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RESEARCH ARTICLE

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Sorption-based treatment of flexographic printing packaging materials ink waste by synthesis of tri-copolymers via gamma irradiation

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Abstract

The treatment or recovery of waste ink constitutes a significant process for the printing and packaging industries, particularly in the flexographic printing of packaging materials. This poses a substantial challenge in the field of waste management science. The application of waste ink recovery, ensuring a safe environment and human health, along with the recovery and sustainability of Earth's resources, has garnered significant global attention. The present research is solely devoted to creating innovative trends without technological barriers for synthesizing a tri-copolymer to be applied as an effective sorption system for waste ink. The Polyethyleneimine-Poly Glycidyl methacrylate-polyethylene glycol diacrylate tri-polymer (PEI-PGMA-PEGDA tri-polymer) was synthesized and thoroughly investigated using FTIR, TGA, and DSC to confirm its chemical structure, thermal stability, and the shift in melting point affected by radiation dose, respectively. SEM analysis showed significant morphological differences in PEI-PGMA-PEGDA tri-polymer samples before and after treatment with flexographic printing ink waste, offering effective strategies for adsorbing waste printing inks from organic solvents. These findings contribute to a comprehensive understanding of the investigated materials and their potential applications. Additionally, the kinetic study of the sorption efficiency of flexographic ink by two sets of tri-copolymers with doses of 20 and 40 kGy indicated that 40 kGy has a more efficient capacity. The highest sorption capacity, approximately 97.6%, was observed for a sample of GMA 15% irradiated by 40 kGy with a sorption amount of 2.5 g L^{-1}. This suggests that the current new treatment strategy can be categorized as highly effective waste ink management and should be advocated for in such domains to ensure a safe environment and preserve Earth's resources. The treatment of printing ink for packaging materials is a crucial step towards achieving green printing technology, which must be supported and advanced through research and industrial application.

KEYWORDS

applications, dyes/pigments, irradiation, packaging, thermal properties

1 | INTRODUCTION

One of the universal challenges is the recovery of resources and the sustainability of industries' output waste. Waste management is a crucial cornerstone in the protection protocol for the environment and human health. Printing manufacturing has a significant background as one of the major contributing activities for all products across various industries. Waste in the printing industry, particularly ink waste, poses a significant environmental threat due to harmful materials such as inorganic substances and non-biodegradable agents, along with toxic compounds like heavy metals and volatile organic compounds (VOCs). These hazardous substances accumulate during the printing process and require proper treatment to mitigate their impact.[1] The escalating environmental protection requirements and economic burden on printing converters further emphasize the urgency to address the problem of flexographic printing ink waste.[2]

Flexographic inks are inks transferred through the process of flexography, primarily used in the printing of packaging materials.[3] The flexographic printing industry is one of the largest consumers of raw materials. Therefore, it is important to recover and recycle the most commonly used materials, especially printed substrates, solvents, and waste ink. The average waste ink from flexographic printing is around 5%, which must be recycled to reuse the solvent before discarding the solid content. To find effective solutions for waste ink management, printing converters, government, industry associations, and other stakeholders must collaborate to explore standardized approaches.

The removal of waste ink from printing solvents promises significant advantages for the industry and fosters the adoption of environmentally friendly practices in packaging materials. Waste inks originate from various substrates, including cartons, plastics, and flexible films, making their management a complex challenge. Specifically, the waste ink issue arising from flexographic printing imposes a considerable economic burden on printing converters due to escalating environmental protection demands.[4] Addressing this problem involves dealing with waste inks and resins that are often present in various solvents.[5] Finding effective solutions to this waste ink problem is essential for promoting sustainable and greener practices in the printing and packaging industries. There are many ways to treat ink wastewater. Depending on the ink content, one will choose a treatment that best matches one's needs. Active carbon,[6] flotation,[7] distillation tower,[8] pyrolysis,[9] flocculation,[10] and filtration[11] are the most common methods to carry out waste treatment of industrial waste.

Many times, a combination of processes is used together to achieve the most effective result. At the end of the day, it's a balance between treatment cost, purification quality, and the stringency of the local environmental regulation.

The Resource Conservation and Recovery Act (RCRA) regulations are in place to protect your business, employee safety, and the environment from hazardous waste at your facility. Whether you are a small, medium, or large quantity generator, you need to understand waste management in the printing industry thoroughly and know RCRA regulations require you to follow certain procedures when generating, storing, transporting, treating, or disposing of hazardous waste. The RCRA is a federal law in the United States that governs the management and disposal of hazardous waste. It establishes a framework for the proper handling, storage, transportation, and disposal of hazardous materials to protect human health and the environment.

A promising avenue for waste reduction lies in the utilization of gamma irradiation synthesis to produce tri-copolymers. Tri-copolymers, with their unique chemical structure composed of three different monomers, offer diverse properties suitable for various applications.[12] Gamma irradiation synthesis provides several advantages, including a fast and efficient process, high product quality, and reduced environmental impact.[13,14,15,16] This paper aims to present a comprehensive overview of the current state of the art in eliminating printing ink waste from packaging materials through gamma irradiation synthesis of tri-copolymers. The discussion will cover the principles and advantages of this synthesis method, the synthesis process, the properties of tri-copolymers, and their potential applications in the packaging industry. The packaging industry can contribute to a more sustainable and eco-friendly future by exploring and implementing these innovative approaches.

2 | MATERIAL AND EXPERIMENTAL

2.1 | Materials

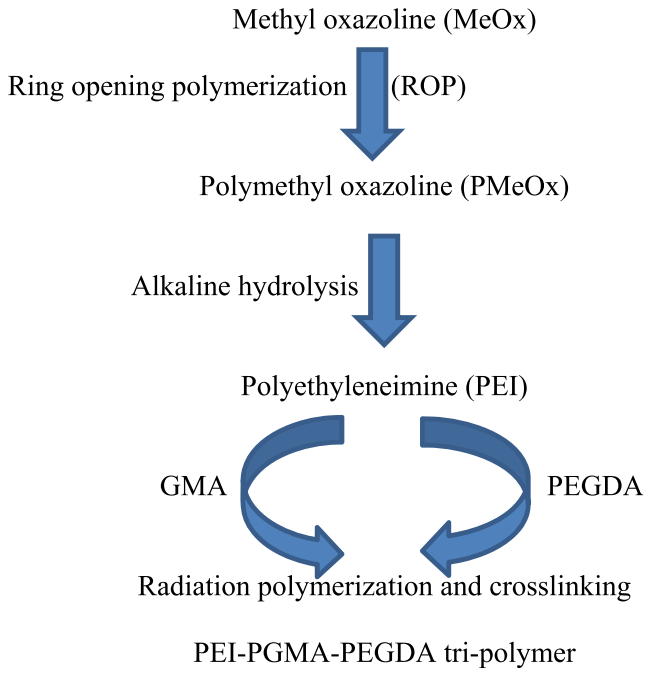
Methyl-2-oxazoline, polyethylene glycol diacrylate (PEGDA), glycidyl methacrylate (GMA), benzyl chloride, acetonitrile and benzonitrile were purified by distillation in the presence of calcium hydride under reduced pressure and stored under dry nitrogen. Polyethyleneimine (PEI) was prepared according to our previous work.[17] DMF, ethanol was used as received without further purification. Flexographic waste ink was collected from local printing converter (Rotographia Masr Co.) as solvent base (ethyl acetate) printing inks.

2.2 | Synthesis of tri-polymer

A solution was formulated using DMF as the solvent, containing 20% PEI and GMA at varying concentrations (0%, 5%, 10%, 15%, and 20%). Additionally, a fixed amount of crosslinker (PEGDA) was incorporated into the mixture. The prepared solution was then subjected to gamma irradiation using a Co-60 gamma cell model 4000 A, sourced from India and located at the Egyptian Atomic Energy Authority, National Centre for Radiation Research and Technology (NCRRT). Under controlled conditions of ambient air, moisture, and room temperature, the specimens of the PEI-PGMA-PEGDA tri-polymer underwent the irradiation process. A radiation dose of 20 kGy was applied at a consistent dose rate of 0.8 kGy/h.

However, it is important to note that PEI and PEGDA are not further polymerized in this process, while GMA acts as a monomer with unsaturation that can undergo polymerization through radiation. The bonding of PEI to the tri-polymer matrix is achieved through a random polymerization process using radiation energy. The specific mechanism of this reaction can vary depending on factors such as the radiation power and the molecular interactions between the components. It is important to note that the actual mechanism for the copolymerization process n result in various stereo forms of the resulting tri-polymer matrix.

2.3 | Scheme for synthesis of polymer networks



Schematic diagram of synthesis process for PEI-PGMA-PEGDA tri-polymer. [Color figure can be viewed at wileyonlinelibrary.com]

2.4 | Step mechanism

The formation of a tri-polymer between glycidyl methacrylate (GMA) and polyethyleneimine (PEI) through radiation-induced grafting involves several steps. Here's a simplified reaction mechanism:

1. Initiation: Radiation (such as gamma rays or electron beams) breaks the C-C bonds in GMA, generating free radicals. One possible initiation mechanism is homolytic cleavage of the double bond in GMA, leading to the formation of GMA radicals.
2. Propagation: GMA radicals react with the amine groups ($-NH_2$) present in PEI, resulting in the formation of a covalent bond between GMA and PEI. This step is often mediated by the abstraction of a hydrogen atom from an amine group by the GMA radical, followed by the formation of a bond between the GMA radical and the nitrogen atom of the PEI chain.
3. Addition of PEGDA: Additionally, polyethylene glycol diacrylate (PEGDA) can be added to the system. PEGDA reacts with the free radicals generated from GMA and PEI, forming covalent bonds between PEGDA and the polymer chains. This leads to the formation of the final tri-polymer P(GMA-PEI-PEGDA), incorporating all three components: glycidyl methacrylate (GMA), polyethyleneimine (PEI), and polyethylene glycol diacrylate (PEGDA).

Regarding the formation of macroradicals on PEI, it's plausible that some radical sites may form on the PEI chain during the grafting process, especially if secondary reactions occur between PEI and other radicals generated in the system. However, the presence and extent of macroradicals on PEI would depend on various factors such as the concentration of free radicals, reaction conditions, and the nature of the polymer chains involved.[17,18,19]

2.5 | Treatment of flexographic waste ink

Practical, easy and efficient technique was selected to can be applied in industrial scale with economic cost. Flexographic waste ink sorption experiments were performed batch-wise in screwed glass tube using crosslinked tri-copolymers under the ambient parameters. The sorption efficiency was study with variation in temperature, time and amount of sorbent tri-copolymer.

3 | MEASUREMENTS AND ANALYSIS

3.1 | Fourier transformation infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR). The attenuated total reflectance (ATR) of a copolymer matrix was examined using a platinum diamond ATR crystal-equipped FTIR spectrometer (Vertex 70, Bruker Optik GmbH, Germany).

3.2 | Ultraviolet–visible spectroscope

UV–VIS spectrophotometer (Shimadzu UV-2550) was used to investigate the color concentration of waste ink before and after treatment with tri-polymers and its kinetics behavior. The sorption efficiency was calculated as a difference between UV–Vis absorption of treatment sample and raw waste sample.

3.3 | Sorption efficiency

The sorption efficiency can be calculated as the percentage reduction in UV–Vis absorption of the waste ink after treatment with the polymer. The formula for sorption efficiency is typically given by:

$$\text{Sorption Efficiency} = [(\text{Absorption of raw waste sample} - \text{Absorption of treatment sample})/\text{Absorption of raw waste sample}]^{\circ} \times^{\circ} 100$$

3.4 | Scanning electron microscope

The cross-section morphology of the PEI-PGMA-PEGDA tri-polymer samples was investigated using scanning electron microscopy (SEM) with a ZEISS EVO 15 SEM instrument from the UK. Before imaging, the samples underwent sputter-coating with gold for 3 min.

3.5 | Thermogravimetric analysis

Thermogravimetric analysis (TGA) was conducted using a Shimadzu TGA-50 instrument from Kyoto, Japan. The analysis was carried out in a temperature range of 20–600°C with a heating rate of 10°C/min. The TGA measurements were performed under a controlled nitrogen flow of 20 mL/min.

3.6 | Differential scanning calorimeter

Nitrogen adsorption/desorption was measured by Nova-TouchLX4 Quantachrome, USA to calculate surface areas of active carbons prepared from waste polymeric packaging materials. DSC131 evo, SETARAM Inc., France was applied to measure the differential thermal behavior for nanocomposites samples. The test was computerized with heating range from 0°C to 200°C with a rising temperature rate 10°C/min. All measured samples were processed using (CALISTO Data processing software v.149).

4 | RESULTS AND DISCUSSION

4.1 | Fourier transformation infrared spectroscopy

Figure 1 shows the FTIR spectra of different samples: Linear polyethyleneimine (LPEI) blank, PEI combined with polyethylene glycol diacrylate (PEGDA), (glycidyl methacrylate) (GMA) and PEI modified with both PEGDA and poly(glycidyl methacrylate) (GMA). The first spectrum represents pure PEI, while the second and third samples represent modifications of the PEI

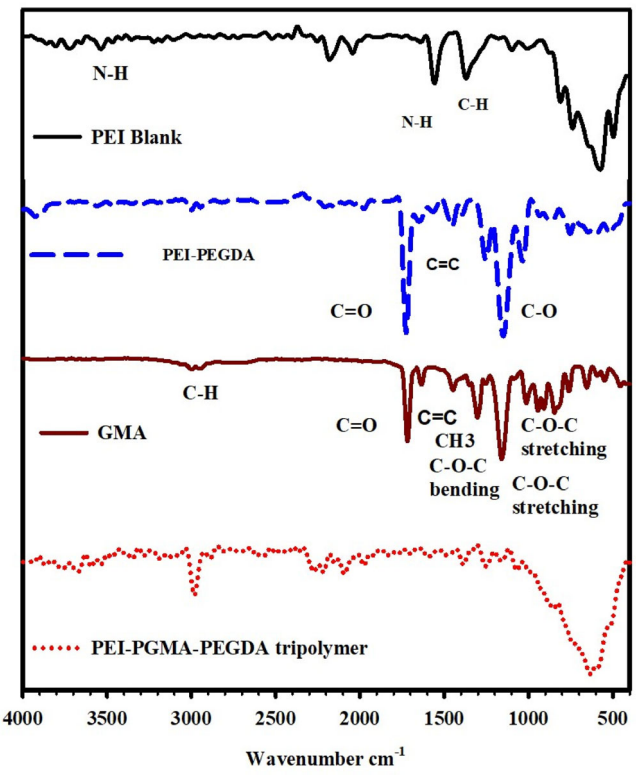


FIGURE 1 FTIR spectra of L(PEI) blank, L(PEI) combined with PEGDA, GMA, and PEI-PGMA-PEGDA tri-polymer. [Color figure can be viewed at wileyonlinelibrary.com]

backbone through the introduction of PEGDA and GMA moieties.

In the FTIR spectrum of linear polyethyleneimine (LPEI), several characteristic bands can be observed. These include: A broad and intense peak around 3300 cm^{-1}, corresponds to the N-H stretching vibration of the PEI backbone. A peak around 2990 cm^{-1}, corresponds to the C-H stretching vibration of the methylene groups in the PEI backbone. A peak around 1650 cm^{-1}, corresponds to the C=O stretching vibration of the amide groups in the PEI backbone. A peak around 1550 cm^{-1}, corresponds to the N-H bending vibration of the amide groups in the PEI backbone. A peak around 1390 cm^{-1}, corresponds to the C-H bending vibration of the methylene groups in the PEI backbone. The figure that shows the comparison of these two FTIR spectra can provide valuable information about the chemical composition of the polymer and the changes that occur upon the addition of PEGDA.[20,21,22] For example, the presence or absence of specific peaks in the FTIR spectra can indicate the presence or absence of certain functional groups. The comparison of the spectra can also provide insight into the interaction between the PEI backbone, PEGDA, and GMA functional groups. The disappearing of broad and intense peak around 3300 cm^{-1}, corresponds to the N-H stretching vibration of the PEI backbone due to the formation of the network structure with the crosslinker. Additionally, the examination of the PEI spectrum provided evidence of hydrolysis reactions that had occurred in the polymer structure. During the analysis of the PEI spectrum, the appearance or disappearance of specific peaks compared to the expected spectrum can indicate the occurrence of chemical reactions. In this case, the presence of additional peaks or shifts in peak position that are not present in the expected PEI spectrum suggests hydrolysis reactions have occurred in the polymer structure.[12] A peak around 2990 cm^{-1}, corresponds to the C-H stretching vibration of the methylene groups in the PEI backbone. A peak around 1730 cm^{-1}, corresponds to the C=O stretching vibration of the acrylate groups in PEGDA and the ester groups in GMA. A peak around 1150 cm^{-1}, corresponds to the C-O stretching vibration of the ether groups in PEGDA and GMA. A peak around 1630 cm^{-1}, corresponds to the C=C stretching vibration of the acrylate groups in PEGDA. A peak around 850 cm^{-1}, corresponds to the C-H bending vibration of the aromatic ring in GMA. The peaks appeared at 850 and 1740 cm^{-1}, indicating the epoxy group and –C=O stretching band of PGMA chains grafted to the PEI backbone polymer.[23] By comparing the FTIR spectra of linear PEI and PEI-PGMA-PEGDA tri-polymer, it is possible to identify the changes in the IR spectrum resulting from the introduction of GMA. This comparison provides valuable insights into the chemical structure of the modified polymer and helps determine its potential applications. The FTIR spectrum of GMA exhibits characteristic peaks corresponding to the functional groups present in the monomer, including the carbonyl group, unsaturated carbon–carbon double bond, epoxy group, and various vibrations of the aromatic and alkyl groups. It is worth noting that the tricopolymer under investigation does not show absorbance attributed to the unsaturation of GMA.

4.2 | Surface area

The surface area and its indices of prepared PEI-PGMA-PEGDA tri-polymer in nitrogen adsorption isotherm branch are presented in Table 1. The performances of prepared PEI-PGMA-PEGDA tri-polymer were examined to confirm the reversible relationship area/ volume. This is due to the packaging effect of adsorbed materials

TABLE 1 Surface area of the prepared PEI-PGMA-PEGDA tri-polymer (20 and 40 kGy) in adsorption isotherm branch.

Sample dose – GMA kGy %	Isotherm branch	Av. pore radius, nm	Slope	BET, m^2/g	Total pore volume (radius, nm)
20–0%	Adsorption	3.34	09.45	72.3	≤100.5
20–5%		1.35	40.51	91.1	≤101.2
20–10%		1.46	64.36	116.5	≤126.3
20–15%		1.38	49.02	113.2	≤109.9
20–20%		1.51	62.01	115.1	≤108.8
40–0%		6.91	18.85	69.8	≤160.4
40–5%		1.43	26.58	132.1	≤104.6
40–10%		1.51	33.08	133.7	≤116.7
40–15%		1.50	56.93	143.5	≤699.3
40–20%		1.50	53.76	119.1	≤409.3

which support the aggregation impact.[24,25] Moreover, the correlation coefficient is nearly ≈0.999. Although, the decreasing in surface area adsorption treatment, the results agree with tri-polymer /adsorbed materials.

On the other hand, density functional theory (DFT) is based on molecular modeling with respect to direct interaction of N_2 with the PEI-PGMA-PEGDA tri-polymer surface. Pore radius can be presented as micropore filling process for all crosslinked samples by both doses. Where the reference samples for two group were presented as microporous filling process as shown in Table 1. The development of the adsorbed film thickness, and capillary adsorption and desorption was described the filling process of pores. Hence, it can model hysteresis in the ads/des micropore, mesopore and macropore region of the isotherm.

Pore size distributions are calculated as shown in Figure 2 for high efficient samples (20–10% and 40–15%). Unimodal pore size distributions for both samples were presented in derivation calculation of pore volume through adsorption isotherm filling process. The cumulative pore volume of sample of GMA 15% irradiated by 40 kGy was nearly double folds than sample of GMA 10% irradiated by 20 kGy which reflected on the sorption efficiency for each sample through the treatment of waste in of flexographic printing industries.

4.3 | Effect of shaken time

The tendency of PEI-PGMA-PEGDA tri-polymer materials for flexographic printing, ink species reduction from crude printing ink waste were evaluated as a function of reaction time ranging 2–600 min (Figure 3). The experimental variables were sorbent dose of 2.5 g L^{-1}, room temperature. The displayed data obvious that both

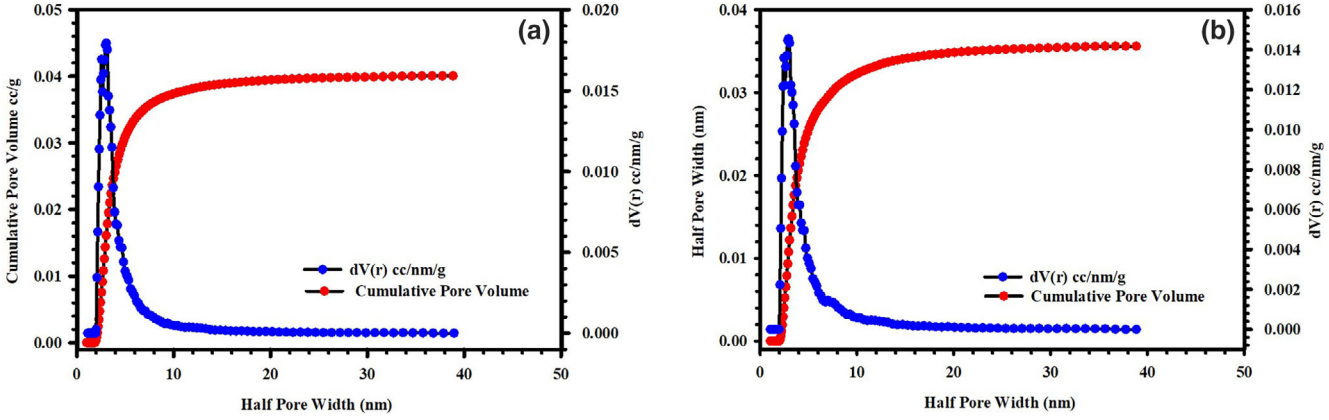


FIGURE 2 DFT method pore volume of (a) 20–10% and (b) 40–15%. [Color figure can be viewed at wileyonlinelibrary.com]

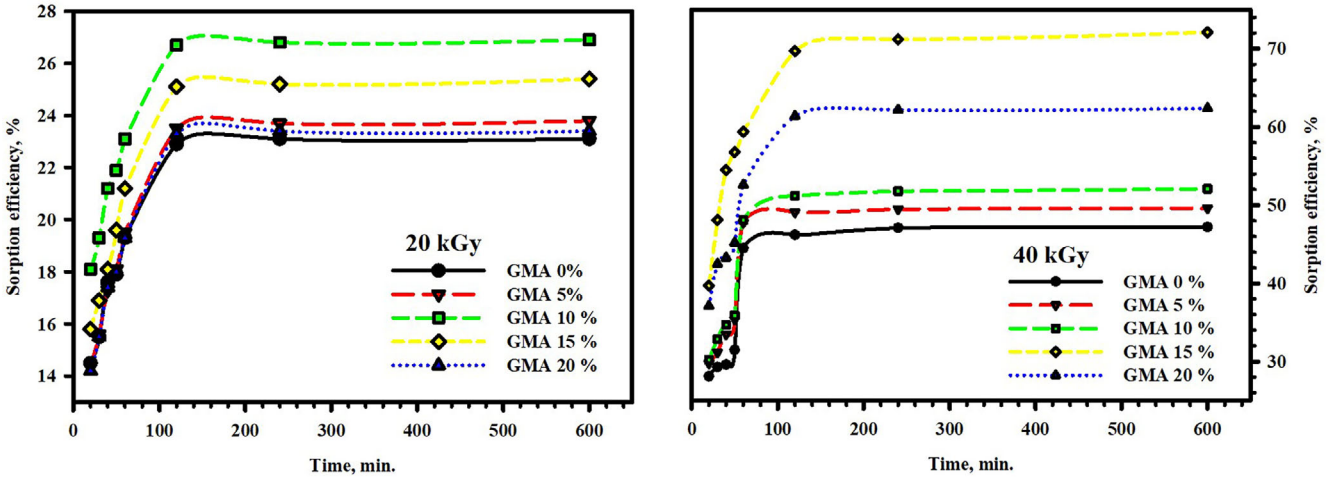


FIGURE 3 Impact of shaken time on PEI-PGMA-PEGDA tri-polymer sorption efficiency, % (2.5 g sorbent/L of flexographic printing ink waste temperature 25 ± 1°C), for 20 and 40 kGy. [Color figure can be viewed at wileyonlinelibrary.com]

sorbents at different crosslinking radiation dose (20 and 40 kGy) exhibit the same kinetic attitude whereas the sorption reaction increase rapidly and reach equilibrium state at 125 min. Extend reaction time after equilibrium obvious a plateau trend for both sorbents. This profile could be owned to the availability of free active function groups on the applied PEI-PGMA-PEGDA tri-polymer materials surface at the beginning of the reaction which means high possibility for binding with flexographic printing, ink waste.[26–28] However, after equilibrium state, most of the vacant surface sites were saturated with waste of ink, and the diffusion of ink particles inside the sorbent pours take place.[26–28]

It is worth noted that tri-copolymer 40 kGy possess higher removal percent (~70%) than tri-copolymer 20 kGy (~27.0). This finding is supported by the characterization discussed of surface area results in which tri-copolymer 40 kGy has higher surface area and pore volume as compared to tri-copolymer 20 kGy which in result, produced higher adsorption capacity towards waste ink. Reaction time of 120 min was selected for other investigation experiments.

4.4 | Effect of temperature

A set of experiments was performed at reaction time of 125 min, sorbent dose of 2.5 g L^{-1}, flexographic printing, ink waste, while different reaction temperature (25–50 ± 1°C) to figure out the impact of temperature on flexographic printing, ink waste efficiency using PEI-PGMA-PEGDA tri-polymer. The attained data shows that waste ink species uptake using PEI-PGMA-PEGDA tri-polymer is an endothermic process whereas the temperature variation slightly improve the sorption process. This reflects that the room temperature is a proper condition for waste ink sorption process, which means that the uptake process is an energy sufficient process.

4.5 | Effect of variation in adsorbent dosage

The dependence of flexographic printing, ink waste sorption percent and capacity on the sorbent dose of 0.6–2.5 g L^{-1} was investigated and displayed in Figure 4b. The selected reaction conditions were fixed at reaction time of 125 min, room temperature. The explored data declares the increment of flexographic printing, ink waste removal percent as the dose of both applied PEI-PGMA-PEGDA tri-polymer up to 2.5 g L^{-1}. This performance could be due to the presence of more active sites as the sorbent dose increases.[29,30] Prolong increase in sorbent dose characterized by a slightly impact on sorbent percent. The solid/liquid ratio of 2.5 g L^{-1} was preferred for other experiments.

4.6 | Morphological study

SEM is a technique used in materials science to analyze and characterize the structure and shape of materials at the micro and nanoscale. The obtained SEM images will provide insights into the size, shape, and distribution of the polymer chains, as well as the presence and distribution of any impurities or defects. By comparing the SEM images obtained at different magnification powers, the performance of the materials in various applications can be optimized. Figure 5 displays the cross-sectional

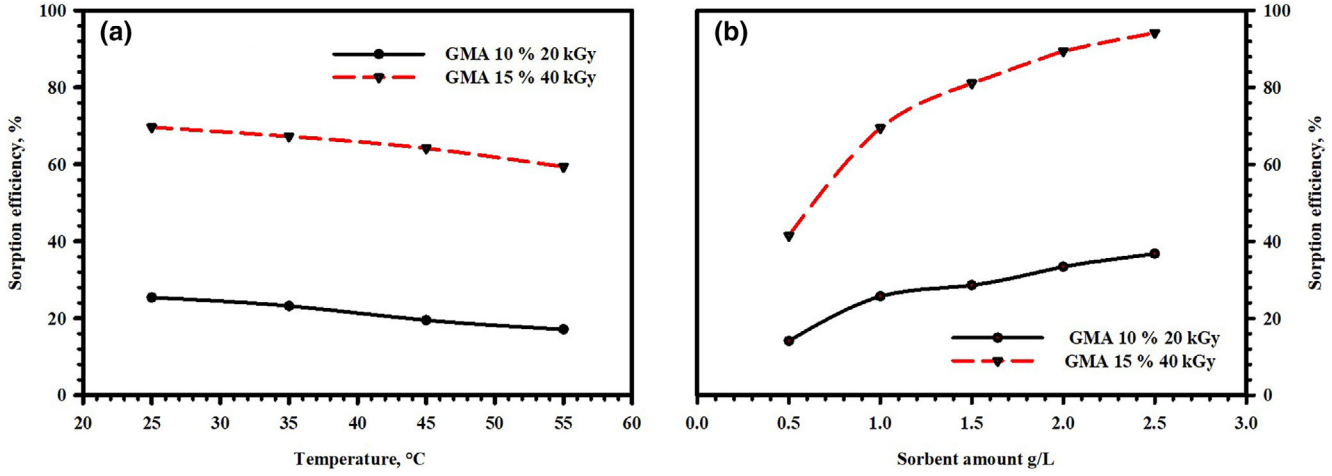


FIGURE 4 (a) Impact of temperature on PEI-PGMA-PEGDA tri-polymer sorption efficiency, % (shaking time 125 min; sorbent dose 2.5 g/L) (b) Effect of sorbent amount of addition on PEI-PGMA-PEGDA tri-polymer sorption efficiency, % and sorption capacity (shaking time 125 min, temperature 25 ± 1°C). [Color figure can be viewed at wileyonlinelibrary.com]

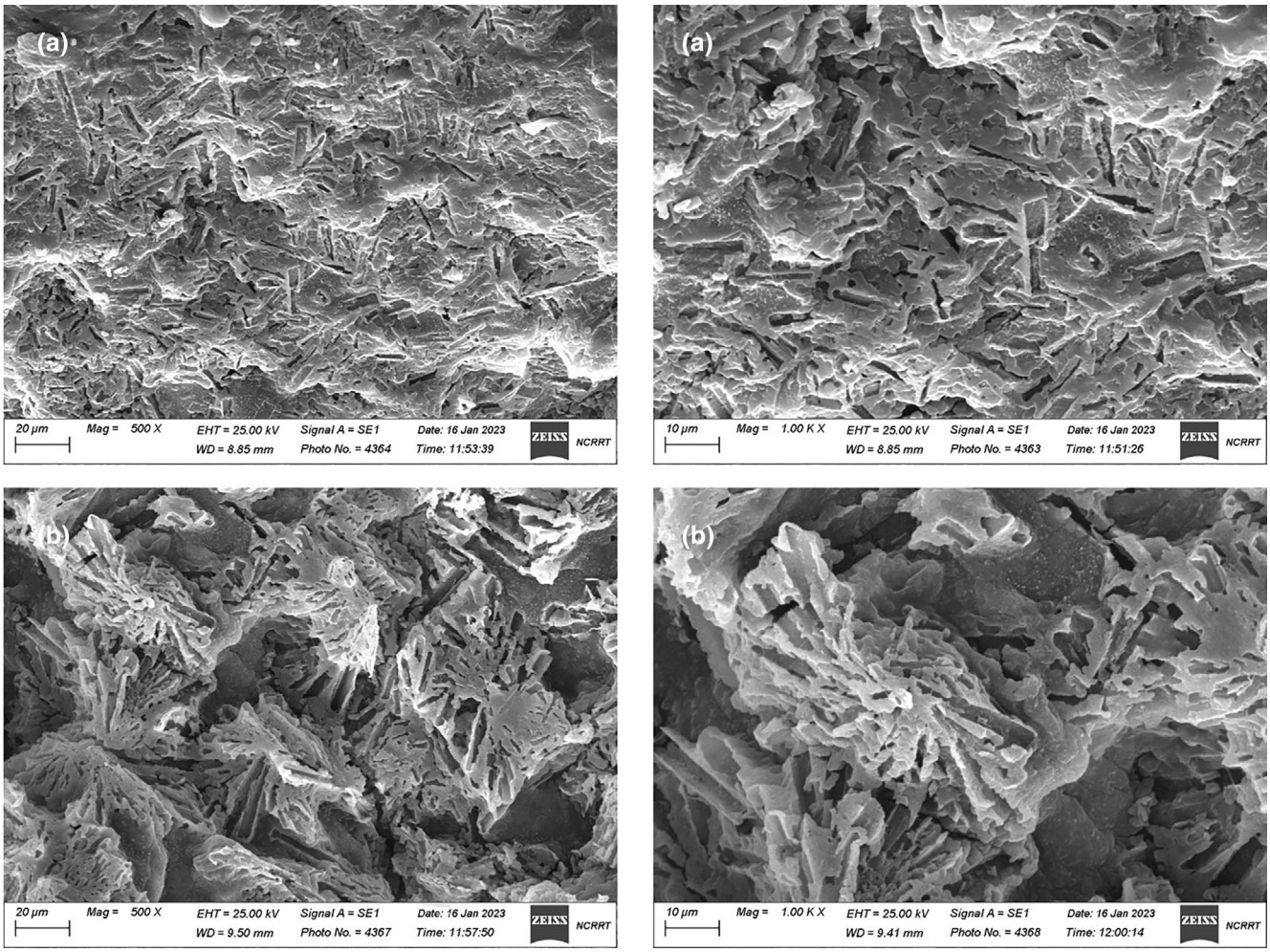


FIGURE 5 SEM cross-sectional of PEI-PGMA-PEGDA tri-polymer (a) before and (b) after treatment of flexographic printing ink waste.

morphology of PEI-PGMA-PEGDA tri-polymer samples (A and B) before and after treatment of flexographic printing ink waste, respectively. Examined samples with GMA concentration of 10% and a radiation dose of 20 kGy were investigated using SEM at magnification powers of 500× and 1000×.

Specifically, topographic character by SEM images of sample (A) without waste and sample (B) containing flexographic printing ink waste were captured. Distinguish forms in the polymer chain structure and orientation were observed between the two samples. In sample (A), the polymer chains were tightly packed as small flower Petals. Additionally, sample (B), the chains had swollen as opened rose petals. The presence of flexographic printing ink waste was also identified by variations in the size, shape, or distribution of the polymer chains 3D structure. Overall, the SEM images provided valuable information about the morphology of the PEI-PGMA-PEGDA tri-polymer samples and the impact of flexographic printing ink waste on their structure as effective tools to adsorb the waste printing inks from organic solvent.

4.7 | Thermal gravimetric analysis

The thermal gravimetric analysis (TGA) results for polyethyleneimine (PEI) and the P(GMA-PEI-PEGDA) tri-polymer, investigated at absorbed doses of 20 and 40 kGy, and various GMA concentrations (5%, 10%, 15%, and 20%), are presented in Figure 6 and the DTG results are shown in Figure 7 and Table 2. Thermal behavior of pure polyethyleneimine (PEI) which is a polymer with high thermal stability, which means it can withstand relatively high temperatures before undergoing significant degradation. For the pure PEI sample, at an absorbed dose of 20 kGy, the first thermal stage (Stage I) shows an onset temperature (T_{Onset}) of 344°C, with a weight loss of 6.5% attributed to the degradation of the polymer. The peak temperature (T_{Peak}) for this stage is observed at 355°C. In the second stage (Stage II), a significant weight loss of 88.1% occurs, starting at 383°C (T_{Onset}) and peaking at 401°C (T_{Peak}). At an absorbed dose of 40 kGy, PEI exhibits similar thermal behavior, but with slightly shifted onset and peak temperatures for both stages.

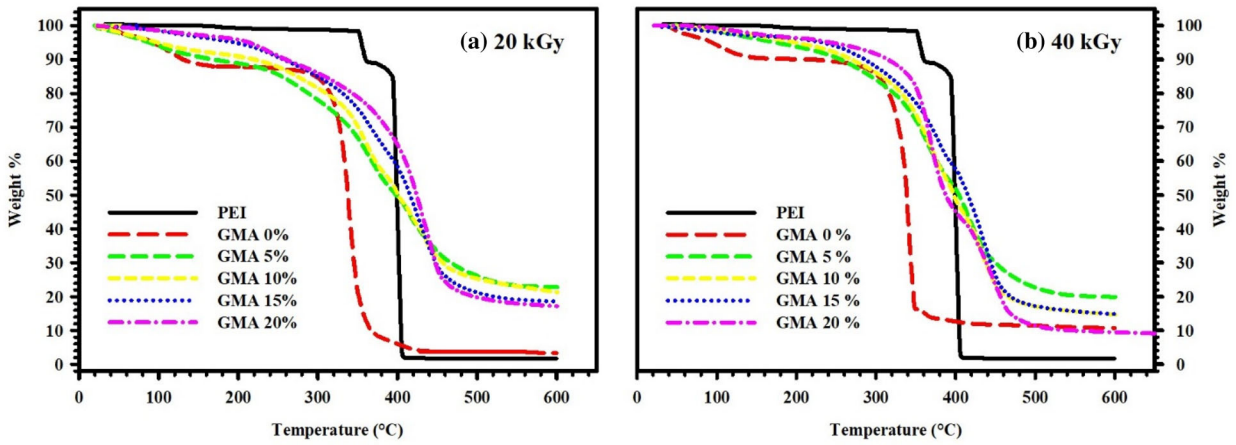


FIGURE 6 TGA results for polyethyleneimine (PEI) and PEI-PGMA-PEGDA tri-polymer at absorbed doses of 20 kGy and 40 kGy, and with varying GMA concentrations (5%, 10%, 15%, and 20%). [Color figure can be viewed at wileyonlinelibrary.com]

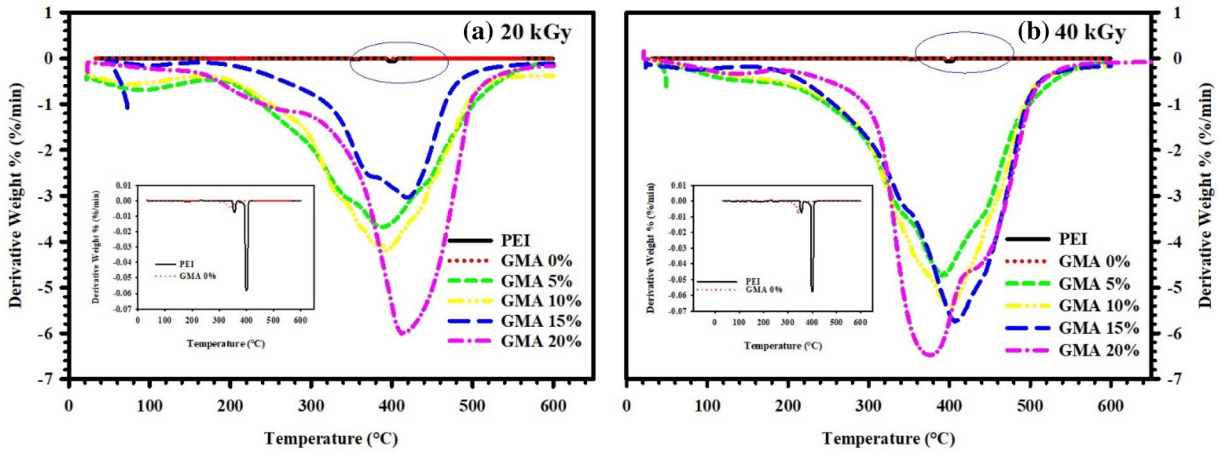


FIGURE 7 DTG results for polyethyleneimine (PEI) and PEI-PGMA-PEGDA tri-polymer at absorbed doses of 20 kGy and 40 kGy, and with varying GMA concentrations (5%, 10%, 15%, and 20%). [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 DTG data for the PEI-PGMA-PEGDA tri-polymer irradiated at 20 and 40 kGy.

			PEI-PGMA-PEGDA tri-polymer									
			20 kGy					40 kGy				
			GMA concentration (%)					GMA concentration (%)				
	Stages	PEI	0	5	10	15	20	0	5	10	15	20
T_{Onset} (°C)	I	344	—	24	30	72	58	295	50	33	28	30
	II	383	—	175	187	204	163	—	193	221	208	217
T_{Peak} (°C)	I	355	295	75	78	104	91	340	125	117	89	120
	II	401	341	380	395	418	416	—	381	390	423	375
Weight loss %	I	6.5	14	11.3	10	6	6	10	8	8	6	6
	II	88.1	85.5	63.6	69	75	76	78	71	76	79	84
Residual mass, (%) at 600°C		1.7	3.3	22.8	21.3	18.5	17.2	10.7	19.9	14.7	14.8	9.5

For the PEI-PGMA-PEGDA tri-polymer samples with varying GMA concentrations, at an absorbed dose of 20 kGy, two distinct thermal stages are observed. In Stage I, the onset temperatures (T_{Onset}) range from 24°C to 72°C, with weight losses ranging from 6% to 11.3%, depending on the GMA concentration. The corresponding peak temperatures (T_{Peak}) for this stage lie between 75°C and 104°C. In Stage II, weight losses ranging from 63.6% to 75% occur at onset temperatures ranging from 175°C to 204°C, with peak temperatures ranging from 380°C to 418°C. The residual mass at 600°C for these samples varies from 3.3% to 22.8%.

At an absorbed dose of 40 kGy, the tri-polymer samples show similar behavior to the 20 kGy doses, with Stage I onset temperatures between 28°C and 163°C, weight losses of 6% to 6.5%, and peak temperatures ranging from 89°C to 163°C. In Stage II, weight losses from 69% to 84% are observed, with onset temperatures ranging from 193°C to 217°C, and peak temperatures ranging from 375°C to 423°C. The residual mass at 600°C for these samples varies from 9.5% to 19.9%.

Comparing the pure PEI with the PEI-PGMA-PEGDA tri-polymer samples were carried out, it is evident that the presence of GMA and PEGDA in the tri-polymer influences its thermal behavior. The tri-polymer shows additional stages of degradation and different weight loss patterns compared to pure PEI. The absorbed dose of gamma radiation has a noticeable effect on the thermal behavior, leading to changes in the onset and peak temperatures, as well as weight losses in both stages of degradation. In summary, the TGA results indicate that the PEI-PGMA-PEGDA tri-polymer exhibits distinct thermal behavior and degradation patterns depending on the absorbed dose of gamma radiation and the concentration of GMA in the polymer matrix. These findings provide valuable insights into the thermal stability and radiation-induced changes of the investigated materials.

4.8 | Differential scanning calorimetry

The thermal behavior of pure polyethyleneimine (PEI) and the PEI-PGMA-PEGDA tri-polymer was investigated using differential scanning calorimetry (DSC) absorbed doses of 20 and 40 kGy and various GMA concentrations (5%, 10%, 15%, and 20%). The DSC thermographs are depicted in Figure 8 and the corresponding data are presented in Table 3. The results reveal important thermal parameters such as onset temperature (T_{onset}), offset temperature (T_{offset}), maximum temperature (T_{max}), and heat of energy (ΔH) for each detected peak. For PEI, three peaks were observed. The first peak had an onset temperature of 46°C, offset temperature of 52°C, maximum temperature of 49°C, and heat of energy of 2.3 J/g. The second peak had an onset temperature of 123°C, offset temperature of 148°C, maximum temperature of 139°C, and a heat of energy of 61 J/g. The third peak had an onset temperature of 195°C, offset temperature of 213°C, maximum temperature of 203°C, and a heat of energy of 52 J/g. Regarding the PEI-PGMA-PEGDA tri-polymer, the DSC results indicated a shift towards lower temperatures for the maximum temperature ($_{Tmax}$) of the second peaks, which could be associated with melting transitions. This shift was observed depending on both the GMA content and the irradiation dose. Higher GMA concentrations and increased irradiation doses contributed to a greater shift in the melting temperatures, an influence on the thermal behavior of the tri-polymer

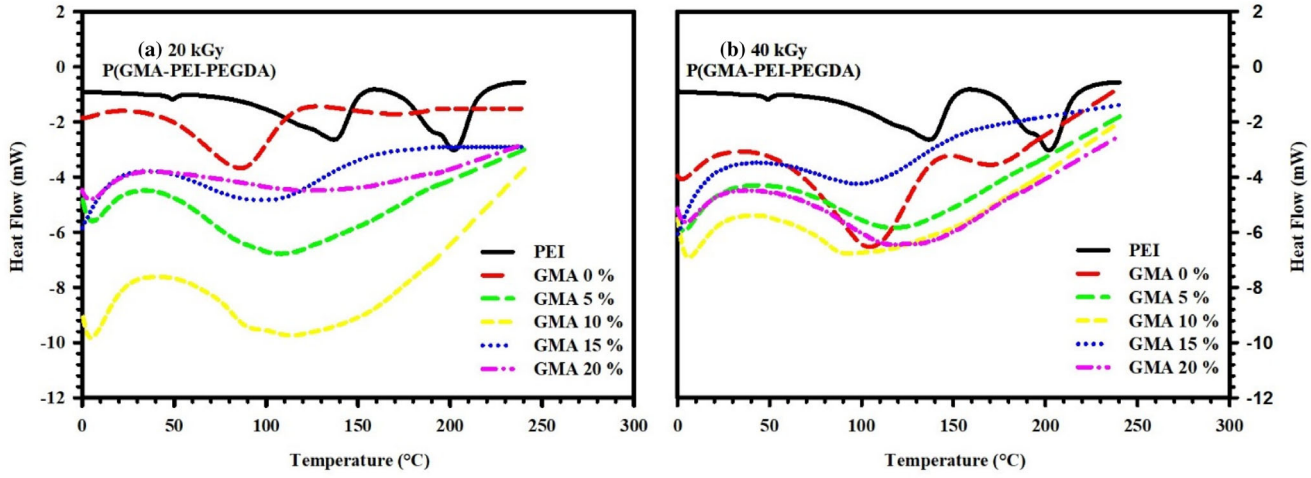


FIGURE 8 DSC analysis of pure polyethyleneimine (PEI) and PEI-PGMA-PEGDA tri-polymer at absorbed doses of 20 kGy and 40 kGy, and with varying GMA concentrations (5%, 10%, 15%, and 20%). [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 3 The change in in thermal parameters for PEI bank and PEI-PGMA-PEGDA tri-polymer, irradiated dose of 20 and 40 kGy.

			PEI-PGMA-PEGDA tri-polymer									
			Dose kGy 20 kGy					Dose kGy 40 kGy				
			GMA concentration (%)					GMA concentration (%)				
Peaks		**PEI**	**0**	**5**	**10**	**15**	**20**	**0**	**5**	**10**	**15**	**20**
1st	T_{onset} (°C)	46	50	0.4	2	55	3	68	1	3	69	2
	T_{offset} (°C)	52	113	119	19	173	16	133	11	22	133	13
	T_{max}	49	87	6	6	105	5	104	3.9	6	102	6
	ΔH (J/g)	2.3	221	6.5	4.7	93	3	154	1.9	6.7	48	1.8
2nd	T_{onset} (°C)	123	—	58	76	—	80	154	81	70	—	89
	T_{offset} (°C)	148	—	174	167	—	165	190	158	156	—	149
	T_{max}	139	—	108	114	—	121	173	118	93	—	119
	ΔH (J/g)	61	—	92	41	—	16	15	35	33	—	36
3rd	T_{onset} (°C)	195										
	T_{offset} (°C)	213										
	T_{max}	203										
	ΔH (J/g)	52										

Note: The missing values (denoted by "—") indicate that the data is not available or not recorded for those specific conditions.

suggesting the internal rearrangements of bonds in the polymeric materials resulting in the release of energy.[31] Overall, these DSC results provide valuable insights into the thermal behavior of PEI and the PEI-PGMA-PEGDA tri-polymer. The recorded parameters help identify the temperature ranges and energy changes associated with specific thermal events or transitions. It was found that the crosslinking between GMA-PEI and PEGDA resulted in two endothermic processes, suggesting the occurrence of multiple reactions during the crosslinking.[32] The shift in the melting temperatures of the irradiated tri-polymer can be attributed to the reduced mobility of PEI and GMA chains caused by the crosslinking process facilitated by PEGDA through gamma irradiation.[12] This reduced mobility disrupts the crystallization process, leading to the observed shift in the melting temperatures.

5 | CONCLUSION

FTIR analysis identified characteristic functional groups in linear PEI and its modifications with PEGDA and GMA, revealing interactions between the components and successful grafting. SEM analysis of PEI-PGMA-PEGDA tri-polymer samples before and after treatment with flexographic printing ink waste showed distinct morphological differences, indicating the waste's impact on the polymer's structure. The TGA results provided valuable insights into the thermal behavior and degradation patterns of the tri-polymer based on gamma radiation dose and GMA concentration. DSC revealed distinct thermal behavior in pure PEI and the tri-polymer, with shifts in melting temperatures influenced by GMA content and irradiation dose. The kinetic study for flexographic ink treatment indicated high sorption efficiency for GMA 10% irradiated by 20 kGy and GMA 15% irradiated by 40 kGy samples. The highest sorption efficiency reached 97% with sample of GMA 15% irradiated by 40 kGy at a sorption amount of 2.5 g L. These previous results encourage the application of copolymer materials in waste ink treatment as environmentally safe resource recovery for flexographic printing industries.

AUTHOR CONTRIBUTIONS

Saber Ibrahim: Conceptualization (equal); data curation (equal); formal analysis (equal); investigation (equal); methodology (equal); resources (equal); supervision (equal); writing – original draft (equal); writing – review and editing (equal). **Hager Fahmy:** Conceptualization (equal); formal analysis (equal); investigation (equal); resources (equal); supervision (equal); writing – original draft (equal); writing – review and editing (equal). **Salah Lotfy:** Conceptualization (equal); data curation (equal); formal analysis (equal); investigation (equal); resources (equal); supervision (equal); writing – original draft (equal); writing – review and editing (equal).

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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