The Study Of Adsorption Efficiency Of Silica nanoparticles hydrophilic For Removal Of Glyphosate Residue

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Abstract :
The current study was conducted in the laboratories of the College of Agriculture, University of Kerbala. The aim of the study was to evaluate the residual of glyphosate Tiller 48% SL in aqueous water with the use of Silica nanoparticles hydrophilic as a water adsorption agent to remove the glyphosate. The result of the study showed that the glyphosate residue for 15 days with three concentrations 10 , 15 and 20 ml/L water. The treated water contained a high concentration of the pesticide after treatment, as it recorded 3520,5600 and 7955 mg L-1, respectively. concentration of the herbicides decreased and within several days reached 1203 mg L-1on the tenth day
. The HPLC was not sensitive to any concentration after 21 days of treatment. The results of the study of the use of Nano-silica as an agent in the removal of glyphosate in aqueous water showed that the concentration 200 mg L-1It achieved the highest rate of herbicide removal with a percentage of 89.37 % , outperforming the other concentrations of 100 and 150 mg L-1, which achieved 63.45 and 82.87%, respectively.
Keywords: Glyphosate , Residue , silica nanoparticles, adsorption .

1. Introduction

Glyphosate (C3 H8 NO5 P) or (N-(phosphonomethyl) glycine) is widely used around the world to combat weeds in agriculture horticulture, and silviculture (Myers et al., 2016). The fate pathways of glyphosate in the soil are complex and attributable to mineralization, degradation, immobilization, and leaching to the rivers, water bodies, and groundwater (Mesnage et al., 2019). It is widely used in protecting crops from weeds (Singh et al., 2020). Increasing the use of glyphosate frequently, often at higher doses than recommended, led to the accumulation of large and excessive amounts in the soil and, consequently, its access to groundwater and trocar water by washing and leaching the soil by rains (Duke,2018 ; Jayasumaua 2014)

Environmental studies related to pollution are growing concerns about the fate of herbicides, especially glyphosate, because of its wide range and use more than once during the season, which leads to the accumulation of herbicides and their drift and leaching into body water and groundwater, there is evidence of its risks for living organisms, including humans (Guyton et al., 2015).

At present time in Iraq, many studies have been conducted to study pesticide contamination and its residual effect on vegetable products and their behavior in the plant and soil (Abu-Duka and Mohammadali 2021; Tulali and Mohammadali 2021).

Adsorption is one of the most promising and efficient processes for removing pesticide residues in water, due to its low cost, high performance, and ease of use (Zhou et al., 2017). Due to the importance of the Glyphosate pesticide in weeds control and also its use in large quantities, many researchers were interested in conducting studies on the mechanism of absorption of the pesticide in water using materials for its absorption (Sophiphun et al., 2022). One of the most used materials in the absorption of water pollutants is carbon, as mentioned in several studies, but it is expensive and difficult to replenish the sorbent in it (Mojiri et al. 2020). Therefore, some studies have suggested the use of silica nanoparticles, which is an alternative material to adsorb glyphosate, and studies have proven its ability to adsorb the herbicide, which is inexpensive and can be prepared and obtained easily (Chindaprasirt et al., 2020). The study aimed to estimate the glyphosate residues in water and to evaluate the efficiency of silica nanoparticles as an adsorbing agent for the herbicide to be removed from the water .

Materials and Methods

Chemicals used and Collection of soil samples

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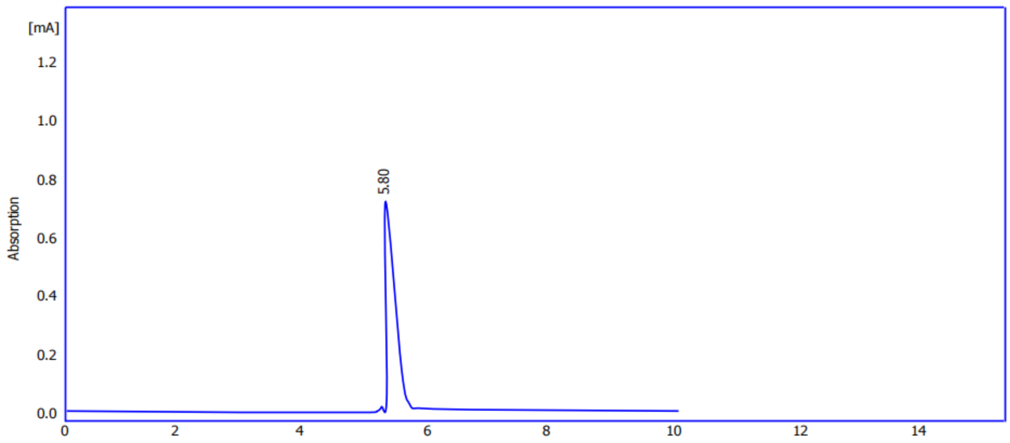
The isopropylamine salt of glyphosate known as Tiller® (containing 480 g active ingredient/L of glyphosate, ASTRACHEM - KSA) was purchased from a local agent in Baghdad, Iraq. Collection of water samples were obtained from the pond water at Agricultural Research Station in the College of Agriculture - Kerbala University - Al-Hussainiya - Kerbala. Three concentrations were used : 10, 15 and 20 ml / L of commercial pesticide. Three samples for each concentration were taken before the treatment, immediately after the treatment and 3, 7, 10 and 15 days after the treatment. The samples were kept in polypropylene tubes in the freezer at a temperature of -20°C until the extraction process was carried out .

QuEChERS Method Extraction

10 gm of the sample were taken in a 100 mL polypropylene centrifuge tube and 10 gm of the sample were taken in a 100 mL polypropylene centrifuge tube and 10 mL of distilled water was added. 10 ml was added for extraction of acetonitrile to the sample and shaking vigorously for 1 min. After the addition of salts (4 ± 0.2 g magnesium sulfate anhydrous, 1 ± 0.05 g sodium chloride, 1 ± 0.05 g trisodium citrate dehydrate , and 0.5 ± 0.03 g disodium hydrogen citrate sesquihydrate), The mixture was vigorously shaken, centrifuged and separated into phases . At least 8 mL of the extract was transferred to a 15 mL single-use centrifuge tube and stored in the freezer (1 h) By the time the extract was almost thawed, an aliquot of 6 mL was transferred to a 15 mL single-use centrifuge tube containing 150 mg primary secondary amine and 900 mg $MgSO_4$, used for the cleanup extract to remove interferences and reduce contamination of the instrument , and was shaken vigorously for 1 min. After an additional centrifugation step, the final extract was transferred to screw-cap storage tubes and stored in a freezer until analysis (Pei et al., 2019).

HPLC model and Conditions :

A high-efficiency liquid chromatography (HPLC) SHIMADZU/LC-20AD was used to detect the residual effect of the glyphosate. Chromatographic column: NH_2 (5μm) 250 mm x 4.6 mm, mobile phase: 85% water solution KH_2PO_4 with 1,5% NaOH 3M : 15% Acetonitrile (80 : 20 V/V) at flow rate 0,8 ml/min, the detector was Fluorescence detection at Ex = 265 nm, and Em = 310 nm. Fig (1) .



Result chromatography Table (Uncal - F:\ Glyphosate (10 PPM)

No	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W 05 [min]	Compound Name
1	5.80	3220.98	985.49	100.00	100.00	0.25	
	Total	3220.98	985.49	100.00	100.00		

Fig. (1) Standard curve substance for the Glyphosate.

Silica nanoparticles hydrophilic as an adsorbing agent for pesticide removal

Silica nanoparticles hydrophilic were provided by US Research Nanomaterials, Inc.USA fig. (2) .

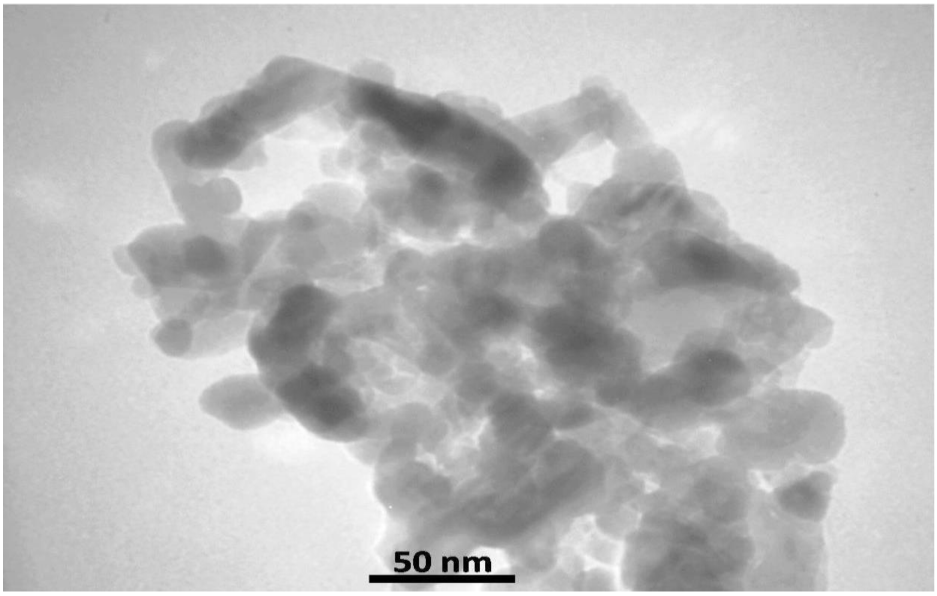


Fig (2) Silica nanoparticles hydrophilic .

For the purpose of estimating the adsorption of glyphosate. The method described by Carneiro et al. (2015) and Sen and Mondal (2020) was followed by the following steps :

Standard Curve

The standard curve for estimating the concentration of Glyphosate was prepared taking different concentrations of 5, 10, 20, 25, 30 and 35 mg . For each of the prepared concentrations, 1 ml of Ninhydrin 5% and 1 ml of sodium molybdate 5% were added, the mixture was incubated in a water bath at a temperature of 100°C for 5 minutes and then left to cool at room temperature, after which the absorbance was read with an EMC-11-UV spectrophotometer at 570 Nm .Fig(2) .

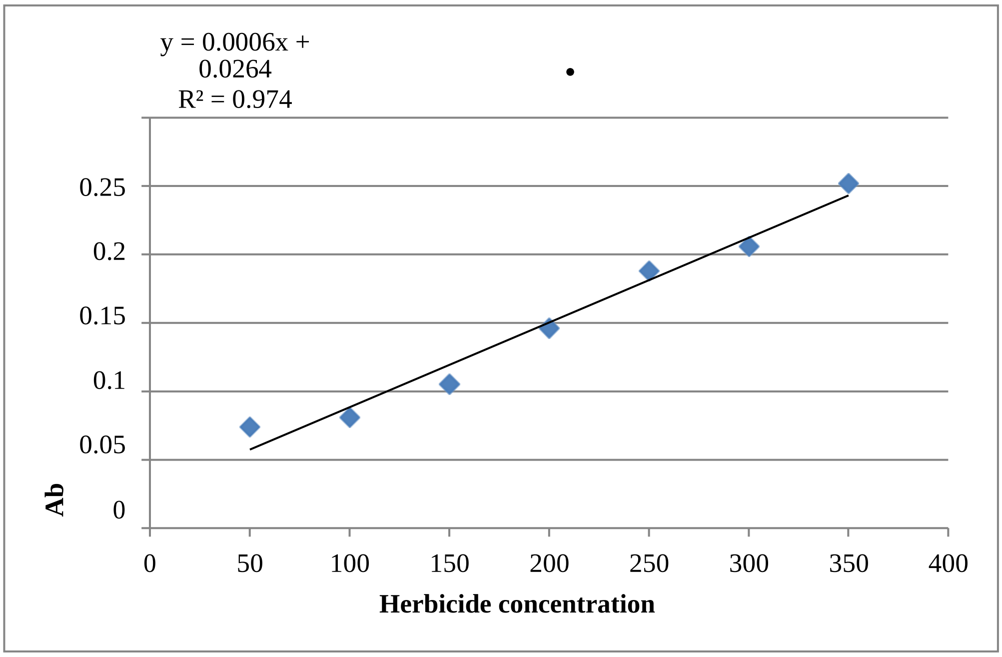


Fig (2) Standard curve for Glyphosate .

Pesticide adsorption using silica nanoparticles hydrophilic
Three concentrations of silica nanoparticles hydrophilic 100, 150 and 200 mg L-1 were prepared, 1 ml of each concentration was added to 2 ml of glyphosate , 1 ml of Ninhydrin %5 and 1 ml of Sodium Molybdate %5 and then transferred to a water bath at a temperature of 100 m° for 5 minutes and then transferred to a shaker for 50 minutes equilibrium time and then the plastic tubes were transferred to a centrifuge 85 minute cycles for 15 minutes, the filtration process was neglect of the precipitate, after calculating the absorbance with a spectrophotometer at 570 Nm, the equation below was applied to find out the percentage of pesticide removed Asouhidou et al. (2009).

$$Remaval\ \text{Herbicide}\ \% = \left\{\frac{\text{Cinitial}-\text{Cadsorpition}}{\text{Cinitia}}\right\} \times 100$$

Results and Discussion
The results of a study of Glyphosate residues in water Fig. (3) showed that the three used concentrations of 10, 15 and 20 ml / L water recorded 3520, 5600 and 7955 mg L-1, respectively, immediately after the treatment, then the concentration of the pesticide began to decrease over the days under study until reaching 822, 2011 and 3652 mg L-1, respectively, on the seventh day .

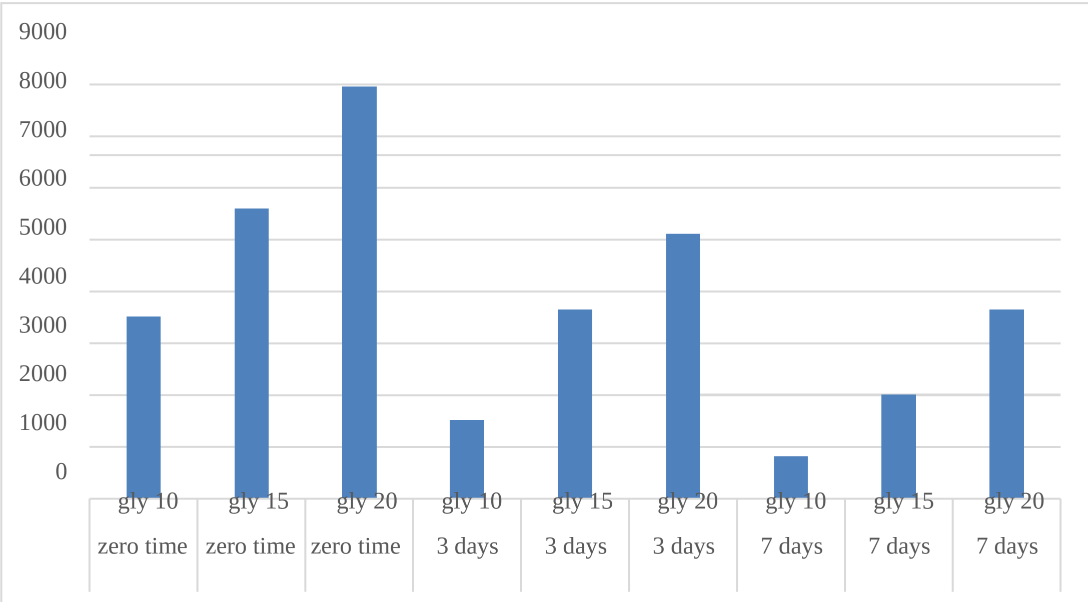


Fig. (3) Determination of Glyphosate mg/L in water using 3 concentrations with the time factor.

The results in Fig. (4) showed that the concentrations decreased on the tenth day, recording 356, 852 and 1203 mg L-1, respectively, and then on the 15th day the HPLC did not detect any concentration of the concentrations used in the water treatment .

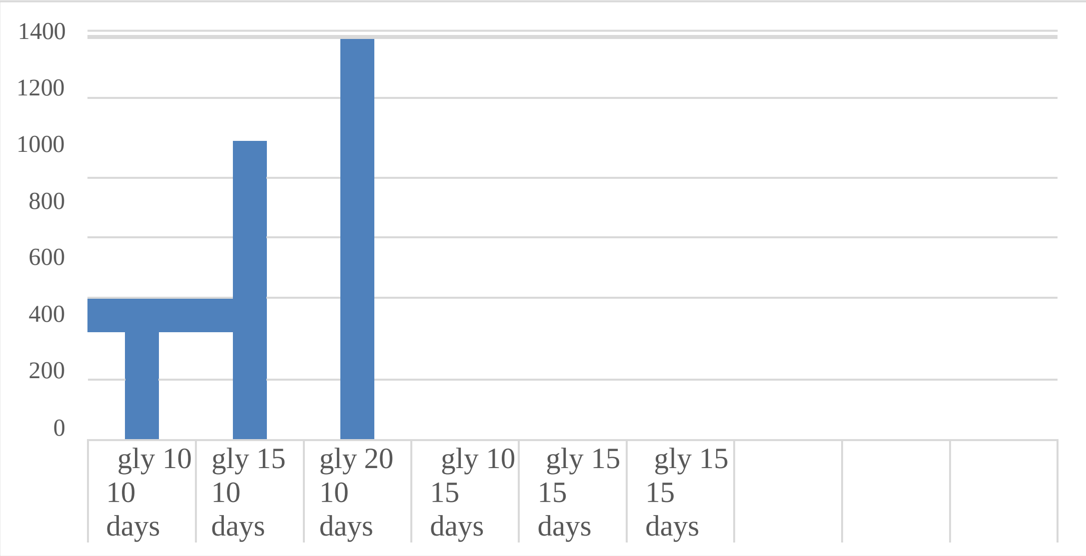


Fig. (4) Determination of Glyphosate (mg/L) in water after 10 and 15 days.

Evandro et al. (2017) indicated in a study conducted to measure glyphosate herbicide residues and estimate the half-time Half-Life in water basins infested with water lily bushes and clean ones in Brazil at the recommended concentration of 7 l / ha, where the Half-Life of the herbicide was estimated at 16 days in water lily ponds and 6 days in clean ponds. Bandana et al. (2015) also conducted a study to determine the fading of glyphosate residues applied at three dose levels in the tea crop in the northwestern Himalayas in India over two consecutive seasons. The presence of glyphosate in the soil persisted for up to 30, 45 and 60 days at concentrations of 0.5, 1 and 2 l / ha, respectively . The half-lives of glyphosate ranged from 5.80 to 19.10 days in the soil of tea fields .

Silica nanoparticles Hydrophilic as an adsorbing agent for pesticide removal

The results showed Table (2) Fig. (5) that the concentrations after 50 minutes at equilibrium, a relative stability occurs, which caused the percentage values of the adsorption efficiency to be fixed, where time 50 achieved the best equilibrium time in the removal of the pesticide reached 81.55%, the results indicated that the equilibrium time begins 50 minutes after the start of the adsorption process for hydrophilic silica nanoparticles and that this stability is due to the absence of unoccupied adsorption sites on the surfaces of the nanomaterial.

Table (1) Estimation of equilibrium time

Glyphosate removal (%)	Glyphosate concentration (ppm)	Time (min)
1.71	344	10
20.98	276.56	20
49.05	178.34	30
67.26	114.58	40
81.55	64.56	50
81.56	64.55	60
81.59	64.45	70
9581.	65.48	80

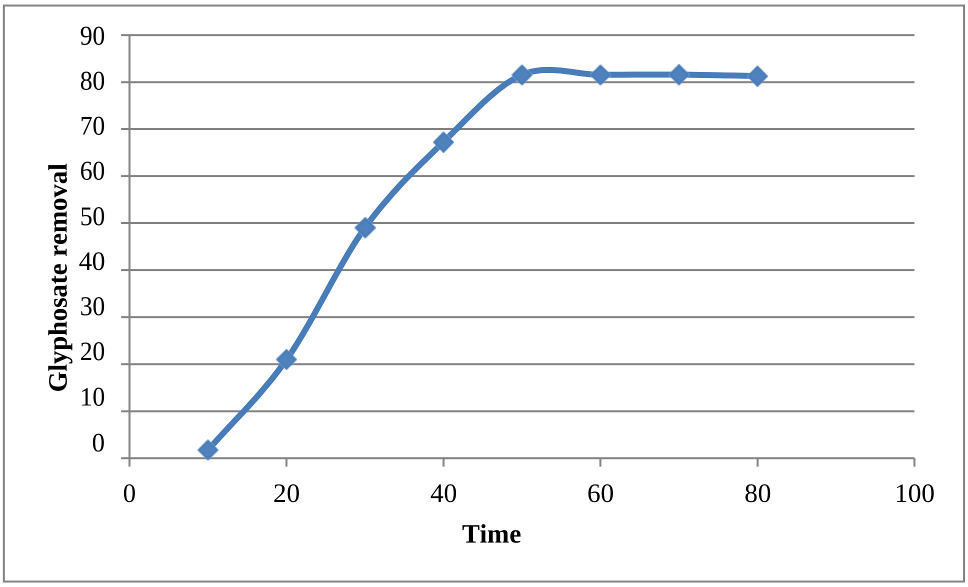


Fig.(5) Estimation of equilibrium time.

The results of the study of the use of silica nanoparticles as a glyphosate removal agent in water Form (6) showed that the concentration of 200 mg L-1 achieved the highest rate of pesticide removal, with a percentage of 89.37, superior to the other concentrations of 100 and 150 mg L-1, which achieved 63.45 and 82.87%, respectively .

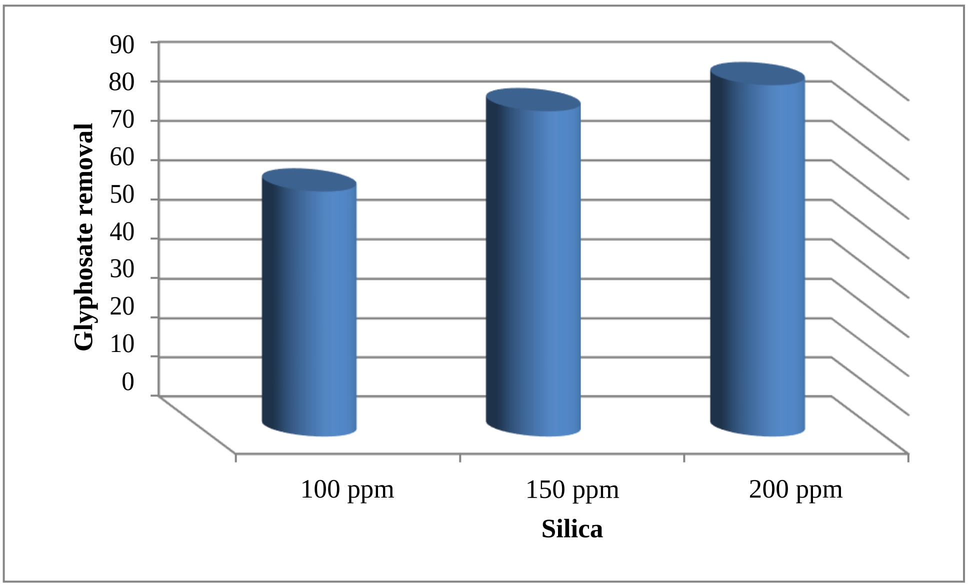


Fig (6) Efficiency of Silica nanoparticles as a glyphosate removal agent in water .

Boruah et al. (2017) found in a study that conducted the adsorption of five herbicides (Ametryn Prometryn, Simazine, Simeton, Atrazine) from aqueous solution using Fe3O4 nanocomposite. The results showed that the nanocomposite had an excellent performance in the adsorption of the five herbicides, recording an adsorption efficiency of 93.6%. Bagheini et al. (2018) indicated that the use of silica-coated magnetic nanoparticles achieved 84% removal of insecticide diazinon after 30 minutes. According to Sophia and Lima (2018) the use of nanocomposite is a promising, low-cost, practical and effective method for removing organic and inorganic pollutants in aqueous solution. Adsorption mechanisms can be a physical action, chemical bonding via a strong covalent bond, weak van der Waals forces, cation exchange, dipole-dipole exchange, or ion-dipole interactions (Mojiri et al., 2020).

Conclusions

According to the study, highly efficient removal may be made possible by properly functionalizing the adsorbent surface and tailoring the experimental setup to the type of herbicide . To sum up the results, Silica nanocomposites are used in a variety of fields because of their porosity, monodispersity, stability, and low toxicity. The latest developments in the synthesis, functionalization, and modification of SINPS are all summarized in this review, with a focus on how pesticide analysis and detoxification are used in these processes.

References :

Abu-Duka A. and Mohammadali M. 2021. Study of the effectiveness of pesticides Thiamethoxam and Acetamiprid against cabbage aphid *Brevicoryne brassicae* and measure the residue of acetamiprid in leaves and soil of cabbage using HPLC . Plant Cell Biotechnology and Molecular Biology 22(19&20):123-129 .

Asouhidou D., Triantafyllidis K. S., Lazaridis N. K., Matis K. A. 2009. Adsorption of remazol Red 3BS from aqueous solutions using APTES- and cyclodextrin-modified HMStype mesoporous silicas. Colloids Surface ,346: 83–90 .

Bagheini A., Saeidi M., Boroomand N.2018. Removal of diazinon pesticide using amino-silane modified magnetite nanoparticles from contaminated water. International Journal Nanosciences Nanotechnology, 14 (1) , pp. 19-32.

Bandana B., Neelam S., Robin J., Ashu G. , Shobha S. 2015. Dissipation kinetics of glyphosate in tea and tea-field under northwestern mid-hill conditions of India. Journal of Pesticide Science , 40(3), 1–5. DOI https://doi.org/10.1584/jpestics.D14-085 .

Carneiro, R. T., T. B. Taketa, R. J. G. Neto, J. L. Oliveira, E. V. Campos, M. A. de Moraes and L. F. Fraceto. 2015. Removal of glyphosate herbicide from water using biopolymer membranes. Journal of environmental management, 151: 353- 360 . DOI: https://doi.org/10.1016/j.jenvman.2015.01.005

Chindaprasirt, P. and Rattanasak, U., 2020. Eco-production of silica from sugarcane bagasse ash for use as a photochromic pigment filter. Scientific Reports, 10, DOI: 10.1038/s41598-020-66885-y .

Duke, S.O. 2018 . The history and current status of glyphosate. Pest. Manag. Sci., 74, 5. Pages 1027-1034 . https://doi.org/10.1002/ps.4652.

Evandro L. C., Luiz L. F., José T. Fi., Edivaldo D. V., Luis M. S., José R. M. 2017. Half-Life of Glyphosate on the Control of Water Hyacinths in Water Tanks . Journal of Water Resource and Protection, 2017, 9, 470-481. DOI: 10.4236/jwarp.2017.95030

Guyton K Z, Loomia D, Grosse Y, El Ghissassi F, Benbrahim-Tallaa L, Guha N, Scoccianti C, Mattock H, Straif K. on behalf of the International Agency for Research on Cancer Monograph Working Group, IARC, Lyon, France. 2015. Carcinogenicity of tetrachlorvinphos, parathion, malathion, diazinon, and glyphosate. Lancet Oncol. 16: 5,490—491.

Mesnage R, Benbrook C, Antoniou MN. 2019. Insight into the confusion over surfactant co-formulants in glyphosate-based herbicides. Food and Chemical Toxicology. 2019;128:137-145 .

Mojiri, A., Zhou, J.L., Robinson, B., Ohashi, A., Ozaki, N., Kinsaichi, T., Farraji, H. and Vakili, M., 2020. Pesticides in aquatic environments and their removal by adsorption methods. Chemosphere, 253, DOI: 10.1016/j.chemosphere.2020.126646.

Myers, J.P., Antoniou, M.N., Blumberg, B., Caroll, L., Colborn, T., Everett, L.G., Hansen, M., Landrigan, P.J., Lanphear, B.P., Mesnage, R., Vanderberg, L.N., Vom Saal, F.S., Wv, Welshons, Benbrook, C.M., 2016. Concerns over use of glyphosate-based herbicides and risks associated with exposures: a consensus statement. Environ. Health 15 (19). https://doi.org/10.1186/s12940-016-0117-0.

Pei Zhang, Mick Rose and Lukas Van Zwieten . 2019. Direct Determination of Glyphosate and its Metabolite AMPA in Soil Using Mixed-Mode Solid-Phase Purification and LC-MS/MS Determination on a Hypercarb Column . Journal of AOAC INTERNATIONAL, Volume 102, Issue 3, 1 May 2019, Pages 952–965, https://doi.org/10.5740/jaoacint.18-0287 .

Sen, K and N. K. Mondal.2020. Facile fabrication of aminofunctionalized silicon flakes for removal of organophosphorus herbicide: in silico optimization. Water Conservation Science and Engineering, 5: 67-80 .

Singh ,S. ; Kumar ,V. ; Gill , J. p. Datta , s. ; Singh, s. ; Dhaka , v. ; Kapoor, d. ; Wani, a.b.; Kumar,m. ; Harikumar, l.s.; and Singh, j. 2020. Herbicide Glyphosate: Toxicity and Microbial Degradation :*17*(20), 7519.
https://doi.org/10.3390/ijerph17207519

Sophia C., Lima E.2018. Removal of emerging contaminants from environment by adsorption Ecotoxicology. Environmental., 150 (2018), pp. 1- 17.https://doi.org/10.1016/j.ecoenv.2017.12.026

Sophiphun O .; Sontichai C. and Chanakan L .2022. Evaluation of Synthesis Method of Fe Loaded Amorphous Silica on the Adsorption of Glyphosate . Current Applied Science and Technology Vol. 23 No. 3(1-12).

Tulail, S. and Mohammadali, M. 2021 . Bio-efficacy of Abamectin against two- spotted spider mite *Tetranychus urticae* Koch and their residues in fruit Cucumber under greenhouse condition. Plant Cell Biotechnology and Molecular Biology 22(33&34), pp. 137-144.

Zhou, C., Jia, D., Liu, X. and Li, C. 2017. Removal of glyphosate from aqueous solution using nanosizes copper hydroxide modified resin: equilibrium isotherms and kinetics. Journal of Chemical and Engineering Data, 62(10), 3585-3592. https://doi.org/10.1021/acs.jced.7b00569.