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Radiation Copolymerization Induced Imprinting Copolymers Applied in Water Treatment Processes for Removal of Herbicides as Pollutants

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Abstract: This research mainly purposes the reducing amount of herbicides used in agriculture, protect human from water carried herbicides which one of the main pollutants that cause serious problems by Molecular Imprinting Technology (MIT) applied for the synthesis of environmental pollutants such as (Glyphosate and Nominee) herbicides. In this study different monomer ratios of Methacrylic acid (MAA) with Styrene (ST) as two function monomers were copolymerized with mixture of; Ethylene Glycol Dimethacrylate (EGDMA) as cross-linker, methanol or chloroform as solvent, and two different types of herbicides as template this mixture initiated by gamma radiation effect at optimum dose 40 KGY. Characterization was performed by Scanning Electron Microscope (SEM), Fourier Transfer Infrared (FTIR), X-Rays Diffraction (XRD), Thermogravimetric analysis (TGA) and Ultraviolet (UV) to study the effect of different parameter in acidic & basic medium at 30°C and thermal study from 30°C-80°C. It give good releasing at 90 /10 MAA/ST in two different types of herbicides after 24 h. From these results, it showed that from 90 to 99% approximately of herbicides can release from Molecular Imprinting Copolymer (MIC).

Keywords: Molecular Imprinting Copolymer; Methacrylic Acid; Styrene; Glyphosate; Nominee

1. Introduction

In recent years, preparation, characterization, and application of Molecularly Imprinted Copolymers (MICs) revealed the gradual maturation of Molecular Imprinting Technology (MIT), and a wider interest on the part of the scientific community in general [1-4]. Molecular imprinting (MI) has been considered as a potentially useful technique for preparing polymer type synthetic receptors. A Molecular Imprinted Copolymer (MIC) receptor that is selective for (Glyphosate, Nominee) herbicides has been recently reported [5, 6]. Affinity and selectivity of the template will be self-increasing as the value concentration increases [7]. Even today, the MICs method is still being developed because it is easy to manufacture polymers; because of its low cost, and is widely used in many biological or chemical target elements, such as those in food or medicine [8, 9]. The synthesis of MIC proceeds in three steps [10]:- (1) the special arrangement of the monomer molecules around the template molecules; (2) polymerization; (3) removal of the template molecule from the copolymer. The first step can be achieved either by covalent or non-covalent interactions between the template and the monomer molecules. Both approaches have been well established and approved by using monomers based on Methacrylic acid (MAA), Styrene (ST) and two different templates (i.e. Glyphosate, Nominee). Glyphosate, which is a weed killing formulation, is a broad-spectrum effective against a large variety of organisms. It is the world's biggest-selling chemical used for weed control in agricultural, silvicultural and urban environments [14-17].

Glyphosate prevents the development of plants by stopping the manufacture of essential aromatic amino acids. Nominee named Bispyribac-sodium, belonging to a pyrimidinylthiobenzoate herbicide [11] is used mainly to control weeds in rice cultivation [12, 13]. The risk of acute exposure to Nominee would be primarily subject to chemical applicators. Minor eye and skin irritation are possible as contact with Nominee can cause respiratory irritation especially upon exposure to high concentrations of it in the air. It is used on crops at a rate of 800cm/acre every 85 days. Radiation-Induced Copolymerization (RIC) carried some merits that can be completed at room temperature, and it does not require the presence of initiators [18]. As the chemical reactions in the processed materials are inhibited by radiation, there is no need to use usually (toxic initiators or other auxiliary substances) [19, 20]. In this article, a feasibility study on the possibility of using an herbicide-specific MIC for controlled release of herbicide into water is described.

2. Experimental

2.1. Materials

Methacrylic acid monomer (MAA) purity 99%, Styrene monomer (ST), both monomers were purchased from (Aldrich Chemical. CO). Two different herbicides (Glyphosate 48%, Nominee 2%) were purchased from (Kefir El Zayat Pesticides-Chemicals Co (S.AE). Methanol and Chloroform 99% were purchased from (El Nasr Chemical. CO), Ethylene Glycol Dimethacrylate (EGDMA) was purchased from (Sigma Co), Acidic and alkaline buffers were purchased from (GB. Chemical). Double-distilled water was used for the preparation of all solutions in this study.

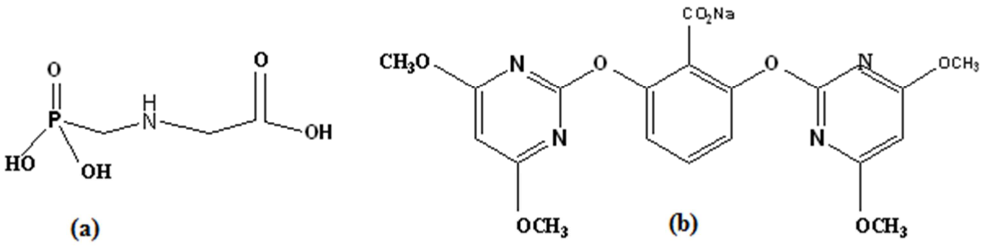

Figure 1. *The chemical structures of two herbicides (a) Glyphosate, (b) Nominee.*

2.2. Preparation of Non-imprinted Copolymer (NIC)

Non-Imprinted Copolymer (NIC) were prepared by mixing different monomer ratios of 50/50, 60/40, 70/30, 80/20, 90/10 MAA/ST monomers with 10 ml methanol and 1 gm of Ethylene Glycol Dimethacrylate (EGDMA) as a cross-linker in 20 ml distilled water and take 5 ml of it. The mixtures were stirring in a glass vessel for 15 min at room temperature then it was bubbled with nitrogen gas to remove the dissolved oxygen for 15 min. The solutions were irradiated with gamma ray at a dose rate of 6.3 KGY/h. After the reactions were completed break the tubes to obtain sticky copolymers and left it to dry in open air for 24 h, it converted into solid copolymers. Then washed it on a hot plate for 2 h, weighed before and after washing to measure the number of monomers were not copolymerized.

2.3. Preparation of Molecular Imprinted Copolymer (MIC)

Molecular Imprinted copolymer (MIC) was prepared in the same manner of NIC with an addition of Glyphosate 0.01 ml (48%) and Nominee 0.25 ml (2%) as a template, then the solutions were irradiated with a gamma ray.

2.4. The Step of Releasing Herbicides from (MIC)

In this step, left copolymers carried herbicides with a known concentration in distilled water for 24 h, measured by UV spectra, to know the concentration of herbicides in water. Using distilled water is slow to get rid of all amounts of herbicides in a matrix of radiated copolymers. Herbicides exit and enter to this cavity again then we must change water after 24 h to reach a low absorbance of herbicides measured by UV spectra. Other solvents were used to measure the number of herbicides released after 24 h and compared by releasing in distilled water at room temperature with different monomers ratio used. Using chloroform as template removal in case of (Glyphosate) & methanol (Nominee).

2.5. Uptake of a Template from Water

In applied part on water obtained from outlet agricultural land of rice crop to measure the ability of MIC which has cavities produced by template removal, take 1 gm of MIC which contains cavities after template removal and soaked it in 100 ml of water carried Nominee and measure FTIR.

2.6. Calibration Curve

Different known concentrations of Glyphosate 48% and Nominee 2% were prepared in mobile phase by diluting the stock solution 5 mg taken from each type of herbicides. Dissolve 0.01 ml of Glyphosate and 0.25 ml of Nominee stock solution in 20 ml distilled water and then take 1ml of this solution in different dilutions 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 ml distilled water, measure the absorbance by UV spectrophotometer.

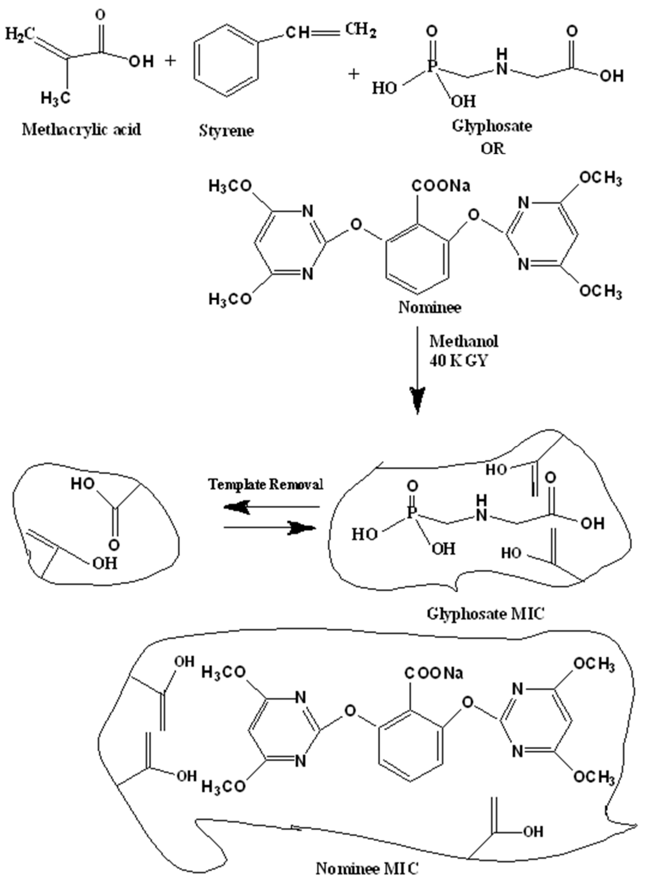

Figure 2. *Represents the steps for preparation of Molecular Imprinted copolymer (MIC) for (Glyphosate, Nominee) herbicides.*

2.7. Characterization and Measurements

All the measurements were carried out at the National Center for Radiation Research and technology, Egyptian Atomic Energy Authority, Nasr City, Cairo, Egypt, (NCRRT).

2.7.1. Gamma Irradiation

Irradiation doses were carried out in ^{60}co gamma cell (Type 4000A, made in India). The dose rate was 6.3 KGY/ h, in the air, in humidity, and at room temperature.

2.7.2. Fourier Transform Infrared (FTIR)

FTIR spectra were obtained in transmission mode using VERTEX 70. The spectra were covered the infrared region 4000-400 cm^{-1}.

2.7.3. X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) analysis was performed at room temperature using XD-DI series using Nickel filtered and Cu-K & target.

2.7.4. Ultra Violet-Visible (UV-Vis)

Absorbance measurements were carried out on double beam UV-Vis spectrophotometer model UV series 2 made by Unicam was used at a wavelength range of 190-900 nm.

2.7.5. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was carried out using a Shimadzu TGA-50 system, Japan. Measurements were carried out from ambient temperature to 600°C at the rate of 10°C/min, Under dry nitrogen at (20 ml/min).

2.7.6. Scanning Electron Microscope (SEM)

The morphology of the samples examined using Scanning electron microscope were taken with a JSM-5400 instrument by JEOL-Japan. A sputter coater was used to pre-coat conductive gold onto the fracture surface before observing the microstructure at 10 KV.

2.8. Gel Fraction

Gel content in the dried sample was estimated by immersing sample in boiling distilled water for 6 h at 100°C, then measuring its insoluble part, Gel fraction was calculated by using the following equation/-

$$\text{Gel (\%)} = {Wd}/{Wi} \times\% \qquad (1)$$

Where W_i is the initial weight of the dried sample after irradiation and W_d is the weight of the dried insoluble part of the sample after extraction from the water.

2.9. Water Uptake Measurements (Swelling Percent%)

The clean, dried crushed solid copolymers of known weights were immersed in distilled water at 30°C until equilibrium. Weighted two samples which carried (Glyphosate, Nominee) and study the water uptake of copolymer alone. Take 1 gm of NIC, MICs for Glyphosate, Nominee and immersed it in 100 ml distilled water. Take read after different hours. Study water uptake in two different shapes of copolymers if using Copolymer as one piece or small crushed pieces. Study the effect of increasing temperature on water uptake% by taking 1 gm of MICs for Glyphosate, Nominee immersed in 200 ml of distilled water. Study the almost water uptake to become constant. The uptake percentage of samples was calculated using the following equation:-

$$\text{Water Uptake\%} = \frac{Ws - Wd}{Wd} \times \% \qquad (2)$$

Where W_d and W_s represent the weights of dry and wet samples respectively.

2.10. Release Studies

Molecular Imprinted copolymers (MICs) were used as fingerprint matrix for release template to make a cavity according to bonds which made by an interaction between MAA/ST/Methanol/EGDMA and two different herbicides which used as a template during gamma ray. Accurately weighted dry sample (2 gm) of each type of MIC was placed in a solution of definite volume (100 ml) and allowed to stand for a period of 24 h at different temperature from 30°C -80°C. The number of herbicides released (mg/g) was calculated using the following equation.

$$q_e = \frac{(Co - Ce)V}{W} \quad (3)$$

where q_e is the number of herbicides released into medium (mg/g), C_o and C_e are the concentrations (mg/l) of the herbicides before and after releasing, respectively, which have been determined using UV-VIS spectrophotometer at identical herbicide's absorbance wavelengths, V is the volume of aqueous phase (L), and W is the weight of dry MAA/ST/Herbicides MIC used (g).

To investigate the effects of the PH of the medium on the release rate and capacity, release for samples under investigation were examined in PH range (1-14). Take 1 gm of MICs for glyphosate, nominee and immersed it in 20 ml of different PH solutions.

To investigate the effect of different monomer ratios on releasing herbicides from MIC to reach optimum release after different time. The concentration of herbicides in aqueous phases were measured using UV spectrophotometer.

3. Results and Discussion

3.1. Preparation of Molecular Imprinted Copolymer (MIC)

Molecular Imprinted copolymers (MICs) were synthesized by reacting different monomer ratios of MAA/ST monomers, cross-linker, solvents, and template were irradiated with a gamma ray. Monomer served as a mold or template. Cross-linker served to form a bond linking the polymer chain with other polymers. While gamma-ray was initiated two monomers to form radicals by breaks each double bond in the two different function monomers used to form a copolymer chain called Poly (Styrene-co-Methacrylic acid). The MIC formed between MAA/ST monomers with a template (Glyphosate or Nominee) occurred in situ in non-covalent interaction. This treatment was useful for hydrogen bond formation, an interaction between two different types of herbicides, MAA, ST, and methanol as solvent, this stage called pre-polymerization. Premix form (Glyphosate, Nominee) mold surrounded by MAA since in the same circumstances, herbicides might also act as the monomer [21]. There was also cross-linker, EGDMA, involves in the reaction of mixture cross-liker called co-polymerization stage. Two different stage pre-polymerization and co-polymerization occurred by a gamma ray. Glyphosate or Nominee MICs effected by radiation dose. Stirring before radiation makes mixture homogeneous and permit formation hydrogen bond between hydroxide groups of two herbicides and a carboxylic acid group of MAA, in the case of glyphosate there is an interaction between secondary amine of glyphosate and a carboxylic acid group of MAA. In case of a nominee, the herbicide may be interaction take place between nitrogen in pyrimidine ring and carboxylic group of methacrylic acid but this bond was difficult to form because tertiary amine in pyrimidine ring can`t break easily. Optimum radiation dose used at 40 KGY to the obtained white solid copolymer. At the end of washing, MIC was expected to produce MIC with specific (glyphosate, nominee) [22]. The good releasing of the largest amount of two different types of herbicides were found in the 90/10 MAA/ST copolymer.

3.2. Study of Different Monomer Ratio Effect on Gel Percent

The Molecular Imprinted Copolymer (MIC) used as the fingerprint of a template. Different monomer ratios were used which affected on releasing process. "Figure 3" Represents the effect of different monomer ratios on gel percent. From the preparation of MAA/ST copolymer at 40 KGY, it was found that; the 90/10 MAA/ST gives high release of glyphosate, nominee herbicides. The higher amount of 90/10 copolymer gives lower gel fraction = 80% selected because its reasonable form, for practical applied, Increasing amount of ST gives higher gel fraction but a low release of herbicide so that there is no insoluble part in distilled water will occur after 24 h.

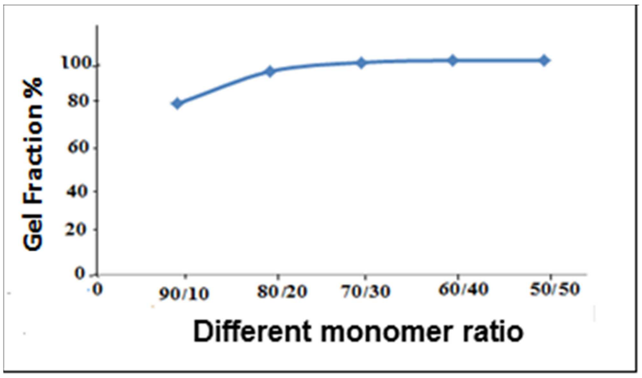

Figure 3. *The effect of different monomer ratio on gell% for the preparation of poly(Styrene-co-Methacrylic acid) at 40 KGY.*

3.3. Water Uptake Swelling%

The ability of copolymer to absorb water was increased with time to become constant after 20 h. Two cases of water uptake studied when using copolymer as one piece, its ability to absorb water was very low but in case of very small pieces of a crushed solid copolymer, its ability to absorb water were increased. From "Figures 4" (a) & (b) it was found that; The (MIC) carried Nominee, its ability to absorb water was higher than (NIC) but lower than (MIC) carried Glyphosate this is because Nominee's structure contains tertiary amine in pyrimidine ring which has lower ability to absorb water than aliphatic amine present in Glyphosate structure. The (MIC) carried Glyphosate have higher water uptake% than (NIC) because Glyphosate herbicide contains secondary amine group which makes interaction with water.

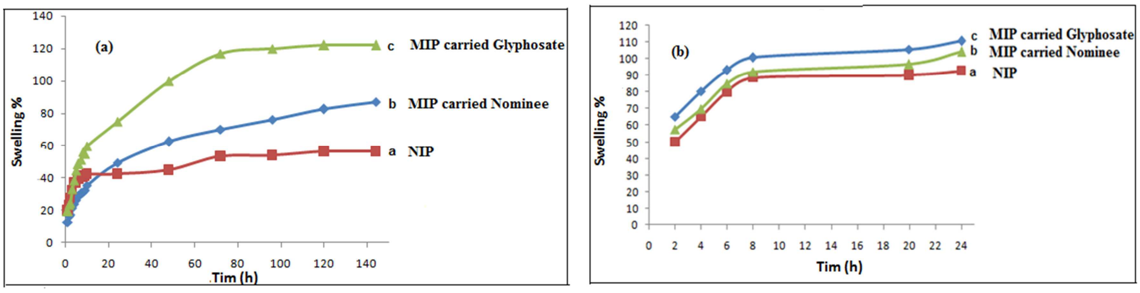

Figure 4. *(a) Show the water uptake% of copolymer as one piece:- (a) NIC, (b) MIC carried nominee, (c) MIC carried glyphosate, (b) Show the water uptake% of copolymer as small pieces:- (a) NIC, (b) MIC carried nominee, (c) MIC carried glyphosate.*

3.4. Effect of Using Different Solvents Characterized by UV

The effect of absorbance on herbicides in different solvents was studied (Glyphosate at λ_{max} 297nm, Nominee at λ_{max} 306 nm) to reach the optimum conditions for high releasing of herbicides. "Figure 5" (a) represents the glyphosate releasing from solid crushed copolymer in distilled water as a solvent. It was found that; optimum release after 24 h at 30°C has occurred because the hydrogen bond between MAA and glyphosate was breaking and dissolved in water (absorbance =1.0792 at λ_{max} 297 nm). In the case of using chloroform as a solvent information of MIC carried glyphosate it gives a good result because of it nonpolar solvent, which allowed for solubility of all components and doesn`t disturb the hydrogen bond. In "Figure 5" (b) it represents the effect of different monomer ratios on glyphosate releasing when using chloroform as template removal, it was found that; the 90/10 MAA/ST copolymer give good releasing after 24 h at 30°C (absorbance = 1.683), but there are problem for using chloroform as glyphosate removal from MIC was highly volatile. "Figure 5" (c) represents releasing of Nominee by using distilled water as template removal at 30°C which gives (absorbance = 0.4803 at λ_{max} 306 nm). But when using methanol as a solvent information of MIC carried Nominee and template removal after 24 h and 36 h, it gives a bad result. Also, we can`t use the chloroform as a solvent information of MIC carried Nominee because it formed two layers. So a good solvent used to the reached optimum removal of Nominee is distilled water.

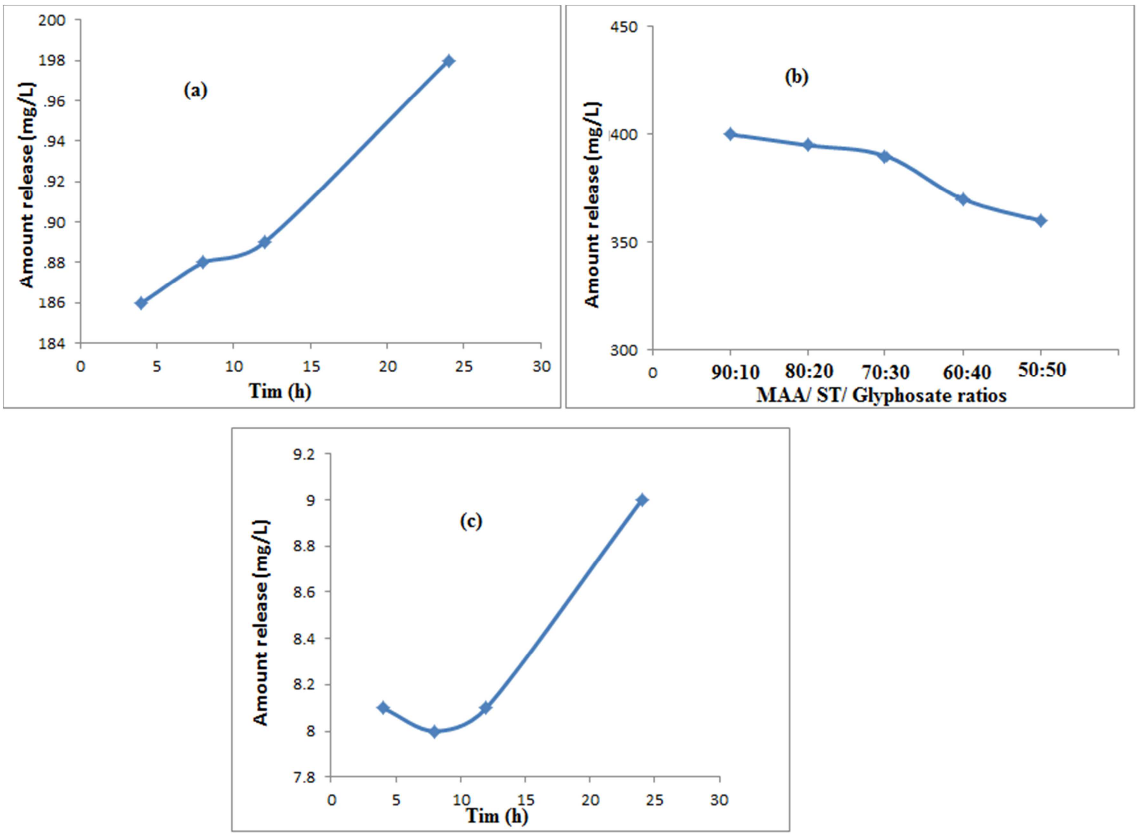

Figure 5. *(a) Different amount of glyphosate released after different times at 30°, (b) Effect of different monomer ratios on releasing of glyphosate from MIC after 24 h at 30°C and (c) Different amount of nominee released after different times at 30°C.*

Calibration curve of the two herbicides graphs were plotted between absorbance and concentration. The curve was found linear up to the lowest concentration range. The calibration chart details are represented in "Figures 6" (a) & (b) given below.

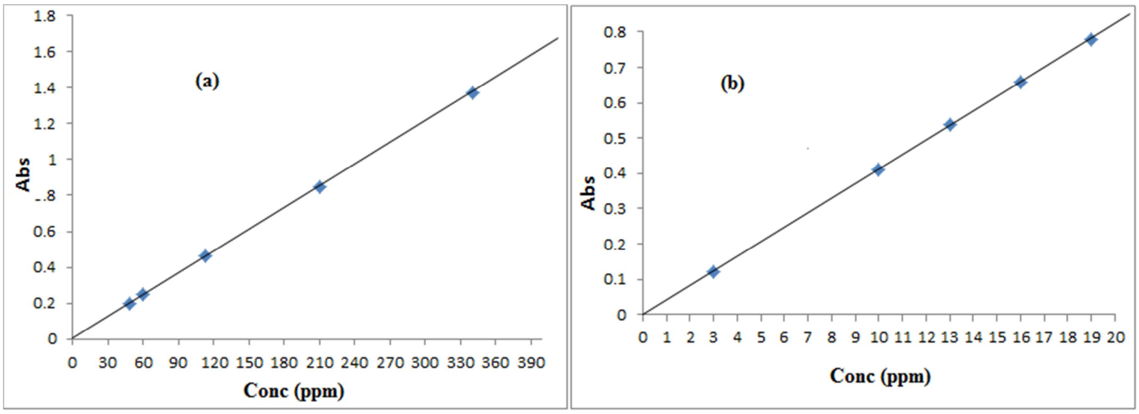

Figure 6. *Calibration curves of: (a) Glyphosate 48%, 5 mg taken from stock and diluted ten times and (b) Nominee 2%, 5mg taken from stock and diluted ten times.*

3.5. Effect of Temperature on Release Capacity

Releasing studies at room temperature. "Figures 7" (a) & (b) Represents the released of glyphosate and nominee herbicides from MIC in distilled water after different hours at 30°C. The results showed that; 90% of herbicides release at room temperature after 24 h.

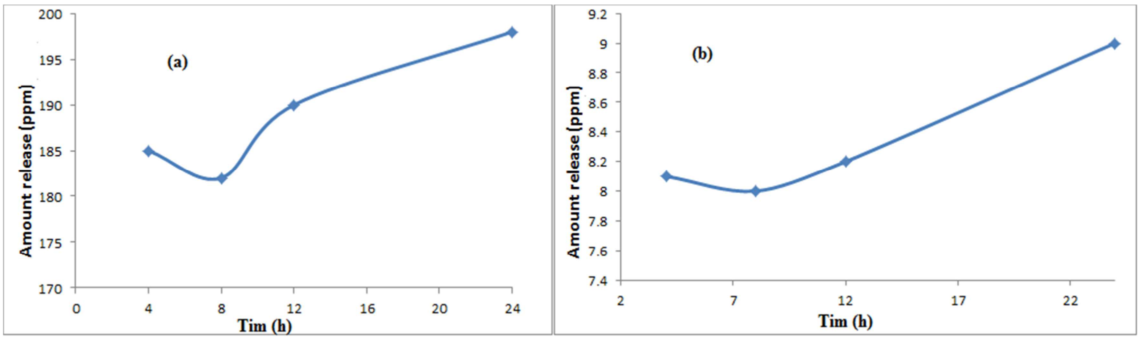

Figure 7. *Shows different amount released after different times at 30°C from (a) glyphosate and (b) nominee.*

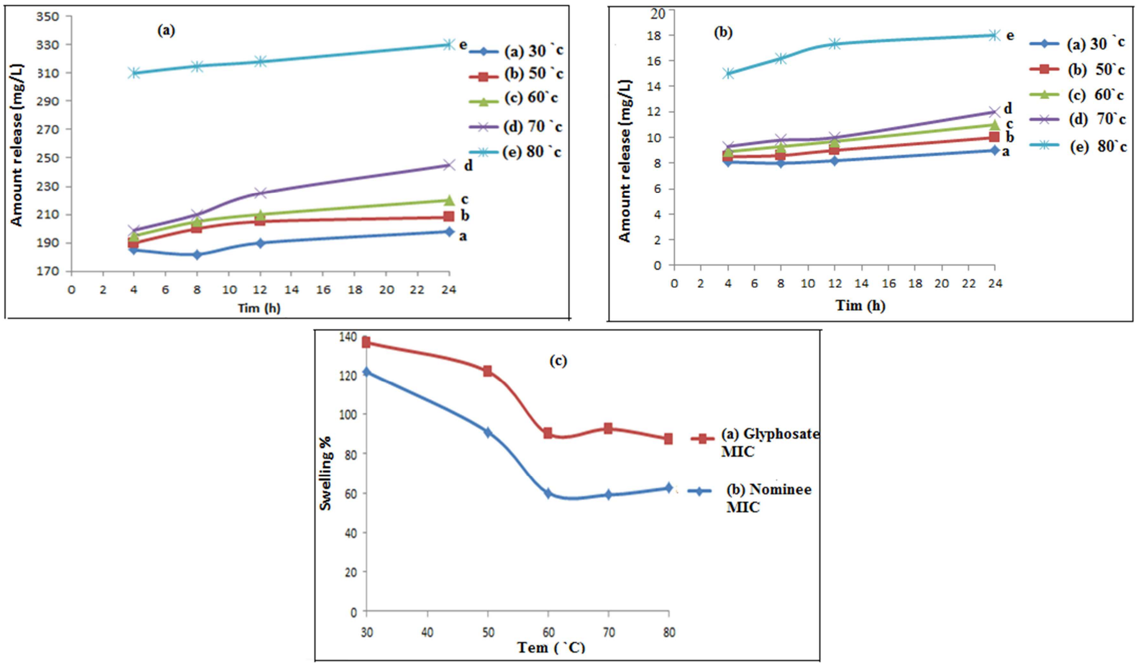

Figure 8. *Shows the Effect of different temperatures on releasing of (a) glyphosate from MIC after 24 h, (b) nominee from MIC after 24 h and (c) water uptake% at temperature range 30-80°C after 24 h, for:- (a) glyphosate MIC, (b) nominee MIC.*

This can be explained by the tendency of the copolymer to shrink however releasing herbicides, in that case, will increase when swelling decrease [23]. “Figure 8” (a) & (b) at higher temperatures this Glyphosate MIC, Nominee MIC display high efficiency, which increases from 30°C to reach 99% of herbicide released at 80°C after 24 h. The increase in a release by the release medium and temperature illustrate that the nature of the release process is endothermic. “Figure 8” (c) it Show water uptake% at temperature range from 30°C to 80°C after 24 h, it was found that; the ability of copolymer to uptake water decreased by increasing temperature this result may be attributed to the competition force affected on copolymer by increase temperature which makes the pores size inside copolymer decreased and makes the ability of copolymer to absorbed water decrease. The ability of glyphosate to uptake water% more than nominee may be because secondary amine in the structure of Glyphosate MIC while in Nominee structure it contains pyrimidine ring which has the low ability to breaks.

3.6. Effect of PH

Study the effect of PH on Glyphosate, Nominee MICs release in Acidic buffer medium (PH 1, 3, 5) and basic alkaline buffer medium (PH 8, 10, 13). “Figure 9” (a) It shows that; in case of glyphosate crushed copolymer in 20ml of different PH ranging from 10-13 PH, it was found that; increasing basicity will increase the release gradually to reach optimum at PH= 13 after 24 h. “Figure 9” (b) It shows that, the Nominee releasing in acidic and basic medium PH=3&10, in the same way, this may be attributed to the presence of pyrimidine ring which is too weakly basic [24] and also contains carboxyl group which are highly acidic, but increasing acidity and basicity make Nominee affected by medium at higher acidity pH=1 release of Nominee decreased and in higher basicity at PH=14 release become the same as in PH=10.

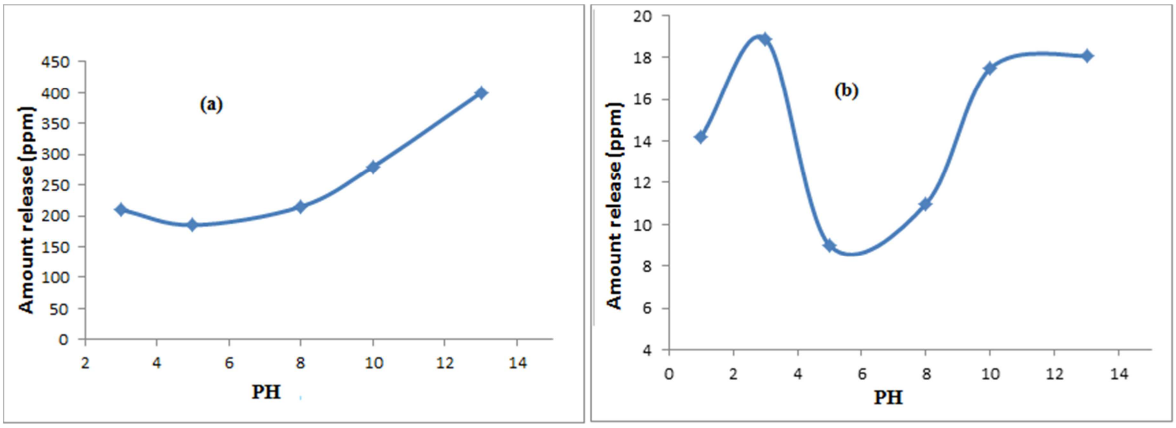

Figure 9. *Shows the effect of changing PH on releasing of (a) glyphosate after 24 h at 30°C and (b) nominee after 24 h At 30°C.*

3.7. Characterization of Molecularly Imprinted by Fourier Transform Infrared (FTIR)

The following FTIR spectra contained NIC or MICs as shown in “Figures 10” (a-j). In “Figure 10” (a) Shows that; the spectrum show broad absorption bands at 3434-3200 cm^{-1} which attributed the stretching of Y OH group of the carboxylic acid. The bands at 3062 & 1533 cm^{-1} are characteristic for benzene ring of styrene [26]. The band at 1711 cm^{-1} is characteristic for the stretching of Y C=O group [25]. The bands at Y 1175 & 1078 cm^{-1} are attributed to the bending vibration of Σ C-O of carboxylic acid. The spectrum indicated that the complete interaction between MAA and ST monomers during gamma radiation to form Poly (Styrene-Co-Methacrylic acid). “Figure 10” (b) Shows the spectrum of glyphosate. “Figure 10” (c) It represents the spectrum of glyphosate MIC, it showed a broad, Stretching band at Y 3734 - 3406 cm^{-1} which attributed to a secondary amine (NH), which is bands to the O-H group of MAA [27]. “Figure 10” (d) It represents the spectrum of release glyphosate from MIC after 24 h at 30°C. “Figure 10” (e) Shows the spectrum indicating the amount of glyphosate released by changing temperature to reach 80°C and the band for NH disappeared. This result was proved also by UV study as shown in “Figure 5” (a). “Figure 10” (f) Shows the spectrum of a nominee. “Figure 10” (g) It represents the spectrum of nominee MIC, it showed a broad stretching band at Y 3597- 3362 cm^{-1} indicating the presence of pyrimidine ring which binds with the O-H group of MAA. The band at 1161 & 1259 cm^{-1} belong to the bending vibration of C-O group of carboxylic acid. “Figure 10” (h) Represents the spectrum of release nominee from MIC after 24 h at 30°C. “Figure 10” (I) Shows the spectrum indicating the amount of nominee released by change temperature to reach 80°C and the band represented for pyrimidine ring disappeared. This result was also proved by UV study as shown in “Figure 5” (b). “Figure 10” (j) It represented a spectrum of poly(Styrene-Co-Methacrylic acid) have cavities produced by releasing of nominee herbicide from it, soaked in water obtained from the outlet of agricultural land of rice crops carried nominee to uptake, Nominee inside fingerprint cavities in copolymer structure after 3 days. The spectrum showed stretching band at Y 3589 cm^{-1} for amine group of pyrimidine ring for Nominee structure. The stretching band at Y 2924 cm^{-1} represent the C-H aliphatic and the stretching band at Y 1689 cm^{-1} which attributed to the C=O group of MAA and Nominee. The conclusion from FTIR spectra are shown about 99% of two different types of herbicides used released after 24 h at 80°C. The also results show that there are different parameters affected on releasing herbicides from MIC, these parameters are, temperature, time, and using fresh water after 24 h.

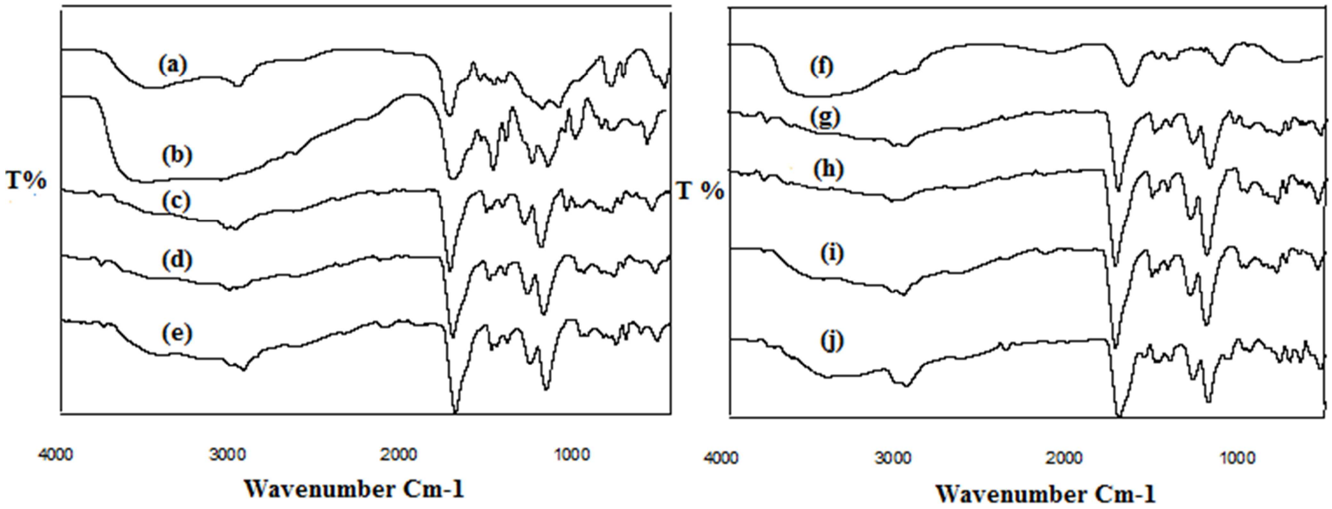

Figure 10. *Shows FTIR spectra of:- (a) Non-Imprinted Copolymer, (b) Glyphosate, (c) MIC carried glyphosate, (d) The release of glyphosate from MIC after 24 h at 30°C, (e) The release of glyphosate from MIC after 24 h at 80°C, (f) Nominee, (g) MIC carried nominee, (h) The release of a nominee from MIC after 24 h at 30°C, (I) The release of a nominee from MIC after 24 h at 80°C and (j) MIC have cavities produced by release nominee from it, soaked in water carried nominee from outlet agricultural land after 3 days.*

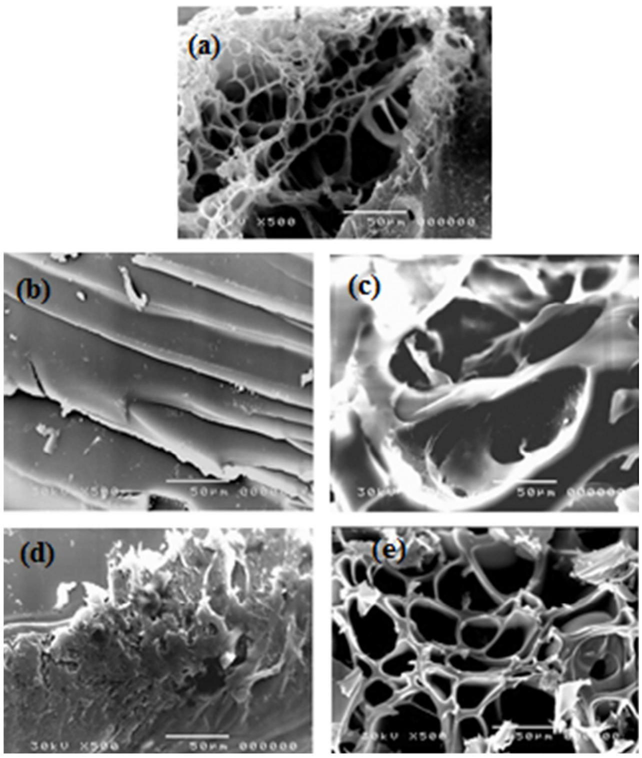

Figure 11. *Show Scanning Electron Microscope (SEM) For: (a) Non-Imprinted Copolymer dry friezed, (b) Glyphosate MIC before washing, (c) Glyphosate MIC after washing dry friezed, (d) Nominee MIC before washing and (e) Nominee MIC after washing dry friezed.*

3.8. Characterization of a Polymer Surface

Scanning Electron Microscope (SEM), this was important information for the synthesis and applications of MICs [28]. The results show SEM of NIP, MICs based Glyphosate and Nominee before, after washing. "Figure 11" (a) Shows dry friezed solid of NIC at optimum swelling after three days, "Figure 11" (b) Shows MIC carried Glyphosate before washing, "Figure 11" (c) Shows MIC carried Glyphosate after washing at optimum release after 24 h dry friezed to keep of cavities which Glyphosate make it after released at 80°C, "Figure 11" (d) Shows MIC carried Nominee before washing, "Figure 11" (e) Shows MIC carried Nominee after washing at optimum release after 24 h dry friezed to keep of cavities which Nominee make it after released at 80°C. After the template removed, the MICs which contain cavities are formed. It is expected that it has the same properties as or similar to those of the template molecules. It is seen that the Glyphosate, Nominee MICs surfaces after template removal is cleaner than before template removal. This finding is indicating that the template removal process is effective [29].

3.9. XRD (X-Rays Diffraction)

X-Rays Diffraction (XRD) technique. "Figures 12" (a-e) Shows XRD patterns of the range 2ϴ = 4.0-90°. In the "Figure 12" (a) Shows the XRD pattern for NIC, it was found that; the peak at 2ϴ= 14° and 17° belong to crystallinity of poly (Styrene-Co-Methacrylic acid) [26], the Strongest two peaks have the highest intensity of NIC which appears at 2ϴ = 77.296° produce more crystalline copolymer. "Figures 12" (b) & (d) Shows XRD patterns for MICs carried glyphosate, nominee, it was found that; the intensity of peak decreased because may be interruption take place in series of copolymer when herbicide make a bond with copolymer during radiation. "Figures 12" (c) & (e) Shows XRD patterns for removal template from MICs, it was found that; the intensity of the peak at 2Θ= 77.296° higher than MICs for Glyphosate and Nominee.

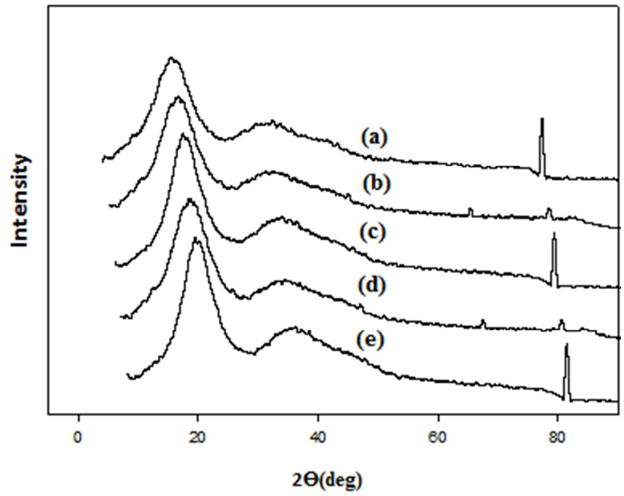

Figure 12. XRD patterns of: (a) NIC, (b) Glyphosate MIC, (c) Release glyphosate from MIC after 24 h at 80°C, (d) Nominee MIC and (e) Release nominee from MIC after 24 h at 80°C.

3.10. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) measurements for MAA/ST NIC and MICs carried herbicides are shown in “Figures 13” (a-e), it rang 25°C-600°C. From these figures we can determine that; the number of herbicides inside the MIC, from thermogravimetric analyzer, can estimate the residual weight, which comparing the weight loss of NIC and MICs particle containing herbicides. The weight remaining against temperature for each composite MAA/ST/methanol NIC, MAA/ST/methanol/Glyphosate MIC and MAA/ST/methanol/Nominee MIC were recorded under nitrogen atmosphere and the corresponding thermogram is illustrated in “Figures 13” (a) & (b) & (d). In “Figures 13” (a-e). It was observed that the slight weight loss occurred at (103-223°C) due to moisture evaporation upon heating. The results shows that; NIC have a thermal stability until 100°C, then the samples become dry by evaporation of water and increases temperature until 200°C, copolymer starts to loss function groups and there are weight loss (7, 5, 6, 6, 3)% for NIC, MIC carry glyphosate, MIC carry nominee, release glyphosate from MIC and release nominee from MIC representatively. In increasing temperature until 500°C, it shows that; NIC loss weight 90% approximately from its original weight. In the case of MIC carried herbicides there are weight loss 73% for glyphosate and 82% for nominee approximately. Also, the study of glyphosate, nominee release cases shows that; 100% weight loss for glyphosate and 85% for nominee. This evidence for the higher thermal stability of the prepared MIC for two herbicides than NIC and releasing cases of two herbicides from the prepared MIC. In Glyphosate release from MIC Up to 500°C, no weight remaining.

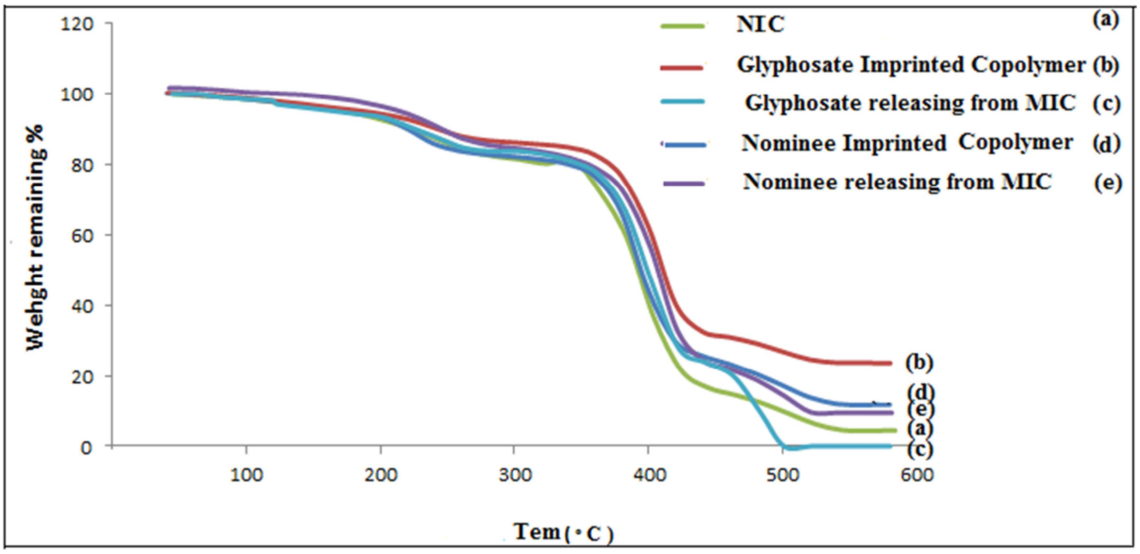

Figure 13. Thermogravimetric analysis (TGA) of: (a) Non-Imprinted Copolymer (NIC), (b) Glyphosate Imprinted Copolymer, (c) Release glyphosate from MIC, (d) Nominee Imprinted Copolymer and (e) Release nominee from MIC.

4. Conclusions

The main focus of this paper is on the development of MIC by using gamma radiation. Its efficiency is enhanced by the template and functional monomers interactions under temperature. MAA/ST/Herbicides MIC are successfully synthesized through in situ polymerization using gamma-ray and Fourier Transformed Infrared (FTIR) measurements revealed in the spectrum of the MIC through the presence of secondary amine group and a carboxylic group derived from Glyphosate and methacrylic acid.

Scanning Electron Microscope (SEM) measurements indicated that; the pore distribution in the MIC after washing was more than MIC before washing indicating that the template removal process was effective and X-Ray Diffraction (XRD) suggests the formation of MIC was successful. An optimal rate of herbicide release can be achieved by controlling the amount of copolymer and the composition of the MIC. It is strongly recommended that more studies on the advantages offered by radiation-induced methodologies would be beneficial in the future. The application of Glyphosate, Nominee contained copolymer could provide a simple method of day-to-day protection of water without exposing the ecological system to excess Glyphosate, Nominee and the consequential potential harm.

Conflict of Interest

This article is the outcome of cooperation between Minofia University under supervision Prof. Dr. Sabrnal H. El-Hamouly and National Center for radiation research& Technology under supervision Prof. Dr. Nabila A. Maziad. There is no conflict of interest between research and any statement. The authors declare that they have no conflict with any previous work.

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