the environmental fate, bioavailability, and efficacy of pesticides in soils: a review. Soil Research, 48 (7), pp.627-637. https://www.publish.csiro.au/SR/SR10007

[23] Poniman, Indratin and Ukhwatul Muanisa 2017 Utilization of biochar and activated charcoal from agricultural waste to reduce pesticide residues in soil and rice Proceedings of the National Seminar on Agricultural Research VII Faculty of Agriculture Gadjahmada University. Pp:228-235

[24] Castelo-Grande T, Augusto PA, Monteiro P, Estevez AM and Barbosa D 2010 Remediation of soils contaminated with pesticides: a review. International Journal of Environmental and Analytical Chemistry, 90 (3-6), 438-467 https://doi.org/10.1080/03067310903374152

[25] Wang X, Song L, Li Z, Ni Z, Bao J and Zhang H 2019 The remediation of chlorpyrifos-contaminated soil by immobilized white-rot fungi J. Serb. Chem. Soc. 84 (0) Pp: 1-12 https://www.researchgate.net/publication/337848314

[26] Islam MS, Ahmed MK, Rakuzzaman M, Habibullah-Al-Mamun M and Islam MK 2015 Heavy metal pollution in surface water and sediment: a preliminary assessment of an urban river in a developing country. Ecological indicators, 48, 282-291. https://doi.org/10.1016/j.ecolid.2018.08.016

[27] Singh DP, Khattar JS, Kaur K, Sandhu BS and Singh Y 2012 Toxicological impact of anilofos on some physiological processes of a rice field cyanobacterium Anabaena torulosa. Toxicological & Environmental Chemistry, 94(7), pp.1304-1318 https://doi.org/10.1080/02772248.2012.703203

[28] Roger PA and Bhuiyan SI 2012 5 Behavior of pesticides in rice-based agroecosystems. Impact of Pesticides on Farmer Health and the Rice Environment, 7, p.111. https://books.google.co.id/books?id=FuhqCAAAQBAJ&lpg=PA111&ots=J9rpC-R5rd&dq=Rajagopal%20BS%2C%20Brahmaprakash%2C%20BR%20Reddy%2C%20UD%20Singh%20and%20N%20Set

[29] Chaplain V, Mamy L, Vieublé L, Mougin C, Benoit P and Nelieu, S., 2011. Fate of pesticides in soils: Toward an integrated approach of influential factors (p. np). In Tech 21(4): 124-32. https://hal.archives-ouvertes.fr/hal-01192228/document [30] Supreeth, M., Chandrashekar, M.A., Sachin, N. and Raju, N.S., 2016. Effect of chlorpyrifos on soil microbial diversity and its biotransformation by Streptomyces sp. HP-11. 3 Biotech, 6(2), p.147. https://doi.org/10.1007/s13205-016-0462-2

[31] Briceno G, Fuentes M S, Palma G, Jorquera M A, Amoroso M J and Diez M C 2012 Chlorpyrifos biodegradation and 3, 5, 6-trichloro-2-pyridinol production by actinobacteria isolated from soil. International Biodeterioration & Biodegradation, 73, 1-7. https://doi.org/10.1016/j.ibiod.2012.06.002

[32] Das S and Adhia TK 2015 Degradation of chlorpyrifos in tropical rice soils. Journal of environmental management, 152, 36-42. https://doi.org/10.1016/j.jenvman.2015.01.025

[33] Filimon M N, Voia S O, Popescu ROXANA, Dumitrescu GABI, Ciochina L P, Mituletu M and VlAD DC 2015 The effect of some insecticides on soil microorganisms based on enzymatic
and bacteriological analyses. *Romanian Biotechnological Letters*, 20(3), p.10439. http://www.rombio.eu/rrbl3vol20/9.pdf

[34] Lo CC 2010 Effect of pesticides on soil microbial community. *Journal of Environmental Science and Health Part B*, 45 (5), 348-59. https://doi.org/10.1080/03601231003799804

[33] Chanika E, Georgiadou D, Soueref E, Karas P, Karanasios E, Tsiropoulos N G and Karpouzas DG 2011 Isolation of soil bacteria able to hydrolyze both organophosphate and carbamate pesticides *Bioresource technology* 102 (3), 3184-92. https://doi.org/10.1016/j.biortech.2010.10.145

[36] Indratin and S Wahyuni 2015 Accelerate degradation of the POPs residue with microbial enrichment *Proceedings of National Seminar XII* The Education of biology, Faculty of Teacher Training and Education Sebelas Maret University. Pp:803-07

[37] Padmini, E., 2010. Physiological adaptations of stressed fish to polluted environments: role of heat shock proteins. In *Reviews of Environmental Contamination and Toxicology Volume 206* (pp. 1-27). Springer, New York, NY. https://link.springer.com/chapter/10.1007/978-1-4419-6260-7_1

[38] Sahitnya K and Das N 2015 Remediation of pesticides using nanomaterials: an overview. *Int J ChemTech Res*, 8 (8), 86-91

[39] Muzammil A, Miandad R, Waqas M, Gehany F and Barakat MA 2016 Remediation of wastewater using various nanomaterials. *Arabian Journal of Chemistry Arabian Journal of Chemistry*. https://www.researchgate.net/publication/309305958