

Radiation Crosslinking of a Mixture of Polyvinyle Alcohol Methacrylic acid and 2-Hydroxyethyle Methacrylate to Removal of Pollutant Dyes from its Aqueous Solution

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HYDROGELS based on polyvinyle alcohol methacrylic acid/2-hydroxyethyle methacrylate [P(PVA-MAAc/HEMA)] were synthesized by gamma-radiation. The prepared hydrogels were characterized by infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and thermal gravimetric analysis (TGA). The results of the adsorption studies reveals the higher adsorption capacity of P(PVA-MAAc/ HEMA), hydrogel for the removal of methylene blue and xylenol orange dyes from aqueous solution.

Keywords: Polyvinyle alcohol, 2-hydroxyethyl methacrylate, methacrylic acid, dyes, γ -rays.

Dyes and pigments are widely used in the textiles, plastics, leather, food and cosmetic industry to colour products. The release of coloured waste water from these industries may present an eco-toxic hazard. Various techniques like precipitation, ion exchange, chemical oxidation, and adsorption have been used for the removal of toxic pollutant from waste water. Methylene blue and xylenol orange are selected as a model of pollutant dyes for evaluating the potential of P(PVA-MAAc/ HEMA) hydrogel to remove pollutant dyes from waste waters.

Superabsorbent hydrogels which can absorb very large amount of water and retain it, even under pressure this superabsorbent hydrogels are composed of homopolymers or copolymers. Irradiation processing is a successful technology for hydrogels preparation (Gu *et al.*, 2007, Jin *et al.*, 2009 and Lin and Metters, 2006). Ionizing irradiation technique offers unique advantages to prepare hydrogels over conventional method, especially for its approach to a clear environment (Chapiro and Claude, 1986 and Saraydin *et al.*, 1997).

Ionizing irradiation (gamma and electron beam) treatment is fast, does not induce a significant increase in temperature, requires minimal sample preparation and does not need any catalyst. In this study, P(PVA-MAAc/ HEMA) was studied for its potential use as adsorbent for removal of a pollutant dye from aqueous solution, factor affecting adsorption, such as, contact time, pH, and temperature was evaluated. There are different techniques such as chemical oxidation, precipitation, ion exchange; adsorption has been used for the removal of pollutant from wastewater (Chiou and Chuang, 2006, Salem and El-maazawi, 2000 and Stephenson and Sheldon, 1996). The first thing for an efficient adsorption process is the search for a low cost adsorbent with high adsorption capacity and second it should be biodegradable (Khattari and Singh, 2009). The constituents of adsorbents are mainly responsible for the removal of any particular pollutants from wastewater (Gao and Pedersen, 2005).

Materials and methods

Materials

All chemicals and reagents were of analytical grade, methacrylic acid (MMA), 2-hydroxyethyl methacrylate (HEMA), Merck, Germany and Polyvinyl alcohol (PVA) were used as received, other chemicals, such as methylene blue, xylene orange, solvents, and other reagents were analytical grade, supplied by Algomhoria Company, Cairo, Egypt and used without further purification.

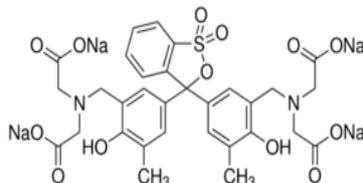


Fig. 1. Structure of xylene orange tetrasodium salt ($C_{31}H_{28}N_2Na_4O_{13}$), MW= 760.6, λ_{max} = 580nm.



Fig. 2. Structure of methylene blue ($C_{16}H_{18}N_3S$), MW= 319.85, λ_{max} = 663nm.

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Preparation of hydrogels

Different concentrations of PVA, 2, 4, 6 wt% are prepared by dissolving it in ionized water at 80°C with stirring until complete solvation. A known volume of MAAc/ HEMA co-monomers of composition ratios (1:1) is dissolved in water is are subjected to different doses of gamma rays until become viscous and then added to different amounts of PVA with stirring. This mixture is placed in test tubes and then degassed by bubbling of pure nitrogen gas for 5 min and subjected to ⁶⁰Co Gamma irradiation. The prepared materials were washed several times with bi-distilled water and then dried in oven at 50°C for 24 h. The product was then grounded and sieved to obtain the desired mesh size of 500µm. The gelation (%) of prepared hydrogel were soaked in distilled water to extract and soluble parts and dried in a vacuum oven at 50°C. The gelation (%) was calculated by the following equation:

$$\text{Gelation (\%)} = \frac{W_e}{W_0} \times 100 \quad (1)$$

Where, W_0 is the wt of dried gel after irradiation, and W_e is the dried wt of the sample after extraction of soluble and unreacted species.

Fourier transforms infrared spectroscopy (FT-IR)

The IR spectrum was measured using ATI MATTFON [Genfis Series, Unicam, England] FTIR spectrometer. Each sample was thoroughly mixed with KBr as a matrix of the mixture was ground and then pressed to give a disc of standard diameter.

Scanning electron microscopy (SEM)

The morphology of the prepared material was studied using SEM. Samples were washed, dried and mounting on support and then made conductive with sputtered gold. The surface observations were made using JEOL JSM-5400 SEM.

Thermal analysis

The thermal properties of P(PVA-MAAc/ HEMA), hydrogels were investigated using Shimadzu-TGA-system of type TGA-50, Japan under nitrogen atmosphere (20 ml/ min). The temperature ranged from ambient to 600°C at heating rate of 10°C/ min. The primary TGA-thermograms were used to determine the rate of thermal decomposition reaction.

Swelling studies

The clean dried hydrogel of pre-weight was soaked in bi-distilled water at room temperature for 24h. The hydrogel was removed and the excess water on the surface was removed by blotting quickly with filter paper and weighed. The swelling ratio was calculated as follows:

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

Where, W_d and W_s are the wt of dry and wet hydrogel, respectively.

Results and Discussions

Characterization of prepared materials

Scanning Electron Microscopy (SEM)

Fig. 1. show the surface morphological structure of P(PVA-AAc/ HEMA), hydrogel and as coarse surface with cavity and groovy structure possesses many largest pore size was obtained for P(PVA-MAAc/ HEMA) hydrogel.

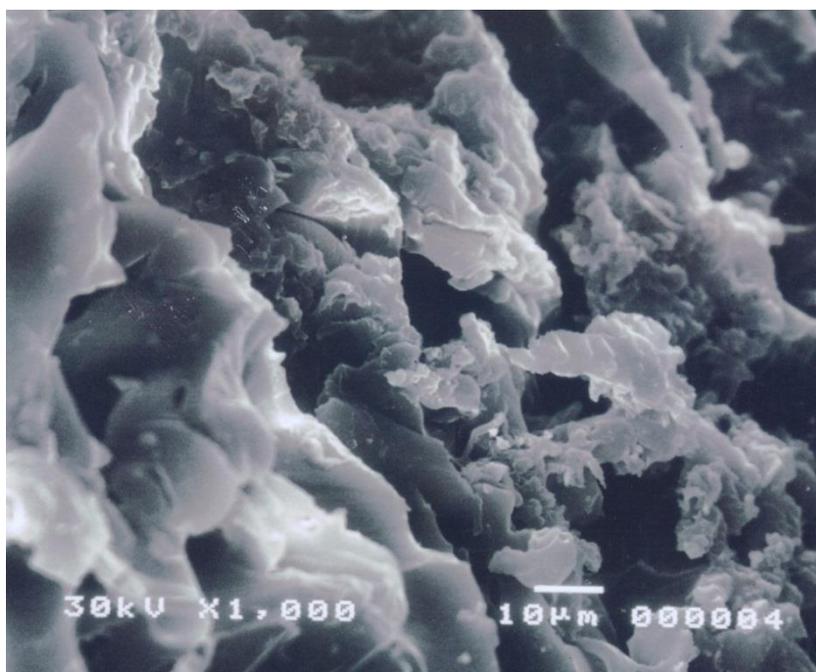


Fig. 3. Scanning electron microscope (SEM) of P(PVA-MAAc/ HEMA).

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FTIR analysis

Fig. 4. show the FTIR spectrum of P(PVA-MAAc/ HEMA), chains appear clearly broad band around $3400\text{-}3500\text{cm}^{-1}$, corresponding to the hydroxyl (OH). The peak at 1760cm^{-1} corresponds to the carboxylic group of AAc. The bands at 1650 and 1780cm^{-1} are attribute to the unsymmetrical and symmetrical stretching vibration of C=O group in carboxylate anion, respectively. This was confirmed by another band at 1420cm^{-1} , which is related to the symmetric stretching mode of C=O in the carboxylate groups (Liang and Liu, 2006).

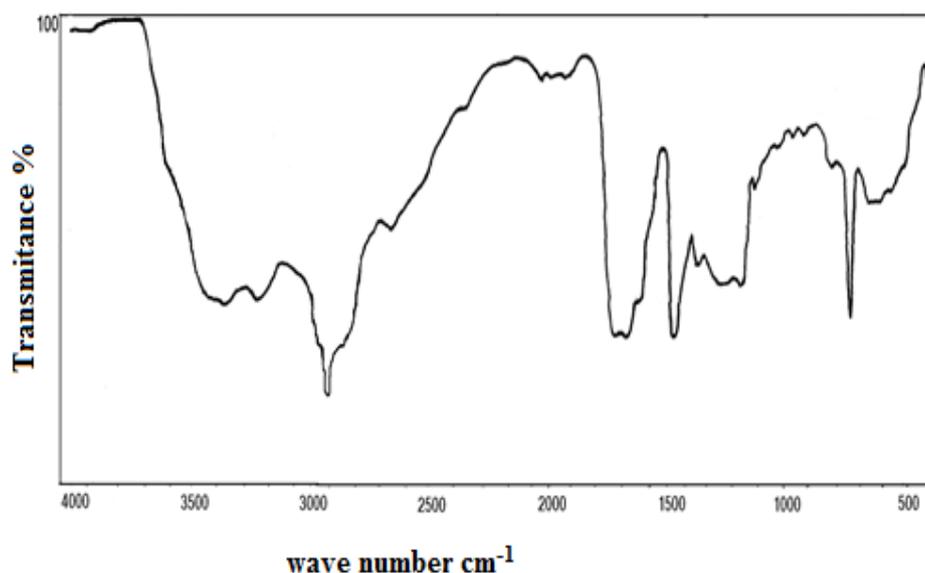


Fig. 4. FTIR of P(PVA-MAAc/ HEMA).

Thermogravimetric analysis (TGA)

TGA was employed to study the effect of thermal behaviour of the copolymer. The TGA of P(PVA-MAAc/ HEMA), hydrogel were studied, as shown in Fig. 5. The thermogram of P(PVA-MAAc/ HEMA), hydrogel shows three decomposition stages, the first decomposition stage within the range $50\text{-}240^\circ\text{C}$ is attributed to the loss of physically adsorbed moisture. The second one within the interval $300\text{-}420^\circ\text{C}$ has been ascribed to the dehydration and decarboxylation of the polymer which leads to the formation of inter- and intra-molecular anhydride. The third decomposition stage within the range $390\text{-}550^\circ\text{C}$ is a result of the degradation of the residual polymer.

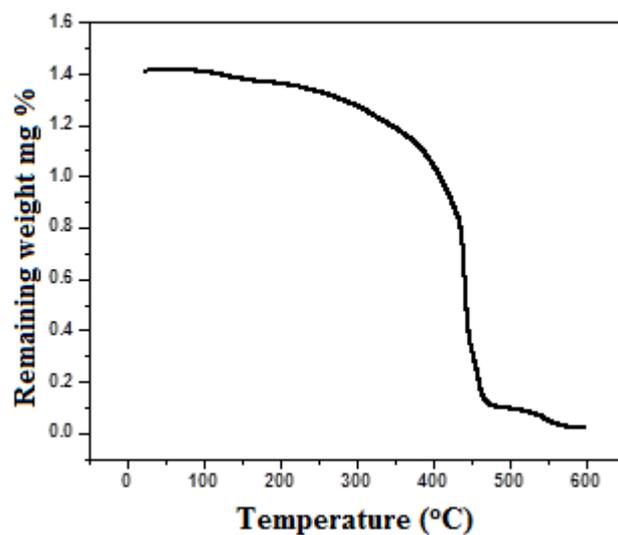


Fig. 5. Thermogravimetric analysis (TGA) of P(PVA-MAAc/ HEMA).

Swelling behaviour

The swelling of hydrogels occurs when the hydrogels are placed in contact with water or buffer solutions, the solution diffuses into the network and a volume phase transition occurs, resulting in an expansion of the hydrogel.

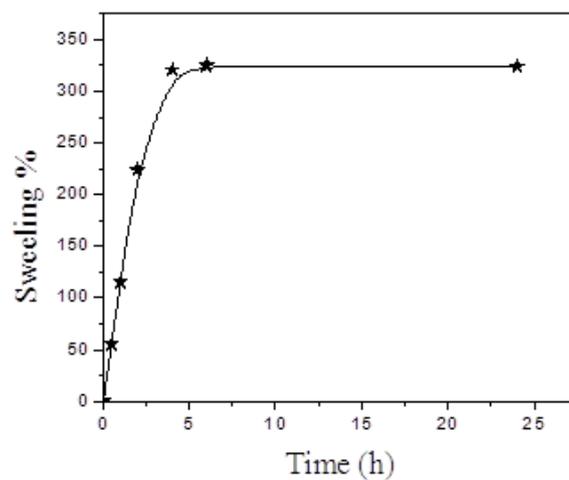


Fig. 6. Effect of time on the swelling % of P(PVA-MAAc/ HEMA) at room temperature, composition of PVA: MAAc-HEMA (1:1).

Fig. 6. show the swelling behaviour of P(PVA-MAAc/ HEMA) hydrogel, as a function of time. They indicate that the swelling (%) increases with time, and reaches the maximum value after 3h. The swelling per-cent of hydrogels depends on the hydrophilicity of the polymer chains and the presence of more ionic groups in the polymer chains which are strongly solvated in aqueous medium. The equilibrium of swelling occurs when the values of the osmotic force driving the solvent into the network and of the elastic force of the stretched sub-chains become equal.

Adsorption of the dyes

Batch adsorption experiments were carried out at different temperatures between 20 and 50°C for the removal of different pollutant dyes from aqueous solutions by shaking 0.05g of the adsorbent with 20.0ml of a required dye concentration at pH from (1-8) in a temperature controlled water bath shaker at 25°C. At the end of the desired contact time the mixture was centrifuged and the residual concentration of each dye was measured. The concentrations of dye at equilibrium C_e were determined using UV-visible spectrometer at wave lengths 663 and 580nm for methylene blue and xylene orange dyes, respectively. Therefore; q_e values are calculated from the following equation:

$$q_e \text{ (mg/ g)} = (C_i - C_e) V / m \quad (3)$$

Where, q_e is the wt in (mg) of the dye adsorbed per gram (g) of dry adsorbent, C_i and C_e are the initial and equilibrium concentrations of dye adsorbate solution in mg/ l while, V is the volume of basic dye solution in (ml) used in the batch adsorption process and m is the mass of adsorbent (g/ l).

Factors affecting on the adsorption of the dyes

Effect of time

The effect of time can be seen from Fig. 7. for the dyes. It is clear that the extent of adsorption is rapid in the initial stages and becomes slow in later stages till saturation is allowed. The final dye concentration did not vary significantly after 1h during adsorption process. This shows that equilibrium can be assumed to be achieved after 1h. It is basically due to saturation of the active site which does not allow further adsorption to take place.

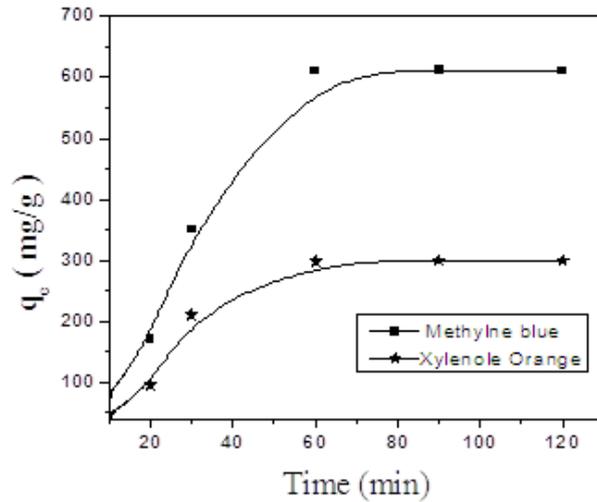


Fig. 7. Effect of time on the adsorption of dyes by P(PVA-MAAc/ HEMA) at room temperature, composition of PVA: MAAc-HEMA (1:1).

Effect of pH solution

Fig. 8. show the effects of initial pH on dye solution of two dyes removal. The adsorption of dyes increase with increasing pH of dye solution and reached the maximum yield at pH 8.

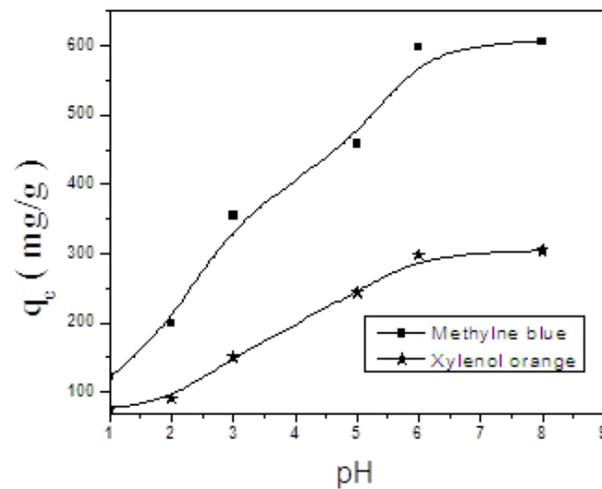


Fig. 8. Effect of pH on the adsorption of dyes by P(PVA-MAAc/ HEMA) at room temperature, composition of PVA: MAAc-HEMA (1:1) at time 1h.

The adsorption of these positively charged dye groups on the adsorbent surface is primarily influenced by the surface charge on the adsorbent which in turn is influenced by the solution pH. The result showed that availability of negatively charged groups at the adsorbent surface is necessary for the adsorption of pollutant dyes. Also, the removal efficiency was found to be highly dependent on the hydrogen ion concentration of solution.

Effect of temperature

The effect of temperature on adsorption of dye solution with initial concentration of 50mg/l at temperatures 25, 30, 40 & 50°C has been determined. The effect of temperature on the adsorption rate of methylene blue and xylenol orange been shown in the Fig. 9. as seen from the curves the rate of adsorption increase with increasing the temperatures for methylene blue and xylenol orange. This may be attributed to increase in the mobility of the large dye ion with temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Furthermore, the temperature affects the adsorption rate by altering the molecular interactions and the solubility. The higher removal due to increasing temperature may be attributed to chemical reactions taking place between the phase's functional groups which are considered endothermic reactions (Hiroyuki *et al.*, (1994).

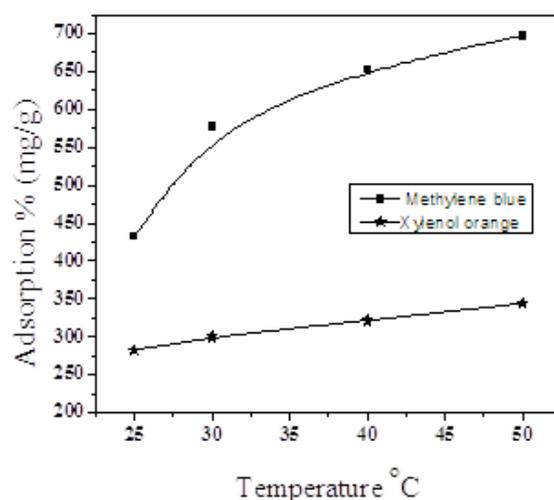


Fig. 9. Effect of temperature on the adsorption of methylene blue and xylenol orange on P(PVA-MAAc/ HEMA).

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Conclusion

Preparation of P(PVA-MAAc/ HEMA) by ionizing gamma radiation was studied and the characterization of prepared hydrogel by different analytical techniques such as IR, SEM and TGA were as investigated, also, studied of different factors affecting on the adsorption of methylene blue and xylenol orange obtained that the preparation of P(PVA-MAAc/ HEMA) can be used as good ion exchange for the removal of pollutant dyes from its solutions.

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البلمره الإشعاعية لبولى فينيل الكحول-حمض المئأكريلك/٢- هيدروكسى إئيل مئأكريلات لإزالة الصبغات من محاليلها

طارق منصور محمد

قسم البحوث الإشعاعية لكيمياء البوليمرات ، المركز القومي لبحوث وتكنولوجيا الإشعاع ، ص. ب. ٢٩ مدينة نصر ، مصر

تم فى هذه الدراسة تحضير هيدروجيل من البولى فينيل الكحول مع حمض المئأكريلك/ هيدروكسى إئيل مئأكريلات باستخدام التشعيع الجامى. و فى هذا البحث تم توصيف البوليمر الناتج عن طريق بعض الاجهزة القياسية مثل الماسح الحرارى الوزنى و الاشعة تحت الحمراء و الفحص بالميكروسكوب الماسح الالكتروني و قد أوضحت النتائج وجود المجموعات المميزة فى البوليمر المحضر. ايضا اوضحت النتائج ان البولمر الناتج ذو ثباتية حرارية عالية. كذلك تم دراسة خاصية الانتفاشية ودراسة عمليات الامتزاز من تلك الصبغات تحت تأثير العوامل المختلفة مثل الاس الهيدروجيني و الزمن و تركيز الصبغات فى المحاليل المائية و كذلك درجات الحرارة و قد لوحظ أن نسبة إزالة الصبغات تزداد بزيادة الاس الهيدروجيني و كذلك زيادة درجات الحرارة تؤدي الى زيادة فى الكفاءة الامتزازية لهذا البوليمر بحيث يمكن استخدامه فى تنقية المياه الملوثة بالصبغات.