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GREEN MODIFICATION OF HYDROGEL AS A NOVEL NATURAL MATERIAL FOR DYE REMOVAL AS A SUSTAINABLE AND RENEWABLE BIORESOURCE FOR WASTEWATER REUSE

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Abstract

The naturally occurring wastes are rich in many active groups, in addition of non-toxicity and biodegradability that may be used as an efficient bio-adsorbent in this study, orange peel (OP) wastes were modified by free radical copolymerization with synthetic monomers to form hydrogel by gamma irradiation (AAM/OP) which is a green polymer able to absorb a high dose of polluted dyes like Congo Red dye (CR) from our studied area. The influence of preparation conditions such as radiation dose and the composition of gel were studied. As a result, the swelling behavior of the hydrogel generated was examined using FTIR, SEM, and infrared spectroscopy to determine how swelling duration, medium pH, and hydrogel content affected the results (FTIR). Congo Red dye (CR) was removed from wastewater collected throughout the experiment using the hydrogel generated. Different operational parameters such as pH, contact time, dye concentration, and temperature have been studied to see how they affect the dye's adsorption ability, and the results show that (CR) can be removed from wastewater with high and ecologically friendly efficiency (OP).

Keyword: Wastewater, hydrogel, Radiation, Orange peel, green polymer, adsorption, drainage.
抽象的

天然产生的废物富含许多活性基团，除了无毒和生物降解性可用作本研究中的高效生物吸附剂外，橙皮 (OP) 废物通过与合成单体的自由基共聚进行改性通过伽马辐射 (AAM / OP) 形成水凝胶，这是一种绿色聚合物，能够吸收我们研究区域的高剂量污染染料，如刚果红染料 (CR) 。制备条件的影响，如辐射剂量和组成凝胶进行了研究。因此，使用 FTIR、SEM 和红外光谱检查了生成的水凝胶的溶胀行为，以确定溶胀持续时间、介质 pH 值和水凝胶含量如何影响结果 (FTIR)。使用生成的水凝胶从整个实验过程中收集的废水中去除刚果红染料

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(CR)。研究了不同的操作参数，如 pH 值、接触时间、染料浓度和温度，以了解它们如何影响染料的吸附能力，结果表明 (CR) 可以从废水中以高且生态友好的效率 (OP) 去除。

关键词：废水，水凝胶，辐射，橘皮，绿色聚合物，吸附，排水。

INTRODUCTION

Water is the substantial necessity for nearly all industries and the wastewater created from industrial methods leads to a critical environmental attention when it is without convenient treatment. the pollution caused by the flowing of industrial wastewater eventually influences on the ecosystem which is an incorporated system that involves water, land, and air. in addition to textiles and rubber, dyes are used in a wide range of other sectors as well, such as printing, food, and medicines 1. chemically synthesized dyes, dyes have a wide range of aromatic structures, and when they interact with a substance, they give it color. dyes considered as aromatic organic compounds with aryl rings in their structures and delocalized electron systems that are ionic and have an aromatic structure. the existence of a chromospheres group determines the dye color. a chromosphere is a radical structure made up of conjugated double bonds and electrons that have been delocalized. a chromogen-chromophore complex is made up of a chromogen and an auxochrome, each of which has benzene, naphthalene, or anthracene rings. in addition to changing the chemical's maximum absorption, auxochromes have a bonding affinity. in the textile and other industries, colored dye wastewater is generated as a by-product of dye production and use. more than 7105 dyes are produced annually all over the world, with over 100,000 commercially available dyes 2. Congo red is the sodium salt of 3,3'-([1,1'-biphenyl]-4,4'-diyl) bis ([1,1'-biphenyl]-4,4'-diyl) bis

([1,1'-biphenyl]-4,4'-diyl) bis ([1,1'-biphenyl]-4,4'-diyl) bis ([1,1'-biphenyl] (4-aminonaphthalene-1-sulfonic acid). it's a dye made from an azo compound. a crimson colloidal solution is created when Congo red is dissolved in water, but its solubility in organic solvents is greater than that. the usage of Congo red, on the other hand, has long been discontinued, owing to its carcinogenic characteristics 3 . it's being looked into as a possible mutagen and reproductive effector. It's irritating to the skin, eyes, and stomach. it can cause somnolence and respiratory difficulties by affecting blood factors like coagulation4. because of their toxicity and endurance, these discharges pose a severe danger to freshwater physicochemical characteristics and aquatic life 5 . the treatments of dye-containing effluents and toxic heavy metals were done previously by various traditional approaches such as chemical precipitation, ion exchange, complications and photo degradation 6-9. because of its economic feasibility, cheap cost, and environmental safety, adsorption has recently become a popular technology for the removal of industrial pollutants10. several natural polymers, such as orange peel (OP), have been used as adsorbents. the most essential components of orange peel are 16.9% soluble sugars, 9.21 percent cellulose, 10.5 percent hemicellulose, and 42.5 percent pectin, as well as lignin, chlorophyll, color, and various low molecular weight hydrocarbons. 11, it's also been utilized to get dyes out of wastewaters 12,13. hydrogels are a network structure made up of cross-linked polymer chains that are encased in

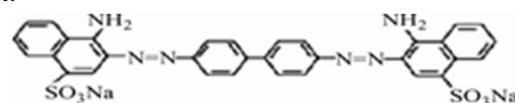
an aqueous solution. 14 . water-absorbing capabilities are good in hydrogels produced from synthetic polymers like poly acrylate. the appearance of hydrogels as matrix, film, or microsphere is determined by the polymerization method used during the production. the presence of polar groups, which can be non-ionic or ionic, contributes to the gel's hydrophilicity¹⁵., superabsorbent hydrogels are hydrogels that can absorb a high amount of water and hold it even under pressure¹⁶ . these materials can absorb hundreds of times their dry weight in water. hydrogels are comparable to real living tissues in their capacity to hold a considerable quantity of water, making them helpful in a number of biological applications ¹⁷ . for the removal of dyes and heavy metals from wastewater, a variety of treatment methods have been used, including physical, chemical, and biological treatments. ozonization, adsorption, chemical precipitation, flocculation coagulation, chemical oxidation, photocatalysis, dilution, ion-exchange, reverse osmosis, ultra-filtration membrane filtration, irradiation, and electro-chemical destruction are examples of physical and chemical treatment methods. these technologies, however, are not extensively employed due to their high cost and limited practicality for small-scale enterprises ¹⁸. due to its efficacy and low cost, adsorption is one of the most often used methods for eliminating heavy metals. ¹⁹ capacities and competence to remove non-biodegradable dyes from large-scale industrial effluents. in our study, we looked at how to make an environmentally friendly hydrogel out of orange peel (OP) as a natural waste copolymerized with acrylamide (AAM) as a synthetic polymer using gamma radiation, and how to use the hydrogels in industrial applications to remove Congo red dye from

wastewater and reuse them. for the purpose of removing the dye Congo red (CR) from wastewater, the hydrogel was employed as an adsorbent, and then the dye-loaded hydrogel was used in a second adsorption cycle to remove the other dye.

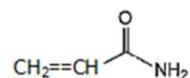
Materials and methods

Materials

A significant byproduct of orange juice production is orange peel (OP), which is collected from the surrounding area throughout the winter months. Two-propenamide (AAM) is an inert colorless non-volatile crystalline solid with Mol.wt :71.08 kDA (99 percent) ⁶⁹⁶ is the Congo red chemical formula, which was bought (by Merck, Germany). Chemical element CR has an atomic mass of 66.8 amu (atomic mass units). Sigma Aldrich was the company that sold u to me, Fig.1. (HCL) solution and/or a (NAOH) solution were used to alter the pH as needed during the test. Nothing needs to be cleaned up as everything is being utilized just as it was given to it.



(A) Congo red (CR)



(B) Acrylamide (AAM)

Fig.1 Congo red and Acrylamide Chemical structure

Treatment of natural polymer (Orange peel)

To eliminate any remaining dirt, (OP) was carefully rinsed with distilled water. After drying

in the sun for 48 hours to remove all moisture, the washed (OP) was crushed and sieved to the required particle sizes. the crushed powder of (OP) was treated with 1 percent sodium hydroxide, rinsed with distilled water, and then dried in the air at room temperature to remove free sodium hydroxide.

Synthesis of Orange peel-based hydrogel

This homogenous 10 percent combination was made by mixing 10 g (OP) with 100 ml distilled water, swirling it around, and then heating it at 80°C for 120 minutes. different AAM concentrations were added after the solution had been cooled to room temperature and agitated continuously for 5 minutes with the solution composition of OP: AAM (1:1, 1:2), and (2:1) monomers at room temperature. one hundred and forty-six kilotons of the solution were bombarded with the Co60 gamma source over the course of an hour. it was washed in excess water to remove unreacted compounds after irradiation and allowed to air dry at room temperature to ensure the hydrogel was clean.

Gel Fraction of the prepared hydrogel

The hydrogel samples were arid in air to a consistent weight before the insoluble components could be identified. It took 24 hours at 70°C to soak the dried pre-weighted samples, which were then rinsed with hot water to eliminate the solubility and dried again to a consistent weight. the following formula was used to determine the gel content gravimetrically:

$$\text{Gel content (\%)} = \frac{W_d}{W_0} \times 100 \quad (1)$$

Wd and W0 are dried sample weight before and after extraction, respectively.

The swelling measurement

The hydrogel was cleaned, dried, and weighed before being submerged in distilled water at room temperature for varying lengths of time. the sample was cleaned using filter paper and then reweighed after the extra water was wiped away. The following equation was used to estimate the degree of edema:

$$\text{Swelling\%} = \frac{(M_s - M_d)}{M_d} \times 100 \quad (2)$$

Md and MS are masses of swelled and dry hydrogel, respectively

Adsorption studies

Experiments on batch adsorption were carried out. exactly 20 mL dye or metal solution (10-80 mg/L) and (50-300 mg/L) with known starting concentrations, the concentration of (CR) was measured when equilibrium was achieved. at nearby pH was shaken with a known dosage of dry hydrogel at suitable time intervals at a certain agitation speed (250rpm). the proportion of dye and metal removed was determined using the formula below:

$$\text{Removal\%} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (3)$$

The adsorption capacity qe (mg/g) at any time was calculated using the following equation:

$$q_t = \frac{(C_0 - C_t)}{w} \times v \quad (4)$$

Color and metal concentrations are set at mg/L for the beginning and mg/L for the end of a time interval, respectively. where qt represents the quantity of metal ion adsorbed (mg/g), V represents the volume of the aqueous phase (L), and w is the amount of dry hydrogel utilized (g).

Instruments

Gamma radiation source

For the irradiation, Egypt's National Center for Radiation Research and Technology (NCRRT) used a Co60 gamma source with doses rates which varies from 1.64 kGy/h to 10-50 kGy.

Infrared analysis

FTIR was used to examine the copolymer's functional groups. In the 400–4000 cm⁻¹ range, the Nicolet IS-10FTIR was utilized to obtain KBr pellet FTIR spectra.

Scanning electron microscopy (SEM)

Hydrogels were scanned with a JEOL-JSM-5400 scanning electron microscope in Tokyo, Japan to assess their morphology. The parts were dried, gold-sputter-coated, inspected, and photographed prior to inspection.

Thermogravimetric analysis (TGA)

The thermal characteristics of the hydrogels were examined in a nitrogen environment (20 ml/min) using a Shimadzu TGA machine (Japan), model TGA-50. the temperature was raised by 10 degrees Celsius each minute starting at room temperature and working up to 600 degrees Fahrenheit. to assess the rate of thermal degradation reaction, primary TGA thermograms were utilized.

Ultraviolet (UV) Measurements

With a wavelength of (190-900) nm, the UV/VIS spectrometer utilized was a German-made UV-Analytic Jena AG specord 210 plus with a quartz cell with an optical length of 1.0 cm, with a maximum CR wavelength of 500 nm and a maximum MO wavelength of 464 nm.

Atomic absorption technique

This technique is used to determine unknown concentration of metals in several

solutions. Absorption at the atomic level was utilized to detect the amount of metal ions left in the solution (Perkin Elmer model 2380)

Results And Discussion

This study concerned with preparation of ecofriendly hydrogel based on natural waste namely orange peel(OP) that was copolymerized with synthetic monomer such as acrylamide (AAM) by gamma irradiation .the prepared hydrogel was employed in industrial applications for removal of Congo red dye (CR) dye .This study concerned with preparation of ecofriendly hydrogel based on natural waste namely orange peel(OP) that were copolymerized with synthetic monomer such as acrylamide (AAM) by gamma irradiation .The prepared hydrogel was employed in industrial applications for elimination of Congo red dye (CR) dye from wastewater.

It's called polymer radiation processing when ionizing radiation is used to alter polymer materials' physical and chemical properties in order to raise their quality 20. High-energy ionizing radiation, such as gamma rays and electron beams, has been used to create unsaturated chemical hydrogels 21. radiation crosslinking is the most efficient way to synthesize hydrogels 22. This method preserves the biocompatibility of the biopolymer23. researchers have looked on radiation polymerization and crosslinking of polymeric materials. it is generally understood that gamma radiation of natural polymers causes link breakage and macromolecule disintegration, as well as the formation of macromolecules with smaller chains (chain scission). In this work, ionizing gamma radiation was used to copolymerize and crosslink AAM onto the backbone of the natural polymer OP in an aqueous solution. radiation-induced co polymer

hydrogel production in aqueous solutions follows a radical process. this polymerization process involves irradiating an aqueous polymer solution, which causes radicals to form on the polymer chains due to the direct impact of radicals produced by solvent radiolysis. hydroxyl radicals attack polymer chains during water radiolysis, resulting in macroradical production as a consequence. Because of an indirect influence, both polymerization and crosslinking are initiated by intermediate products of water radiolysis 24. a study conducted by Saraydin and colleagues showed that acrylamide copolymers may produce macroradicals²⁵. using the same analogy, the current study argues that during the initiation stage, radicals form on OP (or) AAM. furthermore, the product is produced as a result of macroradical propagation. the formation of covalent bonds and, eventually, the formation of a crosslinked structure results from the recombination of macroradicals on different chains. (AAM/OP). gel content is a measure of the quality of a produced hydrogel. several factors influence the gel content, including radiation dosage, monomer concentration, and gel composition.

Gamma radiation Effect on the gel percent

The amount of radiation used has a big influence on how the gel turns out. crosslinking and degradation are two opposing outcomes of gamma radiation dose. it is well known that at high radiation doses, radiation degradation may outpace radiation crosslinking, resulting in a decrease in gel fraction 26. this study's hydrogel was created from radiation-sensitive natural wastes. the impact of radiation dose of various (AAM/OP) hydrogel compositions was studied, and the gelation percent of various (AAM/OP) hydrogel compositions as a function of radiation

dose is shown in Fig (2). As seen in Fig (2), the gel percent grows quickly as the absorbed dosage increases until it reaches the maximal gelation point of 20 kGy. above this amount, the gel percent decreases somewhat. When -rays are used to irradiate AAM monomer in OP solution, free radicals from water and monomers are produced; these radicals promote polymerization and the creation of a network. The quantity of free radicals increases as the irradiation dosage is increased, resulting in high gel content 27. At increasing radiation doses, the gel percent falls, which might be explained by the fact that radiation degradation overrides the crosslinking process at higher absorbed doses²⁸. The gel content of (AAM/OP) hydrogel decreases with increasing the OP content in the hydrogel thus decrease may be attributed to the degradability of OP under ionizing radiation as a natural polymer. The strong tendency of AAM for radiation polymerization and crosslinking, may explain the rise in gel content as the content of AAM in the hydrogel increases.

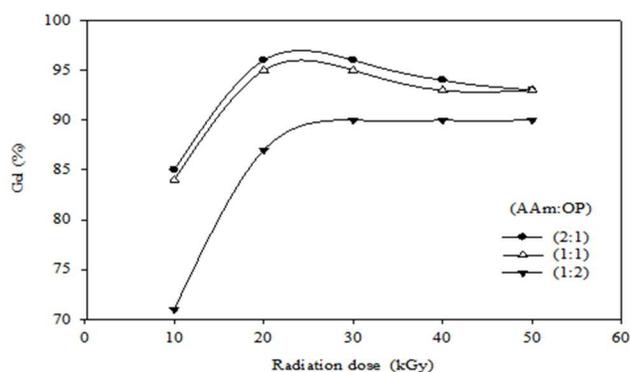


Figure (2): Influence of radiation dose on the gel percent of (AAM /OP) hydrogel at various gel compositions.

Influence of overall concentration on the gel percent

Figure (3), shows the impact of the initial feed concentration on the gel percent of (AAM/OP) for different compositions on the gel percent. When the initial feed concentration increases, the gel content follows suit. Gel percent may have increased as a result of higher monomer concentration due to increased reaction medium viscosity and an increased number of radiation reactive vinyl groups, according to this theory²⁹. It's also worth noting that when the amount of OP in the hydrogel increases, the gel content of AAM decreases. This indicates that when the OP concentration in the hydrogel increases, the gel fraction decreases. Due to the limited likelihood of recombination of the degraded cellulose chains of OP, the main chain scission is the dominating response in this scenario. An increase in the quantity of radiation reactive vinyl groups can be attributed to increased AAM content, and AAM has a high copolymerization and crosslinking capability³⁰.

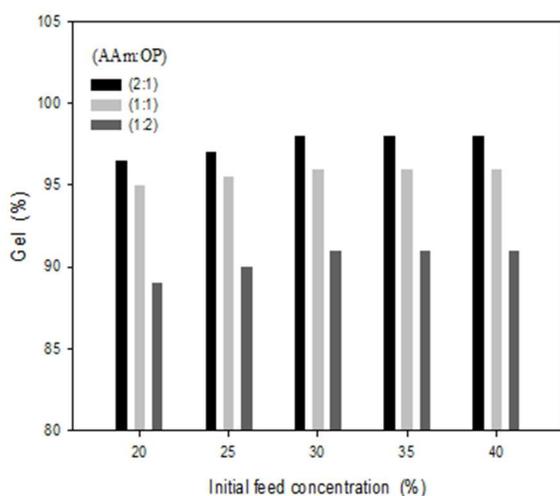


Figure (3): Premier feed concentration effect on gel percent of (AAM/OP) hydrogel at various compositions.

Characterization of the prepared hydrogel FT-IR analysis

The functional group of the synthesized (AAM/OP) hydrogel was shown in Figure (4). It can be observed many numbers of adsorption peaks which represent the complex nature of the observed materials. The FT-IR spectra of the (AAM/OP) hydrogel is dominated by celluloses, hemicelluloses, pectin, lignin, and a number of other low molecular weight molecules³¹, all of which play a role. FT-IR spectra of (AAM/OP) is shown in Figure (4). There is a wide band at 3409.50 cm^{-1} , where alcohol, phenols, and carboxylic acids (O-H) stretching vibrations may be detected, as well as primary amides (NH₂) stretching vibrations in pectin, cellulose, and lignin from OP and AAM. C-H stretching vibrations of -CH₂ groups are shown by bands at 2934 cm^{-1} and 2872 cm^{-1} , respectively. C=O, N-H bending, and C-N stretching are all properties of AAM (CONH₂) group³² in the bands located at 1613, 1603, and 1321 cm^{-1} , respectively. In OP³³: SO₃ from hemicelluloses stretches at 1373 cm^{-1} , whereas CH₃ from lignin does so at 1455 cm^{-1} . Bands in the 1114–1025 cm^{-1} range are generated by stretching vibrations of C-O and C-O-C.

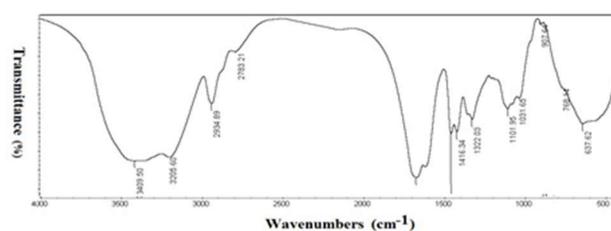


Figure (4): FTIR spectra of (AAM/OP) composite hydrogel.

The Swelling behavior

Hydrogel are water-swollen polymer and copolymer net-works used in different applications, including agriculture, sanitary goods, wastewater treatment, and medication

delivery. The solution diffuses into the network when water or a buffer solution is added to a hydrogel, causing a volume phase transition and the hydrogel to expand. Hydration of the hydrophilic polar groups takes place initially when water is introduced, resulting in the creation of the primary bound water. In this way, the network grows, revealing water-interacting hydrophobic groups. Water that has been hydrophobically bonded is referred to as "secondary bound water" as a result of this procedure. A lot of times, "total bound water" and "primary bound water" are used interchangeably. Due to the osmotic force of the network chains, the network will continue to absorb water indefinitely. The covalent or physical cross-links in the elastic network oppose the additional swelling, causing a retraction force. Assumed to fill space between the network chains and the center of bigger pores, macro pores, or voids 34, "free water" or "bulk water" is surplus absorbed water. As soon as osmotic force and elastic force of stretched sub-chains equal 35, the swelling equilibrium is attained and swelling occurs. Density gain in the crosslink network increases dispersing force variables such as the radiation dose, the polymer composition, and the swelling duration all have an effect on hydrogels' swelling behavior.

Influence of radiation dose on the swelling percent of hydrogel.

(AAM/OP) hydrogel composition swelling percent as a function of radiation dosage used to create them is shown in Figure (5). When the hydrogel's radiation dose is raised, the swelling percent falls as a result of the radiation's higher crosslink density inhibiting water diffusion into the hydrogel (see Figure 5). Excessive crosslinking inhibits polymer chain mobility,

resulting in a decrease in swelling percent 36 and an increase in AAM content in the hydrogel. In other words, when the amount of OP in the hydrogel rose, the percentage of swelling increased because of the presence of hydrophilic groups in OP.

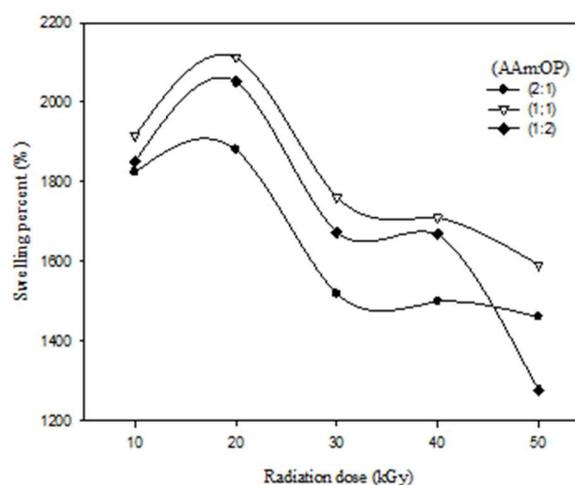


Figure (5): Influence of radiation dose on the swelling percent of (AAM/OP) hydrogel at various compositions.

Influence of premier feed concentration on the swelling percent

The influence of initial feed concentration on the swelling percent of (AAM/OP) hydrogel is shown in Figure (6). The swelling percent of hydrogel decreased as the feed concentration rose, indicating that it was essentially comparable. The viscosity of the reaction medium rose as the number of reactants increased 37, result in a decrease in swelling percent. Increased crosslinking density would slow network development and reduce swelling percent 38. As long as the counter-ion is present in these aggregates, it may condense and reduce osmotic pressure 39, but this does not help the swelling process. Using an irradiation dosage of 20 kGy, Figure (6) depicts the impact of the

premier feed concentration on the swelling percentage of composite hydrogel (AAM/OP).

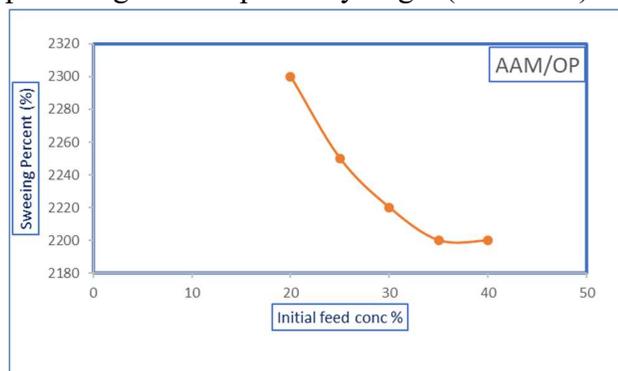


Figure (6): Premier feed concentration effect on swelling percent of (AAM/OP) hydrogel and AAM: OP composition (1:1) and irradiated with a dose of 20 (kGy).

pH influence on swelling behavior

Several factors influence the swelling capacity of hydrogel, including pH. At lower pH values, ionic crosslinking between NH_3 and COO species may result in a form of crosslinking that lowers the swelling percent since most base and acid groups are NH_3 and COO , as well as the hydrogen bonding between the amine and carboxylic groups (AAM/OP) (below the pK_a of carboxylic groups, approximate 4.6). Electrostatic repulsive force (COO^-) increases at pH values over pK_a , causing the carboxylate groups to ionize (>4) and increased swelling. Because of electrostatic repulsion caused by the carboxylate groups deprotonating to $-\text{COO}^-$ at higher pH values than 8, swelling affinity increases. On the other hand, because of the repulsive forces between these anions, the polymer structure is more "open" for water molecule diffusion. The amide groups P(AAM/OP) chains react with strong alkaline to form carboxylate groups 40. Figure 7: depicted the swelling behavior of case (AAM/OP) as a function of pH.

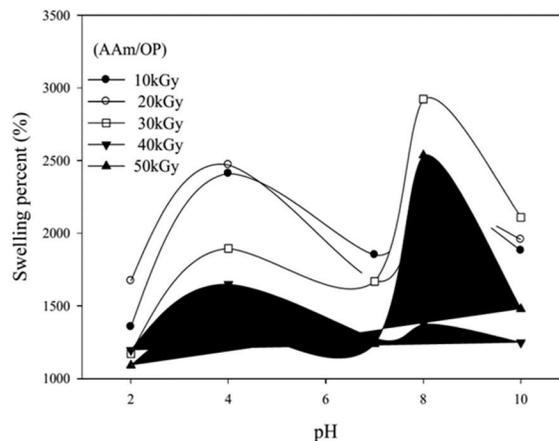


Figure (7): Effect of pH on the swelling percent of hydrogel (AAM/OP), at variety of irradiation doses.

Time Effect on the swelling percent of hydrogel

Swelling time affects (AAM/OP) hydrogel swelling % under different irradiation doses, as shown in Figure (8). In order to increase the irradiation dosage up to 20 kGy, the swelling capacity of (AAM/OP) hydrogel is reduced. This reduces the swelling of hydrogel made from (AAM/OP). n and K were calculated based on the slope and intercept of each line. The findings are given in Table (1). The values of n for all studied hydrogel were found to be less than 0.50, indicating that the water diffusion in the applied hydrogel is Fickian; this indicates that the water diffusion regulates the swelling.

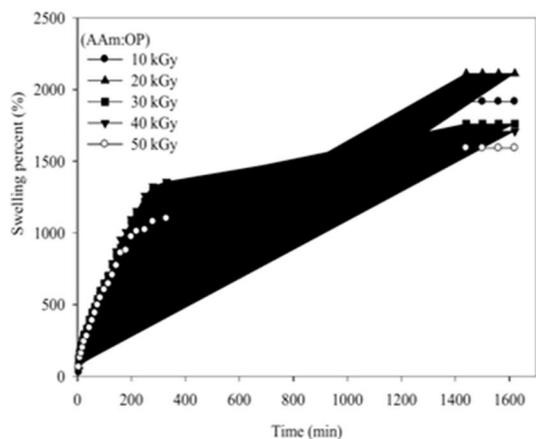


Figure (8): Time effect on the swelling percent of hydrogel at variety of irradiation doses.

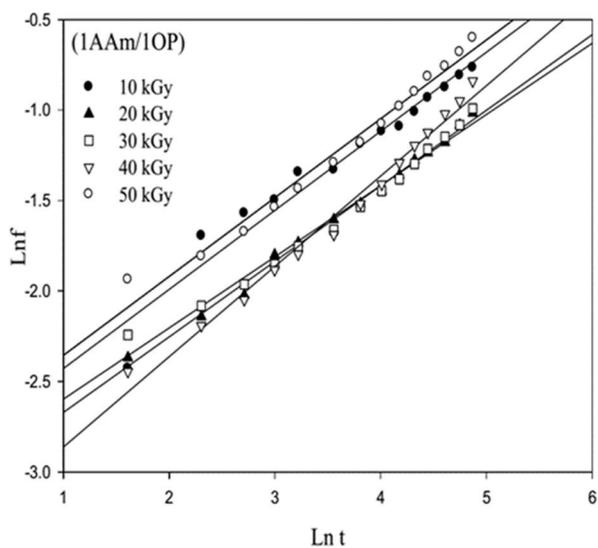


Figure (9): Swelling kinetic curve of investigated hydrogel at variety of irradiation doses.

Dose (kGy)	(AAM/OP)			
	K	n	type	R ²
10	0.06	0.40	Fickian	0.99
20	0.049	0.41	Fickian	0.99

30	0.055	0.39	Fickian	0.98
40	0.049	0.49	Fickian	0.98
50	0.062	0.43	Fickian	0.98

Table (1): Swelling kinetic parameters of investigated hydrogel system at different radiation doses.

Hydrogel Thermal Stability

The thermal stability of the hydrogel is important in establishing the working temperature limit and the ambient conditions for usage, both of which are connected to the temperature and rate of thermal breakdown. The change in thermal characteristics of the produced hydrogel was investigated using thermal gravimetric analysis (TGA) in this work.

Copolymerization results in chemical and physical changes, which are studied and documented. As you can see in Figure 10, (AAM/OP) hydrogel has TGA and thermal breakdown rate (dw/dt) curves from 25 to 600°C. There were three distinct phases of degradation visible. The first stage of breakdown occurs at temperatures between 29 and 130 degrees Celsius, and is caused by the evaporation of physically absorbed water. The intermolecular side chain decomposition and anhydride formation cause the second breakdown stage, which occurs between (130-400) °C. Most of the weight is lost between (400-475)°C in the third stage due to the breakdown of the backbone polymer. (AAM/OP) hydrogel TGA thermogram indicated four breakdown stages. The loss of moisture and the development of certain light weight molecules, notably in orange peel 41, are linked to the first area of decomposition stage in the range of (23-155) °C. The dehydration of polysaccharide rings and the breakage of

glycoside linkages in the main chain of OP which are responsible for the second zone of disintegration⁴¹, which occurs between (155-270oC). The breakdown of amide side groups of AAM in the network is linked to the third zone of decomposition in the range (270-440)oC ⁴². In the region of (440-600) oC, the fourth breakdown stage refers to the polymer's full destruction. The weight loss occurred gradually as the temperature rose, indicating the presence of a stiff structure that shows the hydrogel's thermal resilience. water molecules might interact with the sample if it has hydrophilic areas. The second reaction took place in the (200–381) °C range due to the heat breakdown of hydrophobic side chains along with the imine reaction of a few amide groups. Between 381 and 461 degrees Celsius, amide groups broke down and polymer main chains degraded, and the copolymer was totally destroyed. It's safe to say that the hydrogel (AAM/OP) created is stable up to 200 degrees Celsius, making it suitable for usage. Table 2 shows the rate of heat breakdown and residual weight of several investigations.

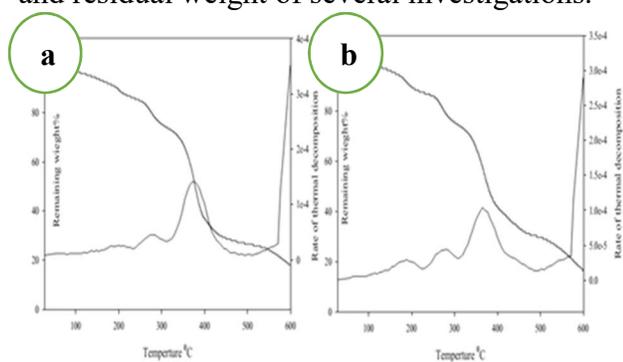


Figure (10): TGA curves and the average of thermal decomposition (dw/dt) of (AAM/OP) hydrogel at 20 kGy and (AAM: OP) (1:1) (a) and (2 :1) (b).

Scanning Electron Microscopy

The surface shape and fundamental physical characteristics of an adsorbent surface are studied using scanning electron microscopy. It may be used to figure out an adsorbent's particle shape, porosity, and size distribution. The surface morphology of (AAM/OP) was detected using (SEM) and the results are shown in Figure (11) examined the surface of OP and discovered that it had an uneven and porous surface shape. OP copolymerization with AAM was carried out at 30kGy in this study⁴³. The SEM images show the structure to be highly porous, with many channels, open heterogeneous pores, and cavities for the adsorption of colors and metal ions, the heterogeneous holes offered a wide exposed surface area. The surface morphology of (AAM/OP) hydrogels with AAM: OP compositions of 1:1 and 2:1 at 20 kGy are illustrated in Fig. 11 a,b, respectively, while the surface morphology of modified orange peel [Fig 11 (a)] has a wide, open, channel-like appearance and a highly porous structure. It's clear that when AAM content increases in the hydrogel the porosity of hydrogel also increases [Fig 11 (b)].

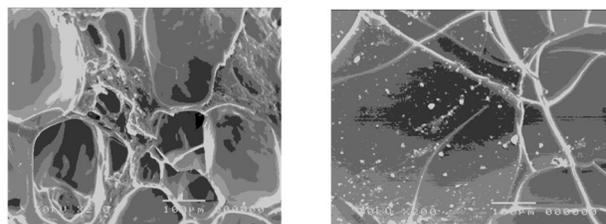


Figure (11): SEM micrographs of hydrogel surfaces of (AAM/OP) at 20 kGy (1:1) (a) and (AAM/OP) (2:1) 20 kGy (b).

Application the prepared hydrogel for wastewater treatment.

Adsorption is a popular and cost-effective process for eliminating dyes from high concentrations. It has several advantages,

including flexibility in sorbent selection and operation, as well as the ability to produce effluents that may be reused. As a result, there has been a surge in interest in developing cost-effective sorbents with high adsorption capacities, rapid adsorption/desorption rates, and ease of separation and regeneration in the previous years 44. The produced hydrogel (AAM/OP) was utilized as adsorbent to remove Congo red (CR) dye from wastewater in this section. The waste water applied in this survey was acquired from the Ismailia Canal (Mostour refinery site): Turbidity (TSS) is (100.7) NTU, pH= (8.32), Temperature= (24.04oC)45,46,47.

Effect of pH

Adsorption procedure and adsorption capacity are both affected by the pH of the dye solution48. The pH of a dye solution affects dye molecular and adsorbent material chemistry 49. Parallel to this, the effects of different pH levels on CR adsorption on (AAM/OP) were studied, and the results are given in Fig (12). Because the dyes precipitated at pH levels below 5, the results were undetectable. As shown in Figure 12, increasing the pH from 5 to 7 increases the adsorption capacity of CR, which thereafter declines somewhat until pH 10 is reached. As a result, the highest quantity of CR adsorbed onto the hydrogel occurs at pH=7. According to some theories, this is due to the fact that at neutral pH levels, as a result, more adsorption tests were performed at pH = 7. The reduction in absorption value at high pH levels might be explained by increased production of OH⁻ ions, which compete with dye anionic species for adsorption sites 50. However, at lower pH levels, the molecular form of the adsorbate is the most often adsorbed species, whereas the ionized form is preferentially adsorbed. The current adsorption

mechanism suggests that at neutral pH, the surface of natural polymer has a predilection for the dye's dissociated species. The hydrogel is made up of heterogeneous polymers of cellulose, hemicelluloses, and lignin that include different functional groups like carboxyl and hydroxyl, among others. The dye molecules' interactions with these functional groups can take on a variety of forms 51. Figure (13) shows that in the spectrum of the (AAM/OP) hydrogel dyed with CR, which has a broad stretching band shift to 3419 cm⁻¹, there is an interaction between this dye and the hydrogel. There is a 2934.9cm⁻¹ shift in the C—N and C=O stretching bands.

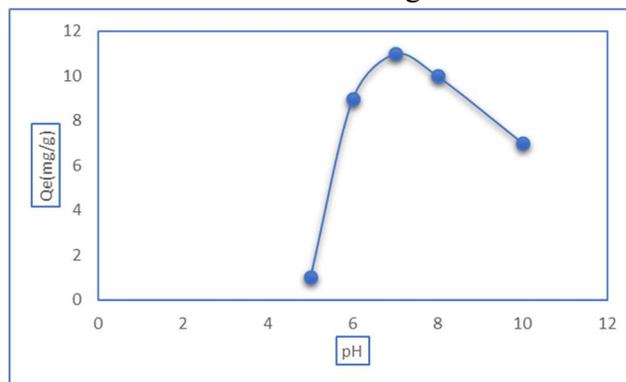


Figure (12): pH influences on the adsorption capacity of CR dye onto hydrogel at premier dye concentration of 25mg/l, contact time 48 hr, at ambient temperature.

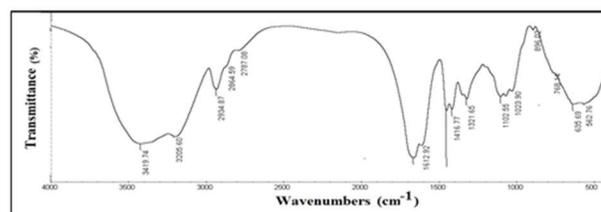


Figure (13): FTIR spectra of loaded hydrogel with CR (AAM/OP).

Effect of preparation of adsorbent dosage.

An adsorbent's efficacy and capacity to adsorb a dye may be estimated using the effect of adsorbent dosage, which can help assess a dye's

economic ability 52. We examined the impact of adsorbent dosage on elimination of CR dye from water by altering the concentration of hydrogel from 0.01 to 0.05 g/L and the results are shown in Figure (14). Increasing the adsorbent dosage improves the CR dye solution's ability to remove color, as demonstrated in the experiment. When the adsorbent dosage is raised, more of the hydrogel's surface area becomes available for adsorption, which improves adsorbate penetration to adsorption sites 53. increasing the adsorbent dose, on the other hand, has no discernible effect on the adsorption efficiency. A dye-adsorbent equilibrium develops as a result of dye molecules attaching almost completely to the adsorbent surface 54 .

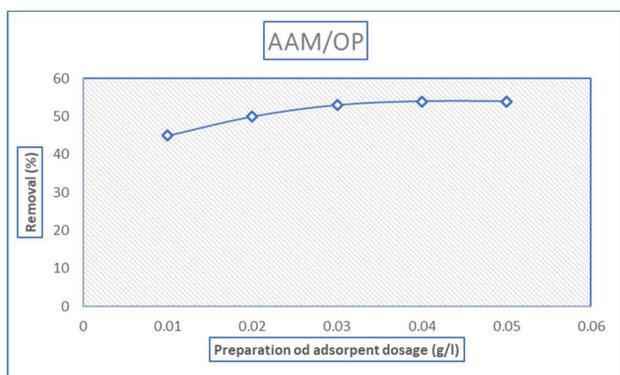


Figure (14): preparation adsorbent dose influence on the adsorption of Congo red dye by the hydrogels at pH 7, premier concentration 25 mg/L and contact time, 48 hr, at ambient temperature.

Influence of initial dye concentration

To some extent, the original dye concentration determines how much dye is eliminated. The initial dye concentration factor's effect is determined by the connection between dye concentration and the obtainable binding sites on an adsorbent surface. From 10 to 80 mg/L dye concentrations, Figure (15) demonstrates how initial dye concentration impacts dye removal in

the hydrogel under investigation. We can observe in figure (15) that the percentage of dye removed from the studied hydrogels reduces as the original dye concentration grows, which might be because the adsorption site saturation on the adsorbent surface 55. Figure (15) shows the impact of the initial CR concentration. Active sites are depleted as the starting dye concentration rises; therefore, the adsorbent surface will contain empty active sites at low concentrations 56. When the initial dye concentration was raised from 10 to 80 mg/L for (AAM/OP) hydrogel, the adsorbent capacity increased from (4 to 15.1) mg/L.

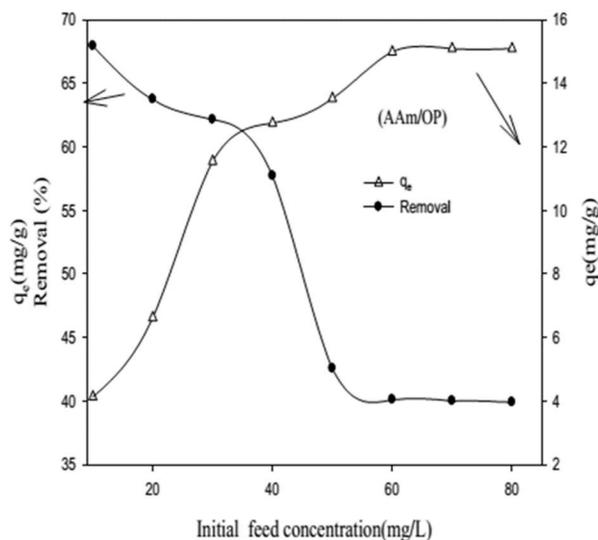


Figure (15): Effect of Congo red dye initial feed concentration on the adsorption of the hydrogel at pH 7, contact time 48 hr and at ambient temperature

Influence of temperature

The adsorption process relies heavily on temperature. The temperature affects the kind of adsorption process, such as exothermic or endothermic. with increasing temperature⁵⁷, adsorption becomes an endothermic reaction.

Because dye molecules become more mobile and adsorption sites increase in number as temperature rises, this might be the case. This impact is heavily influenced by the mobility of dye molecules in different dye classes. In contrast, the fact that adsorption capacity decreases with rising temperature indicates an exothermic nature of the reaction⁵⁸. When temperatures rise, it's possible that the physical connections between dye molecules and the adsorbent's active site diminish, which would explain the reduced dye removal rates found. presented in the form of a Figure (16) adsorption becomes more difficult due to increased^{59,60} solubility of dye as temperature rises, therefore contact forces between solute and solvent are larger than those caused by an interaction between solute and adsorbent. adsorption is easier when the temperature is higher, and it's more beneficial when the temperature is higher⁶¹.

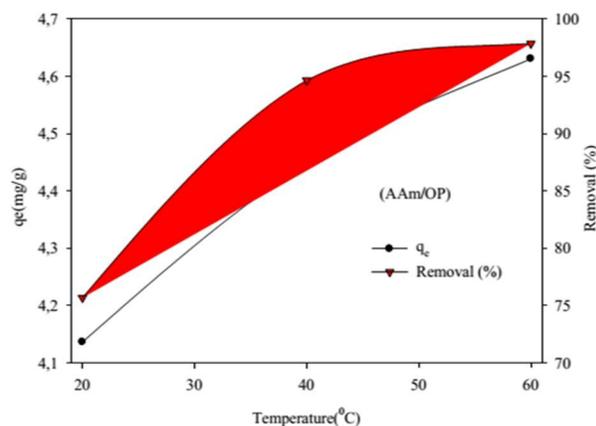


Figure (16) Influence of temperature on the adsorption capacity and elimination percent of Congo red dye onto hydrogels at pH 7, initial concentration 10 mg/L and contact time 48 hr.

Effectiveness of contact time on adsorption process

The amount of dye absorbed by a particular amount of adsorbent at different times may be

determined using contact time experiments. before the dye molecules can react with an active site on the mat, they must first migrate from the bulk solution to its surface (bulk diffusion), then diffuse through the boundary layer to the surface of the material (film diffusion), and then finally diffuse from the surface to the particle's interior (pore diffusion) (chemical reaction). when the starting dye concentration was 10 (mg/L), the amount of CR adsorbed onto the tested hydrogel was measured throughout time at various time intervals. when the contact time is increased, more CR dye is adsorbed and equilibrium is reached in less than 4000 minutes (see Fig. 17), as can be seen. As adsorption progresses, hydrogel functional groups in solution exhaust, slowing the process until it reaches a dynamic equilibrium⁶¹ with its maximum adsorption value (q_{max}), when the rate of adsorption by the hydrogel is equal to the rate of desorption from the hydrogel. A saturation stage was achieved as contact length increased, as the adsorption rate decreased and the dye ions accumulated on the adsorption sites. Total adsorbent surface area decreased and diffusion increased, resulting in the decrease⁶³.

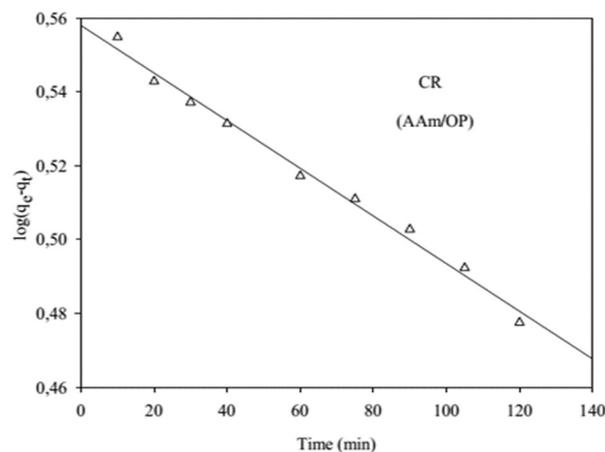


Figure (17): The kinetic plot of Congo red

adsorption onto hydrogel via the Pseudo-first-order model.

Conclusion

The country generates many tones of orange peel (OP) natural wastes that are still dumped every year and reverse an adverse effect on the environment. Modification of physical properties and easy to handle (OP) was done by forming hydrogel with AAM by free radical polymerization using gamma irradiation. the formed hydrogel, (AAM/OP) was characterized by (FTIR), (TGA) and (SEM). Swelling capacity and kinetics of the hydrogel was evaluated. after first adsorption cycle, the loaded hydrogel was applied to second adsorption cycle with good efficiency. From the results obtained the following conclusions can be derived: by raising the irradiation dosage of AAM content in the hydrogel, the gel fraction of OP hydrogel was enhanced. the swelling percent of orange peel-based hydrogel was decreased by raising the irradiation dose of AAM content in the hydrogel. when water was injected into the hydrogel, FTIR validated the functional group in the produced hydrogel, as well as this dye put into, the prepared hydrogel (AAM/OP) was mostly stable up to temperature 200 oC which are suitable for application.

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