



Bioremediation of Synthetic Polyacrylic acid via radiation graft copolymerization with natural based polymers

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Abstract

Starch-g-Polyacrylic acid hydrogel (Starch-g-PAAC) hydrogel was synthesized from starch and Polyacrylic acid (AA_c) via gamma irradiation at dose at 20 kGy. The synthesized hydrogel was examined via Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Scan Electron Microscopy (SEM). The swelling properties were studied at different time intervals and different pH's values. The biodegradability of hydrogels in Soil Burial and the bioremediation in river Nile model of wastewater was investigated over 16 and 4 weeks respectively. Results showed that the biodegradation percent of the starch-g-PAAC (4:1 v/v) hydrogel in Soil Burial 85% compared with pAAc 55% and the bioremediation percent of the starch-g-PAAC (4:1 v/v) hydrogel in the previously engineered wastewater exhibited a biodegradation percent (56%) compared with the synthetic PAAc with 26% biodegradation rate. These results suggest that the prepared starch-g-pAAc (4:1v/v) hydrogels were used as a biodegradable composites and had good better physical characteristics while being more environmentally ecologically friendly.

Keywords: Starch; acrylic acid; Gamma radiation; Biodegradability.

1. Introduction

Every year, synthetic plastic was produced in quantities of three hundred million metric tons, of which fifty percent were released into the environment without any sort of disposal plan [1]. Researchers from all around the world have repeatedly asserted that synthetic materials will persist in the environment ecosystem if they are not properly disposed of [2]. Because diverse synthetic plastic pollutants can spread throughout our ecosystem, it is important to take into account how synthetic plastic degrades. The biodegradable polymeric materials refers to a category of polymers that are designed to degrade through the action of living organisms [3-8]. Numerous efforts have been made in recent years to graft inexpensive and biodegradable natural biopolymers into plastic materials, such as cellulose, starch, and chitin etc [9-13]. Due to their biocompatibility, nontoxicity, and biodegradability, biodegradable polymers have

recently gained popularity as an alternative to synthetic and traditional plastics [14]. By employing polysaccharides and proteins, which are primarily sourced from plants, microbial mechanisms can cause biodegradation of synthetic plastics.

Recently hydrogels have been employed to prepare biodegradable materials, especially for agricultural [15] when polymers biodegrade completely, all of their organic components are broken down [16]. Microorganisms must colonise the polymer surface of hydrogels in order for them to degrade in soil, because of their water absorption capacity, hydrogels have found use in a variety of industries, involving medicine, biomedical engineering and agriculture. In agriculture, hydrogels have mainly been used for soil water retention, [17-18] as slow-release materials for fertilizer [19-20] and heavy metal remove [21]. As a result, they serve a variety of purposes in agriculture as soil supplements. However, there has been discussion about the advantages and disadvantages of employing synthetic and biological hydrogels as modifications

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with regard to their biodegradability. Despite the arguments supporting a shift to bio-based hydrogels (i.e., hydrogels made from natural polymers), few/no studies have compared the biodegradability of synthetic (i.e., hydrogels made from synthetic polymers) and bio-based hydrogels in agricultural soils [22]. Recent reviews have focused on the usage of synthetic and biological hydrogel in a variety of industries [23]. [24] reviewed polysaccharide based hydrogels, their features, synthesis, and use as controlled nutrient-release materials in soil

The amount of synthetic plastics used determines how toxic and potentially deadly they are, and this poses a clear risk to both individuals and the environment. [25]. The dangerous wastes from synthetic plastic resources can be reduced using a few different techniques. Although some of these synthetic materials can disintegrate quickly, others take months. Thermal degradation is unlikely to happen for PAAc if not at high temperatures (400°C) [26]. Mechanisms of degradation under environmental circumstances are expected to be mostly driven by mechanical, chemical and biological. PAAc generally need to be fragmented into smaller fragments by abiotic mechanisms by microorganisms [27]. Some nominated microorganisms have also been defined to successfully degrade cross-linked PAAc under complimentary circumstances [28]. Some bacteria were found to degrade professionally PAAc, in a similar way than the metabolism linked to respiratory chains [29]. The rate degradation of acrylate based hydrogels in compost after about 500 days was 5.9 % under aerobic circumstances. [30] found a mineralization rate of 0.12–0.24 % on 6 months for PAAc in agricultural soil, confirming their slow degradability under common environmental circumstances. A loss of weight of 1.77 % after 12 months was observed by [31] for a PAAc coating in agricultural soil. Similarly, the degradation of another PAAc waterborne coating resulted in a weight loss of 1.69 % after 12 months, when buried in the soil of a wheat field [31]. [32] stated biodegradation of PAAc to range from 1-9 % per year. The authors detailed that such decomposition rate was comparable to that of natural organic matter in forest ecosystems. Since this is comparable to natural humus cycles, SAPs (AAc-based) have often been seen like “artificial humus” and considered to be eco-compatible and thus non-toxic [32].

For instance, biodegradable bags are currently in demand on the market. The characteristics of biodegradable bags are thought to be comparable to those of traditional synthetic plastic bags [33]. Even though biodegradable materials can occasionally have great physical qualities. Agricultural byproducts, vegetable and fruit waste, and other renewable

resources can be used to create biodegradable materials [34]. Depending on the sort of natural material source or biodegradable plastic being utilized, biodegradable polymers can be broken down via aerobic or anaerobic microbial processes. Maximum researchers have employed cellulose and starch as effective substitutes for conventional Acrylic acid (AAc) in a variety of applications. Due to their enhanced favorable characteristics, Starch, Pectin and Chitosan were utilized [35-39]. Other polysaccharides, like chitosan and pectin, have improved qualities like gas barrier properties and ease of handling, which explains why the biodegradable composites were created using these polymers are environmentally benign [40-42]. Recently, There has been a 500-fold growth in the consumption of biodegradable plastics made from natural polymers worldwide. As a result, extensive research has been done to develop biodegradable polymers that can be used, for instance, in packaging for food safety [43–45], biomedical applications [46-52], applications in the automotive industry [53]. In general, biodegradable sources and natural polymers will replace traditional synthetic materials in the future [54-61].

Biodegradation in river water was utilized for the investigate of biodegradation of surfactants, acrylates products and phenols, [62] Moreover, great attention has been paid to the degradation processes of chlorinated aliphatic hydrocarbons, in three European rivers (the Ebro, Elbe and Danube) [63] and polycyclic aromatic hydrocarbons (PAH) in simulated nuclear wastewater . Biodegradations of synthetic polymers as AAC, PVP and AAm with different types of nature waters (river, sea and lake waters), [64] vinyl polymers, such as polyethylene in river water, [65] its blend and copolymers with natural polymers (in activated sludge), [66] poly(ethylene glycols) (PEGs) [67] and different polyurethanes [68] (both in sea water) were also studied.

Therefore, we aimed in this study to develop biodegradable hydrogel via a clean and cheap source of energy like gamma irradiation source without using extra crosslinking agents to shortcut costs and to create an effective and efficient biodegradable composite from starch-based materials as a biodegradable composite to enhance the microorganisms function to enhance the biodegradation process in burial soil environment and the novelty in this research paper is the studying of biodegradation rate of the synthetic bio-based materials through a “bioremediation process” in a previously prepared wastewater from the River Nile in the presence of the most famous water microorganisms, as *Escherichia coli* (*E. coli*), *Pseudomonas*, *Enterobacter* and *Anthrobacter* to enhance the biodegradation rate of PAAc as a model

of abundant synthetic polymers .

2. Experimental

2.1. Materials

Egyptian Starch and Glucose Company in Cairo, Egypt, provided the commercial-grade maize starch. Acrylic acid 99%, (Merck, Germany). Distilled water was used as a solvent. Additional chemicals, like NaOH and HCl were obtained from El-Nasr Co. (Cairo, Egypt). Water sample from the River Nile, was taken from a location near Zamalek Island, Cairo, Egypt. 250g of meat from the Egyptian commercial market, 100g of urea ,100 mg of NaCl and 25 g of CaCl₂ form Lobachemie PVT. LTD, Mumbai, India. Luria-Bertani (LB) plate agar.

2.2 Methodology for Starch-g-PAAc hydrogel

A solution of 3% Starch was obtained by dissolving 3g Starch in 97 mL distilled water and stirred on a magnetic stirrer for one hour at 80°C with the hot plate. After cooling, AAc added to the solution where Starch: AAc composition (4 Starch:1 AAc v/v) and stirring 30 min. Put the obtained mixture was added into a glass tube of 5 mm diameter and they were exposed to irradiated by a Canadian Gamma Cell- 40 ⁶⁰Co gamma irradiation source at dose 20 kGy. The created polymeric cylinders have been eliminated and divide into discs with a thickness of 2 mm. All samples were washed many times with water at 70 °C to discharge the unreacted materials and air dried [69].

1. Characterization of Starch- g-PAAc hydrogel

The IR spectra of Starch-g-PAAc hydrogel was recorded on FT-IR model Bruker, Unicom infra-red spectrophotometer, Germany, at 400–4000 cm⁻¹ wavelength [70]

range.X-ray diffractometer (XRD, Shimadzu XD⁻¹) with a Cu Ka radiation with ($\lambda= 1.542 \text{ \AA}$) at 40 kV operating voltage and 30 mA electric current, at a scanning speed of 8°/min over 2° of range 4° to 90° was used. SEM (JEOL—JSM 5200 SCANNING MICROSCOPE, Japan) was utilized to investigate the surface morphology [71].

4. Swelling at different pH's

At room temperature, hydrogel discs of identified weight were dipped in a solution of HCl and NaOH in distilled at various pH (2, 4, 6, 8, and 10) for 24 h. NaOH and HCl were used for adjustment the pH. The extra water on the turgid sample's surface was

removed using a filter paper then the samples were reweighed again. The proportion of swelling was analyzed via the following formula:

$$\text{Swelling (\%)} = (W_s - W_d) / W_d \times 100 \quad (1).$$

Where W_s is the swollen weight and W_d is the dried weight of hydrogel.

5. Biodegradability testing by soil burial method

The biodegradability of created hydrogels was investigated using a soil burial approach that was carried out at an ambient temperature for 16 weeks. Every week I used to add 200 ml distilled water into the burial soil container which containing the assigned samples. The soil used in the soil burial method was taken from the garden. In the soil-filled pot, 0.05g of synthesized hydrogels were buried three centimeters apart. Samples were removed in order to determine each sample's weight. The equation (2) gave the percentage of weight loss:

$$\text{Weight loss (\%)} = (W_i - W_t) / W_i \times 100 \quad (2).$$

where W_i is initial weight of sample and W_t is weight of sample various times following exposure to soil.

6. Wastewater biodegradation (bioremediation test)

To prepare artificial waste water 2 L of the waste water were mixed with 250gm of meat ,100 mg urea,100mg of NaCl and 25mg of CaCl₂ [72].

. Isolated Bacteria added were Escherichia coli (E. coli), Pseudomonas, Enterobacter and Anthrobacter. Bacterial strains were collected from the Italian Hospital in Cairo. For routine use, the cultures were maintained on Luria-Bertani (LB) agar. All samples of Starch-g-pAAc were put in a mesh, Polypropylene mesh thicknesses was 26 mil and the pore size was 17 mil where (One mil equals 0.0254 mm), then all immersed in waste water. The samples were removed every one week. Then rinsed by distilled water and dried at 40 °C until constant weight. Bioremediation (%) could be calculated by Equation (2). Then the sample re immersed in the fresh artificial waste water again until the same constituents for 4 weeks.

7. Determination of microbial numbers

The microbial colonies were counted using the standard plate count method [73], and used to determine the number colony forming units (CFUs). A bacterial culture is gradually diluted in sterile water flasks and agar plates "The cultures were maintained on Luria-Bertani (LB) agar ". To quantify the number

of microbial colonies related to the concentration of the starch content 1 ml samples from the three different flasks through 30 days after incubation and were transferred with a pipette into 10 ml test tubes containing 9 ml of diluent to obtain a 1/10 dilution. Subsequent serial dilutions were done to obtain a final dilution 1/10⁷. The surface spread method [74] was used to enumerate the microbial counts, Spread the inoculum using a sterile glass spreader over the full surface of each plate beginning with the most diluted sample 1/10⁷ and moving backward. plates should be taped together before being quickly inverted to prevent the water from running to one side. Keep all plates incubated at 37° C until the next laboratory session. Each plate with between 20 and 200 colonies should have a count of the colonies on it. By multiply the total number of colonies by the positive exponentiated dilution factor, you may determine the plate count. The colony forming units (cfu) or cells per milliliter of the liquid under study (water, broth media, etc.) is typically used to represent The population number microbial count were determined for 30 days.

8. Results and discussion

8.1. Formation of the hydrogel

Gamma radiation ⁶⁰Co gamma cell irradiator at irradiation dose 20kGy and at dose rate of 1.66kG/h. This source was installed at the National Center for Radiation Research and Technology (NCRRT), Nasr City, Cairo, Egypt” is a good and straightforward method for producing hydrogel. Radiolysis of water produces (H ·) and (OH ·) free radicals when Starch and AAc are subjected to gamma irradiation [75]. The hydroxyl group assault the chain of the polymer to produce a macroradical. The polymerization of free radicals generated on AAc begins. The AAc fractions are attacked by the macro radicals, resulting in a network structure with crosslinks of Starch-g-PAAc hydrogel. As illustrated in Figure (1), CNF molecules can interact with Starch to generate a Starch-g-PAAc /CNF hydrogel product. Based on earlier research, a 20kGy dose of gamma irradiation was utilised to induce crosslinking and achieve the required level of crosslinking. High irradiation doses are known to cause the creation of extremely crosslinked structures with undesirable characteristics [76-78].

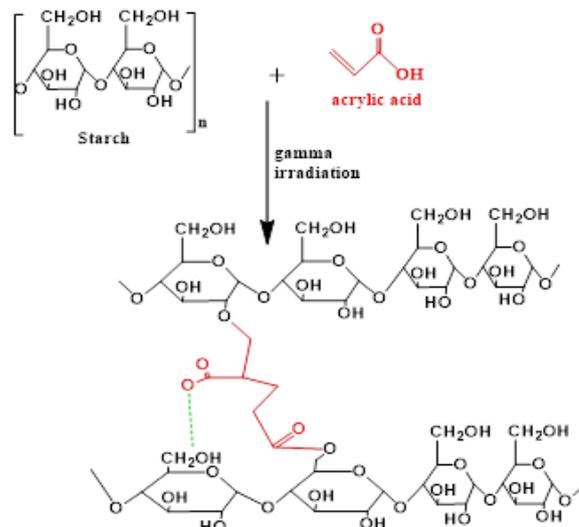


Fig.1. A possible formation reaction of Starch-g-PAAc hydrogel

8.2. Swelling behavior at different Ph

Figure 2 illustrates how pH affects the Starch-g-PAAc hydrogel's swelling (%). By raising pH from 2 to 10, swelling was improved. The COO⁻ group is known to respond to the pH medium. The COO⁻ group protonates up to pH 4.6, which is the PAAc's pKa value, in an acidic media [77]. So, a further rise in pH value creates deprotonation of the COO⁻ group. More water molecules can be absorbed because the negatively charged carboxylate ions repel each other, which improves the swelling [79].

Deprotonation of carboxylic groups increases the amount of carboxylate ions (COO⁻) which consequently increases the repulsion force between the negatively charged ions, more voids appear inside the hydrogel matrix which permits more water to diffuse inside the hydrogel matrix as a result the swelling percent enhanced.

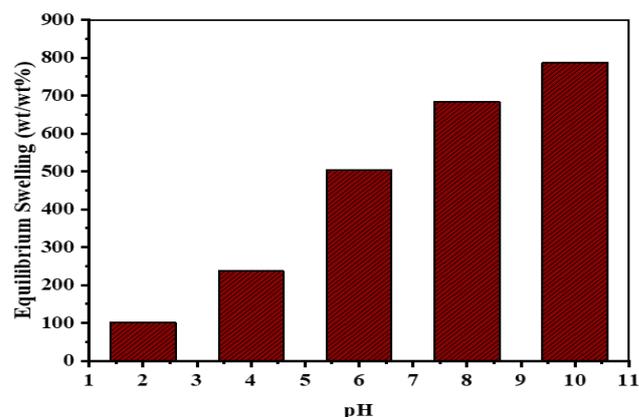


Fig. 2. Swelling performance of the Starch-g-PAAc hydrogel as a function pH.

8.3. FTIR Spectrum

Figure (3) displays the FTIR spectra of pure PAAc, Starch and Starch -g-PAAc hydrogel. The spectrum of poly acrylic acid (PAAc) typically exhibits characteristic absorption bands corresponding to various functional groups present in the polymer chain. O-H stretching vibration carboxylic acid groups (-COOH), which exhibit a broad and strong absorption band centered at 3250 cm^{-1} , corresponding to the stretching vibrations of the O-H groups. The carbonyl group (-C=O) present in the carboxylic acid groups shows a characteristic absorption peak around at 1754 cm^{-1} . The spectrum of Starch showed the presence of peaks at 3249 cm^{-1} and 1640 cm^{-1} due to stretching and bending vibrations of intramolecular OH-groups, respectively. There is a peak at 2933 cm^{-1} assigned for C-H stretching while C-H wagging appears at $\sim 1344\text{ cm}^{-1}$ [80]. The peak at 1005 cm^{-1} due to C-O-C groups. The spectrum of the Starch-g-PAAc hydrogel there a strong peak at 1700 cm^{-1} due to asymmetric stretching in carboxylic group of acrylic acid (AAc) which the band at 1435 cm^{-1} confirms corresponds to the symmetric stretching mode of the carboxylate anion [81]. These findings showed that the COO^- and COOH groups of hydrogels were positively affected by the polymerization of AAc monomers have been grafted onto starch, which improved the swelling behavior of hydrogels [82].

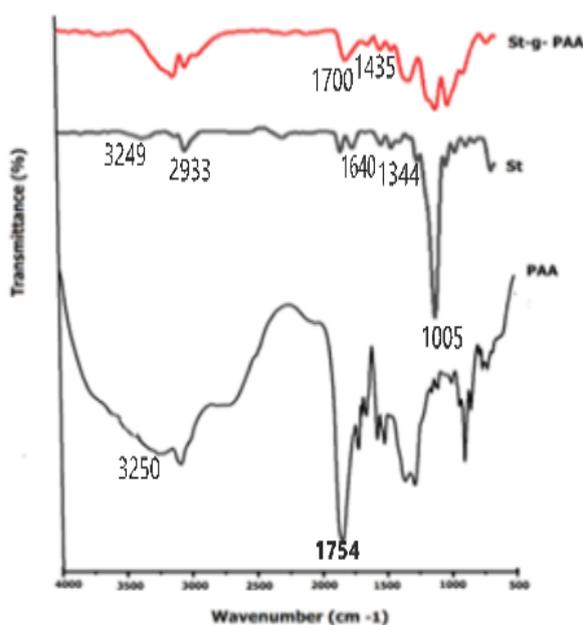


Fig. 3. FTIR spectra of PAAc, Starch, and St-g-PAAc hydrogels.

8.4. X-ray diffraction analysis (XRD)

Amylose, a crystalline phase of starch has a linear structure whereas amylopectin an amorphous phase has a branching structure [83]. The XRD shapes of Starch and Starch-g-PAAc are examined in Fig. 4. Starch pattern showed main diffraction peaks at 2θ of 15.4° , 17.5° and 23.5° that corresponds to A- or C-type crystal [84]. After grafting starch with PAAc, a broad shape of XRD with diffraction peaks at 2θ of 14.5° , and 17.0° was observed indicating a decrease in the crystallinity of Starch-g-PAAc comparing with starch. This might be due to a barrier created by hydrogen bonding between starch chains via PAAc side groups [83,85]. In the other words, the starch structure becomes loosely packed as a result of decreased intramolecular hydrogen bonding. Identical outcomes were found in prior works [86].

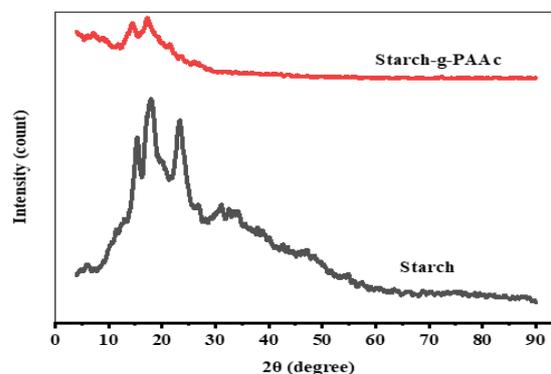


Fig. 4. XRD diffraction patterns of Starch-g-PAAc (4:1) hydrogels.

8.5. Scanning electron microscopy

Figure 5 shows images of Starch-g-PAAc at various pH levels. At pH 2, the hydrogels are not smooth and have numerous pores and globules, whereas, at pH 6, the globules are dimensioned. At pH 10, the surface morphology changes to a more flaky structure with numerous pores because the COO^- group is sensitive to the pH of the medium.

In an environment of acidic medium, the carboxylic group protonates up to pH 4.6. Thus, a further rise in pH causes deprotonation of the carboxylic group. New holes and voids can emerge because of the negatively charged carboxylate ions' repulsion, which enhances the equilibrium of the swelling [87,88].

8.6 Soil Burial Biodegradation

The potential applications of polymers depend on their biodegradability. Solid waste buildup and environmental issues can be solved by using

biodegradable materials, according to experts. The biodegradability of the synthesized starch-g-PAAc (4:1) hydrogel and AAC were examined via the soil burial method by estimating the percentage of weight loss over 16 weeks,[89] as characterized in Figure (6)

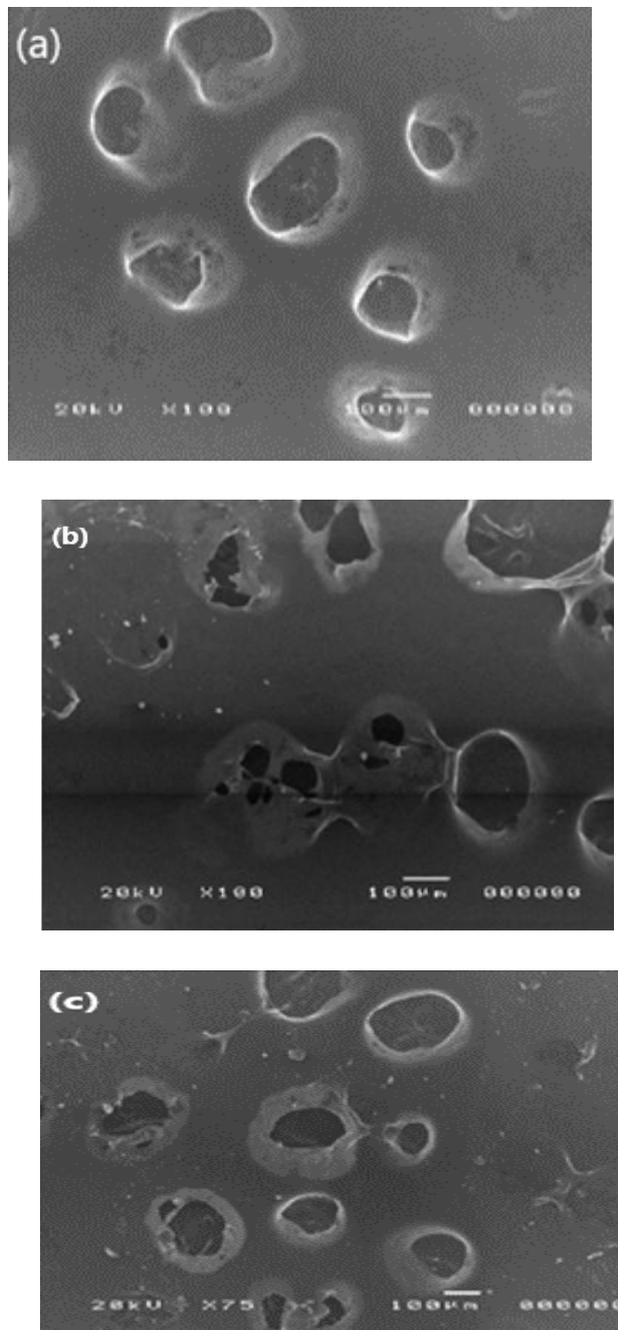


Fig.5. Scanning electron micrograph of Starch-g-PAAc; (a) pH=2, (b) pH=6, (c) and pH=10.

The records of weight loss is an main method to examine the character of biodegradation and the degradation rate of polymeric sources during a soil

burial process. (1) Diffusion of water into the hydrogel matrix samples after preparation causes network swelling and promotes microbial growth on the hydrogel threads, and (2) The weight loss and disintegration of the hydrogel samples are brought on by enzymatic and other types of degradation [89] The percentage of weight loss of the synthesized starch-g-PAAc hydrogel and AAC shown a recorded degradation, and the increased rate of deterioration clearly in the primary 10 weeks. Next that the process of biodegradation continued at a significantly lower rate until the end of the experiment. The weight loss % of the starch-g-PAAc (4:1) hydrogel and AAC were 85% and 55% respectively after 16 weeks. It is suggested that the process of soil burying involves two stages of degradation: (1) Diffusion of water into the hydrogel matrix samples after preparation causes network swelling and promotes microbial growth on the hydrogel threads, [91] and (2) The weight loss and disintegration of the hydrogel samples are brought on by enzymatic and other types of degradation. In the first four weeks of the burying procedure, it was noted that the created hydrogel's color changed from white to yellow. Reddish brown then replaced the previous coloration. These findings concur with a number of other research that documented the biodegradation of the manufactured starch hydrogels [92,93].

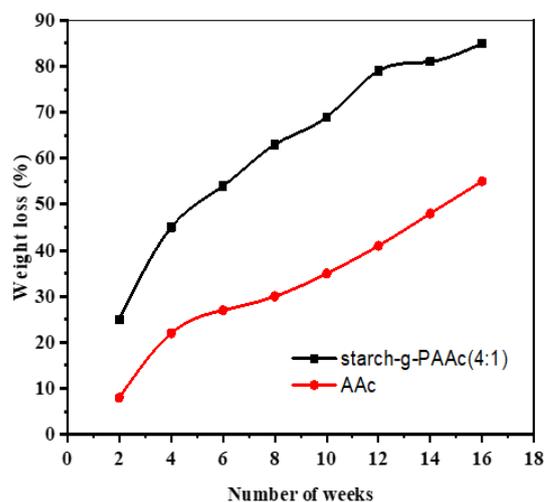


Fig. 6. Biodegradability of the starch-g-PAAc (4:1) hydrogel and AAC over 16 weeks.

8. 7. Wastewater biodegradation.

The results of monitoring biodegradation (bioremediation) of the starch-g-PAAc (4:1) hydrogel in the model of the river wastewater are mentioned

below in fig (7) which indicates the mass loss in the starch-g-PAAc (4:1) hydrogel was significantly high compared with the synthetic PAAc. The mass loss come from the solubility of starch and degradation of the starch by microorganisms which developed in the wastewater during the experiment [94]. The biodegradation process initiated by the diffusion of water into the hydrogel matrix resulting in a network swelling and promotes microbial growth on the hydrogel chains which includes starch.

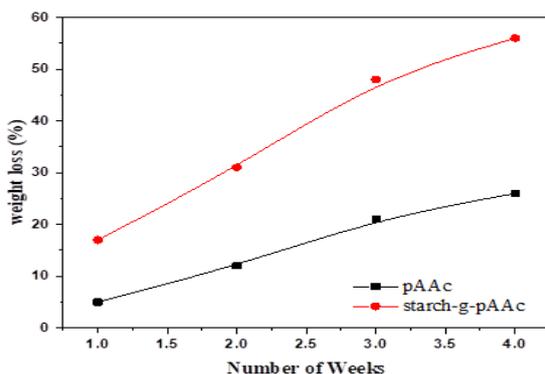


Fig. 7. Biodegradation of the starch-g-PAAc (4:1) hydrogel and pAAc over 4 weeks in wastewater model.

8. 8. Determination of microbial numbers

During the biodegradation test in the Starch -g-PAAc hydrogel (4:1) as shown in Table 1 the number of microorganisms increased in the first three days which attributed to the starch availability. Starch will be dissolved in water which enhance the microorganisms' counts. After the three days the available starch decreased by time, the starch availability in water remained so close till days 14th. After 14th day the microorganisms counts start to decline due to the availability of starch are declined which may be consumed by time or entrapped with the internal copolymer chains and microorganisms could not reach to it.

8.9. Biodegradation Mechanism

The biodegradation mechanism started by microorganisms attack on starch species. After of the consumption of the starch content the intermolecular spaces between AAc moiety starts to appears, which will enhance the PAAc chains to dissolved faster so PAAc degradation process enhanced[95-98].

Table 1.Number of colonys Log (CFU/ML⁻¹) of Starch -g-PAAc (4:1) over 28 days.

Starch -g-PAAc (4:1)						
Days	1	3	7	14	21	28
Log (CFU/ML ⁻¹)	6.5	9	8	6	3	1

9. Conclusion

Biodegradable hydrogel was prepared from Starch and AAc by Gamma irradiation at dose 20 kGy. The synthesized hydrogel was examined by FTIR, XRD and SEM. The swelling properties were studied at different time intervals and different pH's. The biodegradability of hydrogels in Soil Burial Biodegradation and bioremediation in river Nile model of wastewater was investigated over 16 and 4 weeks respectively. Results showed that the biodegradation percent of the starch-g-PAAc (4:1 v/v) hydrogel in Soil Burial 85% compared with pAAc 55% and the bioremediation percent of the starch-g-PAAc (4:1 v/v) hydrogel in the previously engineered wastewater exhibited a biodegradation percent (56%) compared with the synthetic PAAc with 26% biodegradation rate. These results suggest that the prepared starch-g-pAAc (4:1v/v) hydrogels were used as a biodegradable composites and had good better physical characteristics while being more environmentally ecologically friendly.

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