

Synergistic effect of titanium dioxide (TiO₂) and ionizing radiation on thermal and mechanical properties of carboxymethyl cellulose (CMC) for potential application in removal of basic dye from wastewater

Yasser Gad (✉ yasser2uk@yahoo.com)

National Centre for Radiation Research and Technology <https://orcid.org/0000-0002-6973-0701>

Hussein E. Ali

National Center for Radiation Research and Technology

El-Sayed A. Hegazy

National Center for Radiation Research and Technology

Original Research Full Papers

Keywords: carboxymethyl cellulose, TiO₂, composite films, γ -radiation, Basic violet 7 dye

Posted Date: February 2nd, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-161064/v2>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Synergistic effect of titanium dioxide (TiO₂) and ionizing radiation on thermal and mechanical properties of carboxymethyl cellulose (CMC) for potential application in removal of basic dye from wastewater

Yasser H. Gad¹, Hussein E. Ali² and El-Sayed A. Hegazy¹

¹*Polymer Chemistry Department, National Center for Radiation Research and Technology, Atomic Energy Authority P.O. Box 29, Nasr City, Cairo, Egypt*

²*Radiation Chemistry Department, National Center for Radiation Research and Technology, Egyptian Atomic Energy Authority P.O. Box 29, Nasr City, Cairo, Egypt.*

Abstract: Carboxymethyl cellulose (CMC)/titanium dioxide (TiO₂) was prepared using gamma irradiation at different doses. Carboxymethyl cellulose was used as a matrix and TiO₂ in different contents was added (0.25, 0.5, 1, 1.5 wt %) as a filler. The polymer composite film were irradiated at doses of 5, 10 and 15 kGy using ⁶⁰Co γ -ray to form crosslinked network structure. The prepared composite films were described by different diagnostic procedures including X-ray diffractometer, scanning electron microscope (SEM), FTIR as well as thermal and mechanical properties measurements. CMC/TiO₂ composite films was used for removal of basic Violet 7 dye. The adsorption of the dye match with the Langmuir model across chemical monolayer adsorption performance. Adsorption kinetic of dyes was set up to be regular to pseudo second order kinetic model. The results showed that the prepared composite films significantly removed this basic violet 7 dye with maximum absorption capacity (123.6 mg/g).

Keywords: carboxymethyl cellulose, TiO₂, composite films, γ -radiation. Basic violet 7 dye.

corresponding author: yasser2uk@yahoo.com, tel. 002-22746791 and fax. 002-22749298.

1. Introduction

Water contamination happens in various ways, however an enormous quantity of water pollution, as a product of different industrial effluents, happens during the pollution with organic, inorganic and high volume of dyes and this causes the contamination of environment and the orderly health problems for living frameworks [Khan, & Lo, 2015]. Nevertheless, the pollution of water by dangerous dyes has become a crucial problem, universal because of their persistent bioaccumulation, low degradability and their high harmfulness [Sahraei & Ghaemy, 2017]. There are various methods, for example: biodegradation, catalytic degradation and oxidation, for the elimination of pollutants [Khanday et al. 2017]. Nevertheless, these procedures are more responsive and consistent, anyway additional time-consuming, costly, cumbersome, laborious and tedious. Henceforth, sensitive, a simple, direct analytical and economical process is the adsorbent technique. In the adsorbent technique, hydrophilic polymeric hydrogels can assume a fundamental role in the elimination of pollutant from the waste water [Sahraei & Ghaemy, 2017]. Hydrogels have three-dimensional, tissue like network, crosslinked and insoluble [He et al., 2016, Wang & Wang, 2016]. These characteristics are high sorption capacity, important for water safeguarding and the removal of pollutants. In the advancement of such system, polysaccharide polymers are supplementary attractive than the synthetic polymers, on account of their functional properties, for example; great hydrophilicity, biocompatibility and biodegradation [Sharma et al., 2015]. Carboxymethyl cellulose (CMC) has been broadly utilized for the preparation of new designed hydrogels [7,8]. This is for the reason that CMC is a biodegradable natural anionic polysaccharide and biocompatible that can be highly soluble in the water and thus, rising the viscosity of the water [9]. The consolidation of a

limited quantity of inorganic particles can improve the exhibition of thermal, mechanical, electrical, optical, antimicrobial and catalytic properties of the polymer structure [10-12]. TiO₂ is notable for its numerous favorable circumstances, Titanium dioxide (TiO₂) is generally utilized in a variety of medical, food and biological yield [13]. The incorporation of TiO₂ particles into polymeric network is being considered extensively in light of their significant properties, for example, hydrophilic properties, good stability, UV blocking ability, excellent photocatalytic, high oxidation power, liberated from contamination, non-toxic, exhibit antimicrobial activity and chemically inert material [14].

Numerous crosslinkers are generally utilized for polymers crosslinking yet these crosslinkers are either poisonous or costlier and furthermore the crosslinking occur in the presence of organic solvents. Citric acid (CA) is a crosslinker has low toxicity and cost compared with the different crosslinkers. Along these lines, it has been utilized to improve the properties of cellulose in materials applications [15, 16]. There are various techniques to improve the surface properties of polymeric materials or to incorporate new useful natural based polymer.

The critical character of plasticizers is to upgrade the processibility and flexibility of natural polymer such as starch and CMC by reducing the strong intermolecular interactions between polymer molecules [17]. consequently, increases the mobility of polymeric chains, which enhances the flexibility, ductility and extensibility of plasticized composite films. Actually, the addition of plasticizers decreases mechanical resistance of the polymer. In addition, plasticization is especially significant on biopolymer composite films, since the dehydration of these structures produces a highly cohesive composite with poor mechanical properties [18]. Since most plasticizers contain hydrophilic groups, these compounds can interface by methods for hydrogen bonds with polymer framework as well as with water particles, increasing the polymer water adsorption [19]. The majority familiar plasticizer utilized for starch based polymers are polyols such as glycerol and sorbitol. The enthusiasm for the utilization of glycerol is because of glycerol properties which lessens the intermolecular forces and increment the mobility of the polymer chains. It can likewise modify the mobility of water because of its ability to decrease the surface energy of aqueous solution [20].

Radiation polymerization has a lot of advantages over other conventional strategies' science it does not involve the utilization of the catalysts or added substances to start the reaction, no compelling reason to include any initiator or crosslinker, disinfection, no waste, more environment friendly and generally low running expense [21,22]. In this manner, in contrast to the chemical initiation technique, the radiation prompted technique leaves no chemical residues, is free of pollution, consequently the purity of the processed yield can be kept up. In the majority cases of polymerization initiated by high energy radiation, easy to control, the processes are homogeneous and the reactions are not temperature dependent [23, 24]. Additionally, ionizing radiation has been known as an advantageous tool for improving the polymeric materials through grafting, crosslinking and degradation strategies [25].

In this study, preparing of dyes adsorbent composite films based on CMC and TiO₂, which are neither harmful nor costly polymer composite film were done utilizing a direct radiation method. The properties of unirradiated and irradiated composite films were evaluated by utilizing different analytical devices, for example, FTIR, XRD, TGA and SEM. The adsorption isotherm model and kinetic studies for adsorption of the basic violet 7 dye onto CMC/1.5 TiO₂- 10 kGy hydrogel composite film has been investigated. The results showed that the prepared composite films significantly removed this dye with maximum adsorption capacity (123.6 mg/g).

2. Experimental

2.1. Material

- **Basic Violet 7 dye** (Astrazon Red 6B), molecular formula ($C_{24}H_{30}N_2Cl_2$), molecular weight (416), was supplied by Dystar (Cairo, Egypt).
- **Carboxymethyl cellulose (CMC)** (purchased from El Gomhoria company, Cairo, Egypt).
- **Titanium dioxide** (TiO_2) was produced from KARMA for food colors flavors & Fragrances, code No. 77891, Cairo, Egypt.
- Citric acid E.P (monohydrate) $C_6H_8O_7 \cdot H_2O$, M.W= 210.14 Mfr. By ALPHA CHEMIKA,INDIA, was used as crosslinker to prevent CMC from dissolution.
- Glycerol 99.5 % , (Mwt = 92.09) was provided from Gomhoria pharmaceutical company, Egypt. glycerol was used as plasticizer to make the composite film more flexible.

2.2. Preparation of CMC/ TiO_2 Composite films:

CMC (3.0g) was added to 100 ml of deionized water with stirring for about 4 h. until complete miscibility. The desired amount of glycerol (20%) was added as a plasticizer. At that point 5 % citric acid (CA) was added to the solution to reduce the solubility of the prepared composite films (just as a crosslinking agent). During the stirring the required amount of TiO_2 was included with various proportions(0.25, 0.5, 1.0, 1.5 wt %) to the solution. Then placed in sonicator for 30 minutes to get enormous homogeneity. The composite film was removed, the foam was skimmed off and the composite film was poured in leveled polystyrene petri dishes then irradiated at doses of 5, 10 and 15 kGy using ^{60}Co γ -ray to form crosslinked network structure and after that dried for 48 h. at room temperature to form the composite films.

2.3 Irradiation method:

Irradiation was completed at a dose rate of 0.33 Gy/s in air using ^{60}Co gamma cell facility situated at National Center for Radiation Research and Technology (NCRRT), Cairo, Egypt.

2.4 Characterization

2.4.1. Mechanical testing:

Mechanical properties such as elongation at break and tensile strength of the prepared CMC/ TiO_2 composite films were carried out utilizing a Mecmesin equipment (model 10-I, Britain) utilizing a crosshead speed of 5 mm min^{-1} and load 500 N as per ASTM D-638 standards.

2.4.2. Morphology and topography measurement:

The fracture surfaces SEM micrographs were taken with a JSM-5400 electron microscope, JEOL, Japan. A sputter coater was utilized to pre-coat conductive gold onto the fracture surfaces before watching the micrographs at 30 kv.

2.4.3. Thermogravimetric analysis (TGA):

The TGA thermograms were performed by a Shimadzu TGA instrument (Kyoto, Japan)

2.4.4. FTIR Spectroscopy:

The infrared spectra were performed utilizing the Thermo scientific Nicolet iS 10, USA.

2.4.5. X-Ray Diffraction (XRD):

The XRD of plasticized CMC/ TiO_2 composite film before and after irradiation were carried out by a completely automated x-ray diffractometer (Shimadzu type XD-DI). X-ray diffraction pattern was recorded in the range of 2θ on Philips Pw 1730. The diffraction

patterns were performed with nickel filter (Cuka) $\lambda = 1.45 \text{ \AA}$. The x-ray diffractogram was gotten utilizing the following conditions: filament current = 28 mA, voltage = 40 kv, scanning speed = 20 mm/min.

2.5. Application:

- Uptake of basic violet 7 dye onto irradiated CMC/TiO₂ composite film:

Basic violet 7 dye is a cationic water soluble dye; it was chosen as a model dye to investigate its uptake using CMC/TiO₂ composite film. The dye stock concentration (500 mg/l) in proper extents to the required concentrations (10-250 mg/l) were set up by dilution of the stock solution. 100 mg of polymeric composite film was included into 59 ml of dye solutions of definite concentration in each test bottle. The bottles were shaken in a thermostatic mechanical shaker at 30 °C with a speed (100 rpm) for time intervals extend (1-28 h.). The effect of the initial pH of dye solution on the adsorption onto the prepared composite films were studied, for a pH range (2 - 11) at initial dye concentration (100 mg/l) and contact time 4 hours to determine the optimum pH. After each experiment, the dye concentration was determined by measuring its absorption at $\lambda_{\text{max}} = 544 \text{ nm}$ by using UV/Vis double beam Unicam UV2 spectrophotometer. The removal (%) efficiency and the amount of dye adsorbed (q) (mg/g) were determined by the following equations:

$$\text{Removal (\%)} \text{ efficiency} = \frac{(C_o - C_e)V}{C_o} \times 100 \quad (1)$$

$$\text{Amount adsorbed (} q_e \text{)} = \frac{(C_o - C_e) V}{m} \quad (2)$$

$$\text{Amount adsorbed (} q_t \text{)} = \frac{(C_o - C_t) V}{m} \quad (3)$$

Where C_e (mg/l), C_o (mg/l), q_e (mg/g) and q_t (mg/g) are the equilibrium and initial concentrations (mg/l) and the amount adsorbed of the dye at equilibrium and at the time (t), respectively; m (g) is the weight of polymer composite film and V (l) is the volume of the basic violet 7 dye solution.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy (FTIR).

As a result of stretching vibration of –OH groups, pure CMC represented a broad absorption band at 3350-3415 cm^{-1} . Also, stretching vibration band at 2912 cm^{-1} for C-H bonds was belonged. Two intense peaks become obvious at 1460 and 1605 cm^{-1} were appointed to symmetric and asymmetric stretching of carboxylate groups and absorption band at 1320 cm^{-1} associated with –OH bending frequency [26]. The bands at 1175, 1605 and 1023 cm^{-1} corresponded to C-O stretching frequencies of (C-O-C), which are stereotypical of the polysaccharide backbone. As can be seen in figure 1, the FTIR spectra of the prepared composite films were equivalent to the pure CMC composite film with low difference in peaks intensity. This suggests that the added TiO₂ particles have not actuated fundamental changes in the composite film structure [27]. The absorption band at 3415 cm^{-1} which was doled out to –OH group stretching vibration, moderately moved to 3375 cm^{-1} with adding 1% wt of TiO₂. This may be due to formation of hydrogen bonding between CMC and surface hydroxyl groups upon TiO₂ [28]. Likewise, after the addition of TiO₂, absorption bands at 692, 765 and 1062 cm^{-1} were shifted to 735, 796 and 1092 cm^{-1} , respectively. The bands at 1605 and 1572 were disappeared and a new bands at their interval were appeared on 1.5% TiO₂ formed composite films and a new bands at 452- 800 cm^{-1} appeared for CMC based composite film which is due to TiO₂. In affirming this, the spectra of the nanocomposite film (Polycaprolactone/Starch/TiO₂) bands at 412, 532 and 656 cm^{-1} were identified for TiO₂

particles. Besides, the bands in the range 400 - 850 cm^{-1} have been associated with Ti-O-Ti inorganic particles [29,30].

3.2. Mechanical properties

The tensile strength and elongation at break are the mechanical properties that studied in this segment and the effect of irradiation dose and the content of TiO_2 as a filler on this properties were studied. The variation in tensile strength of unirradiated and irradiated CMC samples containing different TiO_2 content are represented in figure 2. It is shown that the TS values of irradiated samples CMC/ TiO_2 samples were higher than the unirradiated sample. Additionally, it was seen that the TS increases as irradiation dose increase up to 10 kGy and it tends to decrease at higher doses above 10 kGy at a given amount of TiO_2 . This increase in TS values is a result of radiation crosslinking in the prepared composite film up to 10 kGy, through at higher doses degradation occur. Meanwhile, the higher the content of TiO_2 the higher the TS at a given irradiation dose. The reinforcement of TiO_2 might be credited to the higher surface area of TiO_2 that in contact with CMC causing a decent dispersion of TiO_2 in the polymer network and strong interaction between TiO_2 and CMC. In this manner, high stress between CMC and TiO_2 is relied upon to happen showing the reinforcing effect of TiO_2 [31]. The TS values increases with introducing TiO_2 in CMC is due to compatibility between TiO_2 and CMC matrix of the composite film. From the data we found that an increase in the stress related to TiO_2 content as a result of irradiation. This gives another factor for the improvement in TS. Also, due to irradiation with addition of TiO_2 the function groups of intercalation agent may support extra additional sites for crosslinking. The TS increase as a result of irradiation CMC of composite film may be due to the formation of free radicals that joined with each other to form crosslinked structure or with TiO_2 through hydrogen bonding.

The change in the elongation at break of the prepared composite film samples relies on the nature polymer and the degree of crosslinking, which limits the movement of polymer chains against the applied force. Figure 3 represent the effect of irradiation dose and TiO_2 % on the elongation at break. It tends to be seen that an orderly decrease in Eb is observed due to the increase of TiO_2 content, this is something contrary to TS. This may be due to reinforcement at low TiO_2 content causes a decrease in the elongation. Additionally, clearly Eb decreases consistently for all CMC/ TiO_2 composite film with increasing the irradiation dose. This is ascribed to the formation of crosslinking network structure in the polymer, Which limited the mobility of the molecular chains through drawing [31]. At higher doses degradation is predominant, which gives another factor contributes a lot in decreasing the values of elongation at break.

3.3. X-ray diffraction investigation (XRD)

XRD was done to perceive the change in the morphology of the composite film by means of checking the position and intensity of reflection as appeared in figure 4. XRD sample of CMC/ TiO_2 showed an intense diffraction peak characteristic to TiO_2 at $2\theta = 25.6^\circ$ (101). While the blank CMC showed a broad peak at $2\theta = 20.8^\circ$ indicating a semicrystalline structure and becomes more comprehensible with addition of TiO_2 . Also, the intensity of the CMC beak of the prepared composite film decreased due to interaction between CMC and TiO_2 particles and the crystallinity of TiO_2 particles does not change during the preparation process. Additionally, the decrease of the composite film crystallinity could be the indication of formation of hydrogen bonding between CMC and TiO_2 [31-33]. Generally, γ -irradiation at 10 kGy for CMC/1.5 % TiO_2 composite film caused a reduce in the

crystallinity of the composite films, which may be due to formation of crosslinked composite film.

3.4. Surface morphology (SEM)

The surface micrographs of blank CMC, unirradiated and irradiated CMC/TiO₂ composite films were produced in figure 5 at a magnification power of 1000 X. The figure indicates that the surface feature of blank CMC is smooth, soft, homogenous and coherent. Addition of TiO₂ particles to unirradiated CMC led to roughness with aggregated white spots, indicating the convenient distribution of TiO₂ particles into the hosting polymer network. Meanwhile, the irradiated CMC/TiO₂ composite films displayed better interfacial adhesion with the polymer matrix.

3.5. Thermal stability

Figures 6,7 showed the thermal stability of CMC, unirradiated and irradiated CMC/1.5% TiO₂ composite films. Which represented that the irradiated samples is thermally more stable than the corresponding polymer from which it was synthesized. The degradation of blank CMC starts at 225 °C with 20 % degradation. In comparison, the degradation of unirradiated CMC/TiO₂ started at 230 °C with just 17 % weight loss and the irradiated sample started at 234 °C with 15 % loss, which making it more stable than the native material from which it was synthesized. From table (1) it can be seen that the unirradiated and irradiated CMC/TiO₂ composite films display higher T_{max} than the neat CMC and T_{max} increases with irradiation. Which pointed that the thermal stability of irradiated CMC/TiO₂ composite films is higher than that of the unirradiated ones. The thermograms concludes higher degradation temperature for the irradiated than the blank CMC and the unirradiated samples. That is might be confirming improvement in the thermal stability ascribed to the formation of crosslinked structure.

3.6. Uptake of basic violet 7 dye on CMC/TiO₂ composite film

The uptake of the dyes from discharge wastewater is a significant issue for the environment. In this study we used the irradiated CMC-20% glycerol, CMC/1.5% TiO₂ and CMC/1.5% TiO₂-10 kGy hydrogel composite films for the uptake of basic violet 7 dye from wastewater. Figure 7A represents the change in the absorbance of the dye solutions by blank CMC, unirradiated and irradiated composite films after 24h., which decreases to approach zero, demonstrating the total removal of the dye by the irradiated CMC/TiO₂ composite film and confirmed by figure 7B that shows the effect of the adsorbent type: (A) blank CMC, (B) unirradiated CMC/TiO₂ and (C) irradiated CMC/TiO₂ composite film.

3.6.1. Effect of initial pH and initial concentration on the adsorption of the dye

Figure 8 represents effect of initial pH on the adsorption of basic violet 7 dye onto CMC/TiO₂ composite film. In this study, 0.2 g of composite film was included into 50 ml of dye solution of definite concentration 100 mg/l in each experimental bottle. The data represented that as the pH increases the dye uptake increases until reaches a maximum value at pH = 8, and afterward remained practically consistent over the range (9 – 11.0). At lower pH values in acidic medium, there will be a competition between the positively charged dye and H⁺ of the aqueous medium toward the carboxylic groups of CMC. As the pH increased (neutral and basic medium), a net negative charge formed on the surface of CMC due the dissociation of carboxylic groups onto CMC, which enhance the attraction between the composite film and the dye. The chosen optimum pH for the adsorption process was pH = 8 as shown in figure 8. Also, Figure 8 represents the effect of initial concentration of the basic violet 7 dye (25 – 250 mg/l) on the adsorption capacity (mg/g) of the dye onto the irradiated CMC/1.5% TiO₂ composite film. The results represented that the adsorption capacity increases as the initial dye concentration increases. Actually, the adsorption capacity of

CMC/TiO₂ toward the basic violet 7 dye is strongly affected by the initial dye concentration. The higher the initial concentration of the basic dye, the stronger the driving forces of the concentration gradient and afterward the higher the adsorption capacity. The adsorption capacity of composite film for the basic violet 7 dye was found to be about 123.8. mg/g at pH = 8, initial concentration of dye = 100 mg/l and temperature = 30 °C after 420 min.

3.6.2. Effect of contact time and temperature on the dye uptake

Figures (9) represent the effect of contact time between the dye solution (initial conc. 100 mg/l) and the prepared CMC/TiO₂ polymer composite film at pH = 8 at different temperatures, which indicates that the adsorption process could be considered as quick process since the amount adsorbed reached 123.6 mg/g after 420 min. From the figure we observed the adsorption increased with time till reaches equilibrium after 420 min. this may be due to rapid attachment between the dye and the composite film at the first stage. Then after that, the attachment becomes slow because many of the available external sites of the polymeric composite film were occupied and, slow diffusion of the dye molecules into the pore spaces of the irradiated CMC/TiO₂ composite film. Temperature is an important factor on the adsorption process as shown in figure 9. Where amount adsorbed (mg/g) of the dye onto the irradiated CMC/1.5 % TiO₂ were studied at 298, 308 and 318 °K at pH = 8 and adsorbent dosage = 0.2 g. The adsorption capacity (mg/g) increased when the temperature increased from 298 to 308 °K, which represented that the adsorption process is an endothermic process. When the temperature reached 318 °K a small change in the adsorption process occurred. This may be due to the thermal motion of the dye molecules increased and could run away the interaction and this process reaches balance.

3.6.3. Adsorption isotherm

The adsorption isotherms of basic violet 7 dye for the irradiated CMC/ 1.5 TiO₂ at different temperatures are represented in figure 10. The data are fitted with the generally used Langmuir and Freundlich models, and the fitted parameters are exposed in Table 2. The Langmuir model is expressed in equation 4. What is more, the Freundlich isotherm describes the reversible adsorption and is not confined to the development of the monolayer is expressed in eq. (5).

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (4)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)$$

where K_L and K_F are the binding constants in the Langmuir and Freundlich models, respectively and $1/n$ is empirical parameter in the Freundlich model.

The Langmuir model correlation coefficients (R^2) for the basic violet 7 dye adsorbed onto the irradiated CMC/1.5 % TiO₂ at different temperatures 298, 308 and 318 °K were 0.9962, 0.9969 and 0.9972, respectively. These values are higher than those acquire from the Freundlich model, for example, 0.7173, 0.6268 and 0.6878, respectively. Furthermore, the obtained empirical parameters ($1/n$) from the Freundlich model for the adsorption of the basic violet 7 dye are all under 1.0, which are in general not compatible with the experimentally calculated adsorption values, while the q_m values resulted from the Langmuir model are fitted with the experimental data in Table 2. This proposes that the adsorption of the dye follows the Langmuir model as opposed to the Freundlich model, representing a monolayer adsorption behavior of the investigated dye onto the irradiated CMC/1.5 % TiO₂.

3.6.4. Adsorption kinetics

The kinetics of basic violet 7 dye adsorption are determined to understand the adsorption behaviors for the irradiated CMC/ 1.5 TiO₂ at different temperatures represented in figure 11. As regards, the irradiated CMC/1.5 TiO₂, the data reveal that, at various temperatures, during the first 420 min, the adsorption plateau showed up the adsorption amounts of 123.6, 138.6 and 142.7 mg/g, respectively. While after 420 min, the adsorbed amounts of the dye didn't change significantly (126.1, 138.7, and 143.2 mg/g, respectively). The kinetic adsorption of the basic violet dye for the irradiated CMC/1.5 TiO₂ was linearly evaluated utilizing the pseudo-first-order (eq. 6) and pseudo-second-order kinetic (eq. 7) and the fixed data were shown in figure 11.

$$\log (q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (6)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (7)$$

where $K_1(\text{min}^{-1})$ and $K_2(\text{min}^{-1})$ are the pseudo-first-order and pseudo-second-order rate constants.

The kinetic parameters fitted from the experimental data were summarized in Table 2. The linear correlation coefficients (R^2) resulted from the pseudo-second-order kinetics for the adsorption of the basic violet 7 dye at various temperatures 298, 308 and 318 °K are close to 1.0 (0.9911 or 0.9971 and 0.9909, respectively). These values are higher than those acquired from the pseudo-first-order, for example, 0.5049, 0.9141 and 0.9256, respectively. Moreover, the determined equilibrium adsorption values ($q_{e,cal}$) obtained from the pseudo-second-order kinetic model for irradiated CMC/1.5 TiO₂ composite film towards the dye are 129.8, 179.8, and 148.9 mg/g, respectively. Where, ($q_{e,cal}$) obtained from the pseudo-first-order kinetic model in general not compatible with the experimentally calculated adsorption values. For that reason, the fitted and the experimental values illustrate considerable consistence here when the pseudo-second-order kinetic model was used.

It is significant that the prepared Fe₃O₄/SiO₂/GMA/AN(amidoxime) nanocomposite film in this work have superior adsorptivity for the basic red dye than that for other CMC polymeric nanocomposite film as Adsorbents., as listed in Table 3.

4. Conclusion

CMC/TiO₂ composite film with various content of TiO₂ were prepared using gamma irradiation source which and characterized by FTIR, TGA and SEM. Additionally, Also, the mechanical behavior of the developed composite films was investigated and the dose yielded best values was adopted to use for the application of interest. The possibility of using the 10 kGy irradiated CMC/ 1.5 % TiO₂ in the removal of basic violet dye from wastewater was examined under the following conditions: optimum irradiation dose 10 kGy, adsorbent CMC/TiO₂ amount: 0.2 g, contact time: 420 min., initial dye concentration: 100 mg/l and pH 8. In this investigation, CMC/1.5 % TiO₂ demonstrated excellent adsorption capacity (123.6 mg/g) for uptake of basic violet 7 dye from its solution. The adsorption of the dye follows the Langmuir model a with chemical monolayer adsorption behavior. Adsorption kinetic of dyes was set up to be regular to pseudo second order kinetic model. Hence, the CMC/TiO₂ composite film can be potentially used for the uptake of dye in addition to industrial applications.

6. References

1. Khan, M., & Lo, I. M. C. (2015). Removal of ionizable aromatic pollutants from contaminated water using nano γ -Fe₂O₃ based magnetic cationic hydrogel: Sorptive performance, magnetic separation and reusability. *Journal of Hazardous Materials*, 322, 195–204. <http://dx.doi.org/10.1016/j.jhazmat.2016.01.051>

2. Sahraei, R., & Ghaemy, M. (2017). Synthesis of modified gum tragacanth/grapheneoxide composite film hydrogel for heavy metal ions removal and preparation of silver nanocomposite film for antibacterial activity. *Carbohydrate Polymer*, 157,823–833. <http://dx.doi.org/10.1016/j.carbpol.2016.10.059>.
3. Khanday, W. A., Asif, M., & Hameed, B. H. (2017). Cross-linked beads of activated oil palm ash zeolite/chitosan composite film as a bio-adsorbent for the removal of methylene blue and acid blue 29 dyes. *International Journal of Biological Macromolecules*, 95, 895–902. <http://dx.doi.org/10.1016/j.ijbiomac.2016.10.075>
4. He, S., Zhang, F., Cheng, S., & Wang, W. (2016). Synthesis of sodium acrylate and acrylamide Copolymer/GO hydrogels and their effective adsorption for Pb²⁺ and Cd²⁺. *ACS Sustainable Chemistry and Engineering*, 4(7), 3948–3959. <http://dx.doi.org/10.1021/acssuschemeng.6b00796>.
5. Wang, L. Y., & Wang, M. J. (2016). Removal of heavy metal ions by poly(vinylalcohol) and carboxymethyl cellulose composite film hydrogels prepared by a Freeze-Thaw method. *ACS Sustainable Chemistry and Engineering*, 4(5),2830–2837. <http://dx.doi.org/10.1021/acssuschemeng.6b00336>.
6. Sharma, R., Kaith, B. S., Kalia, S., Pathania, D., Kumar, A., Sharma, N., & Schauer, C.(2015). Biodegradable and conducting hydrogels based on Guar gum polysaccharide for antibacterial and dye removal applications. *Journal of Environmental Management*, 162, 37–45. <http://dx.doi.org/10.1016/j.jenvman.2015.07.044>.
7. Kono, H., Ogasawara, K., Kusumoto, R., Oshima, K., Hashimoto, H., & Shimizu, Y.(2016). Cationic cellulose hydrogels cross-linked by poly(ethylene glycol):Preparation, molecular dynamics, and adsorption of anionic dyes. *Carbohydrate Polymers*, 152, 170–180. <http://dx.doi.org/10.1016/j.carbpol.2016.07.011>.
8. Wang, Z., Ning, A., Xie, P., Gao, G., Xie, L., Li, X., & Song, A. (2017). Synthesis and swelling behaviors of carboxymethyl cellulose-based superabsorbent resin hybridized with graphene oxide. *Carbohydrate Polymers*, 157, 48–56. <http://dx.doi.org/10.1016/j.carbpol.2016.09.070>.
9. Raafat, A. I., Eid, M., & El-Arnaouty, M. B. (2012). Radiation synthesis of superabsorbent CMC based hydrogels for agriculture applications. *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms*, 283, 71–76. <http://dx.doi.org/10.1016/j.nimb.2012.04.011>.
10. Jordan, J., Jacob, K. I., Tannenbaum, R., Sharaf, M. A. and Jasiuk, I.(2005). *Materials Science and Engineering: A*, 393 (1-2), 1-11.
11. Viswanathan, V., Laha, T., Balani, K., Agarwal, A. and Seal, S. , *Materials Science and Engineering R* 54 (2006) 121–285.
12. Damodar, R. A., You, S. J. and Chou, H. H., (2009) *J. Hazard Mater*,172(2-3), 1321-1328.
13. Kaewklin, P., Siripatrawan, U., Suwanagul, A., Lee, Y.S., 2018. Active packaging from chitosan-titanium dioxide nanocomposite film for prolonging storage life of tomato fruit. *Int. J. Biol. Macromol.* 112, 523–529.

14. He, Q., Zhang, Y., Cai, X., Wang, S., 2016. Fabrication of gelatin–TiO₂ nanocomposite film and its structural, antibacterial and physical properties. *Int. J. Biol. Macromol.* 84, 153–160.
15. Gawish, S. M. Abo El-Ola, A. M. Ramadan AAAE-KN (2012),” Citric acid used as a crosslinking agent for the grafting of chitosan onto woolen fabric“ *Journal of Applied Polymer Science*, 123, 3345–3353.
16. Reddy N, Yang Y. “Citric acid crosslinking of starch films”, *Food Chem.* 2010;118(3):702–11.
17. Aguirre, A.; Borneo, R.; León, A.E. “Properties of triticale protein films and their relation to plasticizing–antiplasticizing effects of glycerol and sorbitol”. *Ind. Crops Prod.* 2013, 50, 297–303.
18. Melissa Gurgel Adeodato Vieira, Mariana Altenhofenda Silva and Marisa MasumiBeppu, “Natural-based plasticizers and biopolymer films: A review”, (2011). *European Polymer Journal.* 47(3): p. 254-263.
19. Sandra Rivero, L Damonte, María Alejandra García, A Pinotti, “An insight into the role of glycerol in chitosan films”, (2016). *Food Biophysics.* 11(2): p. 117-127.
20. Lavorgna, M., Piscitelli, F., Mangiacapra, P., and Buonocore, G. G., (2010). Study of the combined effect of both clay and glycerol plasticizer on the properties of chitosan films. *Carbohydrate Polymers*, 82: 291–298.
21. Tabata Y., Ito S. and Tagawa S., “CRC Handbook of Radiation Chemistry, CRC, Baston”, (1991) p. 742.
22. Abd El-Mohdy H.L., Hegazy E.A., El-Nesr E.M., and El-Wahab M.A.,” Synthesis, characterization and properties of radiation-induced Starch/(EG-co-MAA) hydrogels“, *Arab J. Chem.*, 9, S1627 (2016).
23. Barsbay, M., Kodama, Y., Güven, O., 2014. Functionalization of cellulose with epoxy groups via initiated RAFT-mediated grafting of glycidyl methacrylate. *Cellulose* 21,4067–4079.
24. Rymuszka, D., Terpiłowski, K., Sternik, D., Tomczynska-Mleko, M., Goncharuk, O., 2017. Wettability and thermal analysis of hydrophobic poly(methyl methacrylate)/silica nanocomposite films. *Adsorpt. Sci. Technol.* 35 (5–6), 560–571.
25. El-Arnaouty M.B., Abdel Ghaffar A. M. , Abdel Baky A. A. and Shama S. A., “ Radiation synthesis of hydrogels based on carboxymethyl cellulose and its application in removal of pollutants from wastewater”, *J. Vinyl& Additive*, (2017), 25, S1, E35-E43.
26. Damodar, R. A., You, S. J. and Chou, H. H.,” Study the self cleaning, antibacterial and photocatalytic properties of TiO₂ entrapped PVDF membranes.“, (2009) *J. Hazard Mater*,172(2-3), 1321-1328.
27. A.Abdel-Galil· H.E.Ali· A.Atta and M.R.Balboul “Influence of nanostructured TiO₂ additives on some physical characteristics of carboxymethyl cellulose (CMC)” *Journal of Radiation Research and Applied Sciences*, 7, (1), 2014, 36-43.
28. Jinbao Zhang, Nick Vlachopoulos, Yan Hao, Thomas W. Holcombe, Gerrit Boschloo, Erik M. J. Johansson, Michael Grätzel, and Anders Hagfeldt,” Efficient Blue-Colored Solid-State Dye-Sensitized Solar Cells: Enhanced Charge Collection by Using an in Situ

- Photoelectrochemically Generated Conducting Polymer Hole Conductor”, *ChemPhysChem* 2016, 17, 1441 – 1445.
29. Jordan, J., Jacob, K. I., Tannenbaum, R., Sharaf, M. A. and Jasiuk, I.” Experimental trends in polymer nanocomposite films - A review“, (2005). *Materials Science and Engineering: A*, 393 (1-2), 1-11.
 30. Lei, Y., Zhang, L. D. and Fan, J. C. “Fabrication, characterization and Raman study of TiO₂ nanowire arrays prepared by anodic oxidative hydrolysis of TiCl₃“, (2001). *Chemical Physics Letters*, 338(4-6), 231-236.
 31. Oleyaei, S. A., Zahedi, Y., Ghanbarzadeh, B. and Moayedi, A. A.,” Modification of physicochemical and thermal properties of starch films by incorporation of TiO₂ nanoparticles“, (2016). *International Journal of Biological Macromolecules*, 89, 256-264.
 32. Ren, J., Wang, S., Gao, C., Chen, X., Li, W. and Peng, F. , “TiO₂-containing PVA/xylan composite films with enhanced mechanical properties, high hydrophobicity and UV shielding performance“, (2015). *Cellulose*, 22(1), 593-602.
 33. Sreekumar, P., Al-Harhi, M. A. and De, S.,” Reinforcement of starch/polyvinyl alcohol blend using nano-titanium dioxide“, (2012). *Journal of Composite film Materials*, 46(25), 3181-3187.
 34. Tayeb Benhalima , Hafida Ferfera-Harrar, Djahida Lerari,” Optimization of carboxymethyl cellulose hydrogels beads generated by an anionic surfactant micelle templating for cationic dye uptake: Swelling, sorption and reusability studies”, *International Journal of Biological Macromolecules*, 105(1), (2017), 1025-1042
 35. Zirak, M., Abdollahiyan, A., Eftekhari-Sis, B. *et al.* “Carboxymethyl cellulose coated Fe₃O₄@SiO₂ core-shell magnetic nanoparticles for methylene blue removal: equilibrium, kinetic, and thermodynamic studies”. *Cellulose* 25, 503–515 (2018).
 36. C. Liu, A. Omer, X.-k. Ouyang, “Adsorptive removal of cationic methylene blue dye using carboxymethyl cellulose/k-carrageenan/activated montmorillonite composite film beads: isotherm and kinetic studies”, *Int. J. Biol. Macromol.* 106 (2018) 823–833.
 37. K. Kaur, R. Jindal, “Self-assembled GO incorporated CMC and chitosan-based nanocomposite films in the removal of cationic dyes”, *Carbohydr. Polym.* 225 (2019), 115245
 38. J. Liu, H. Chu, H. Wei, H. Zhu, G. Wang, J. Zhu, J. He, “Facile fabrication of carboxymethyl cellulose sodium/graphene oxide hydrogel microparticles for water purification”, *RSC Adv.* 6 (2016) 50061–50069.

Figures

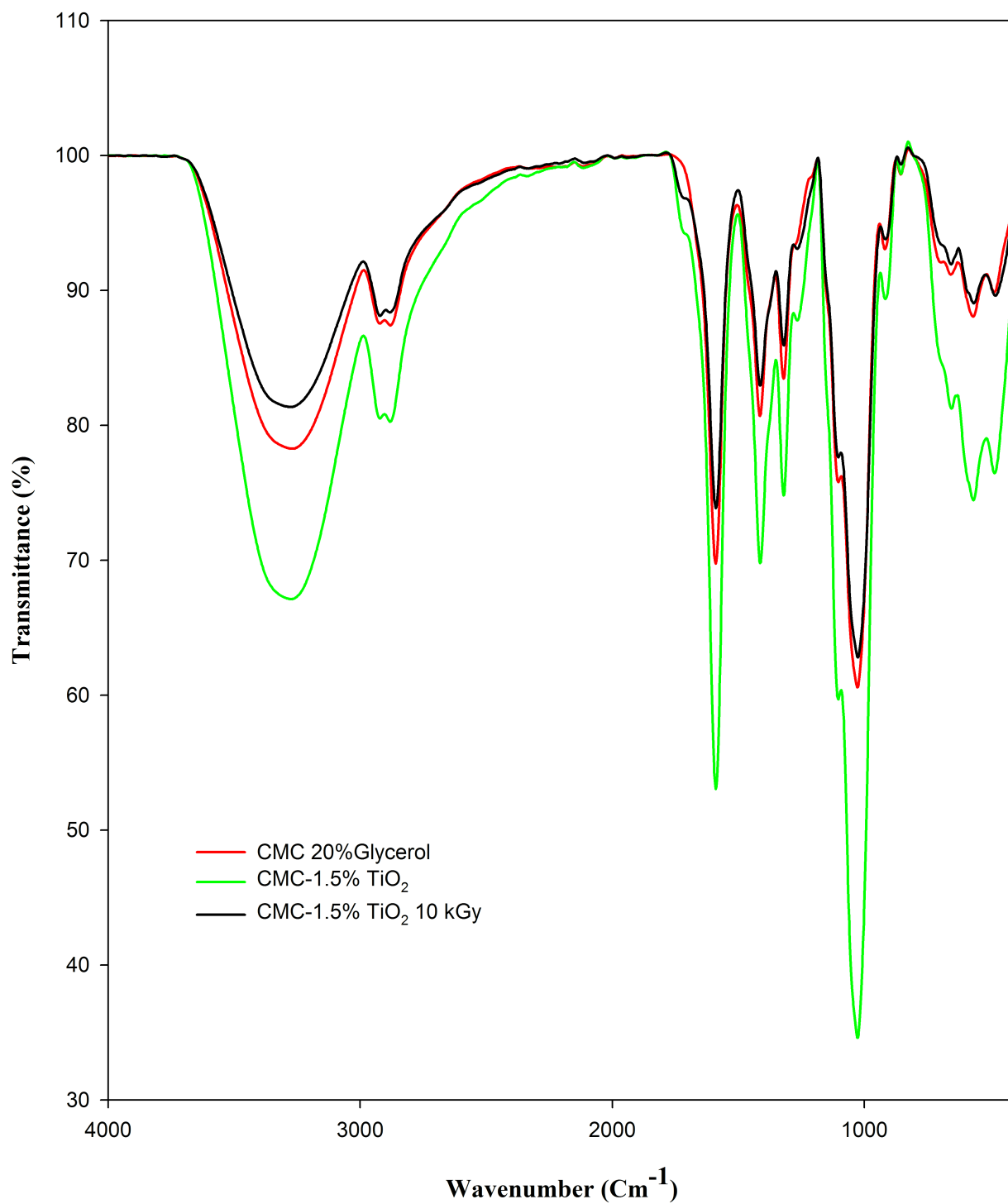


Figure 1

FTIR spectra of CMC-20% Glycerol, CMC/1.5% TiO₂ and CMC/1.5% TiO₂ - 10kGy.

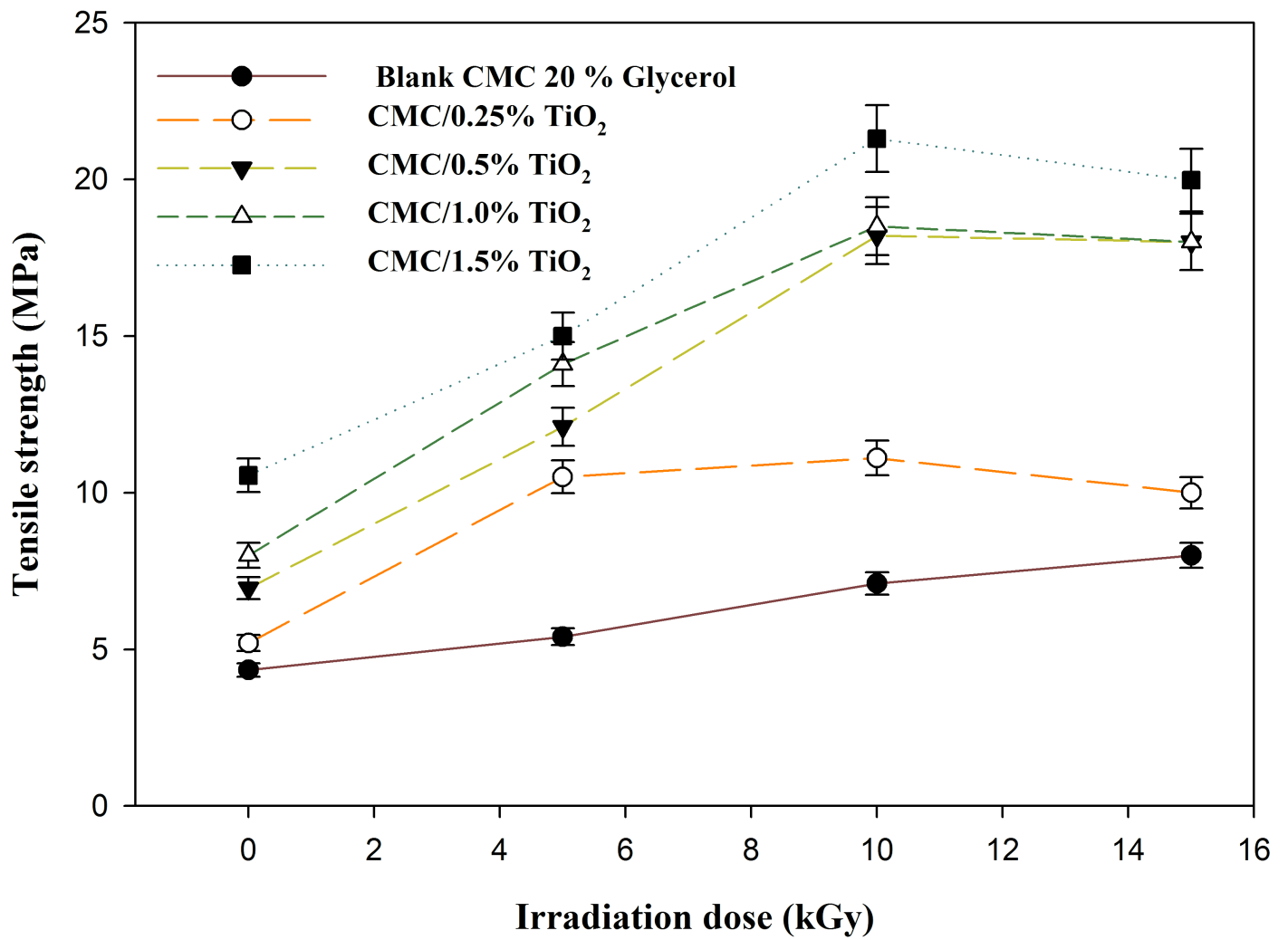


Figure 2

Effect of Irradiation dose (kGy) and TiO₂ (%) content on the Tensile strength (MPa) of carboxymethyl cellulose (CMC) films.

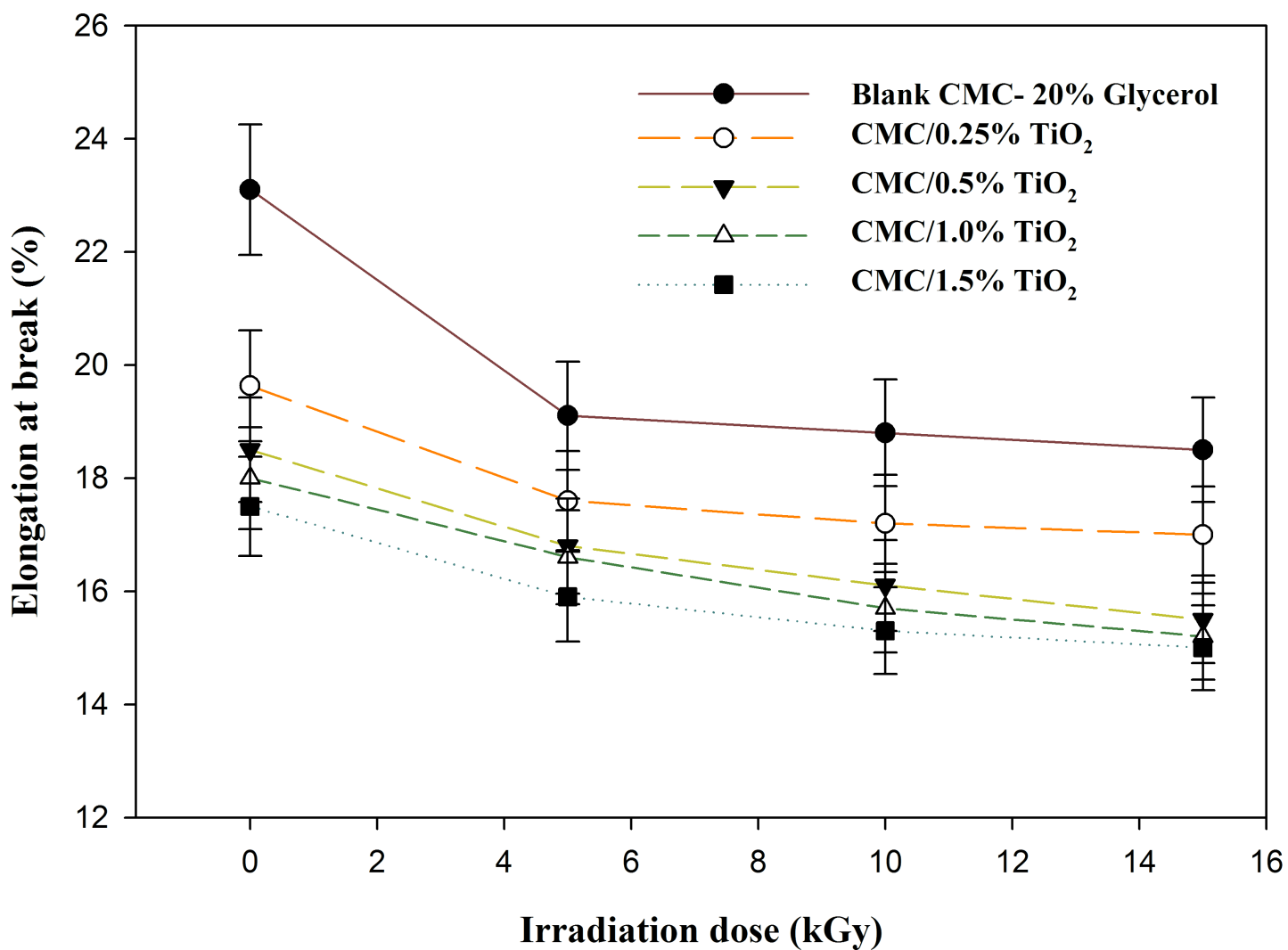


Figure 3

Effect of Irradiation dose (kGy) and TiO₂ (%) content on the Elongation at break (%) of carboxymethyl cellulose (CMC) films.

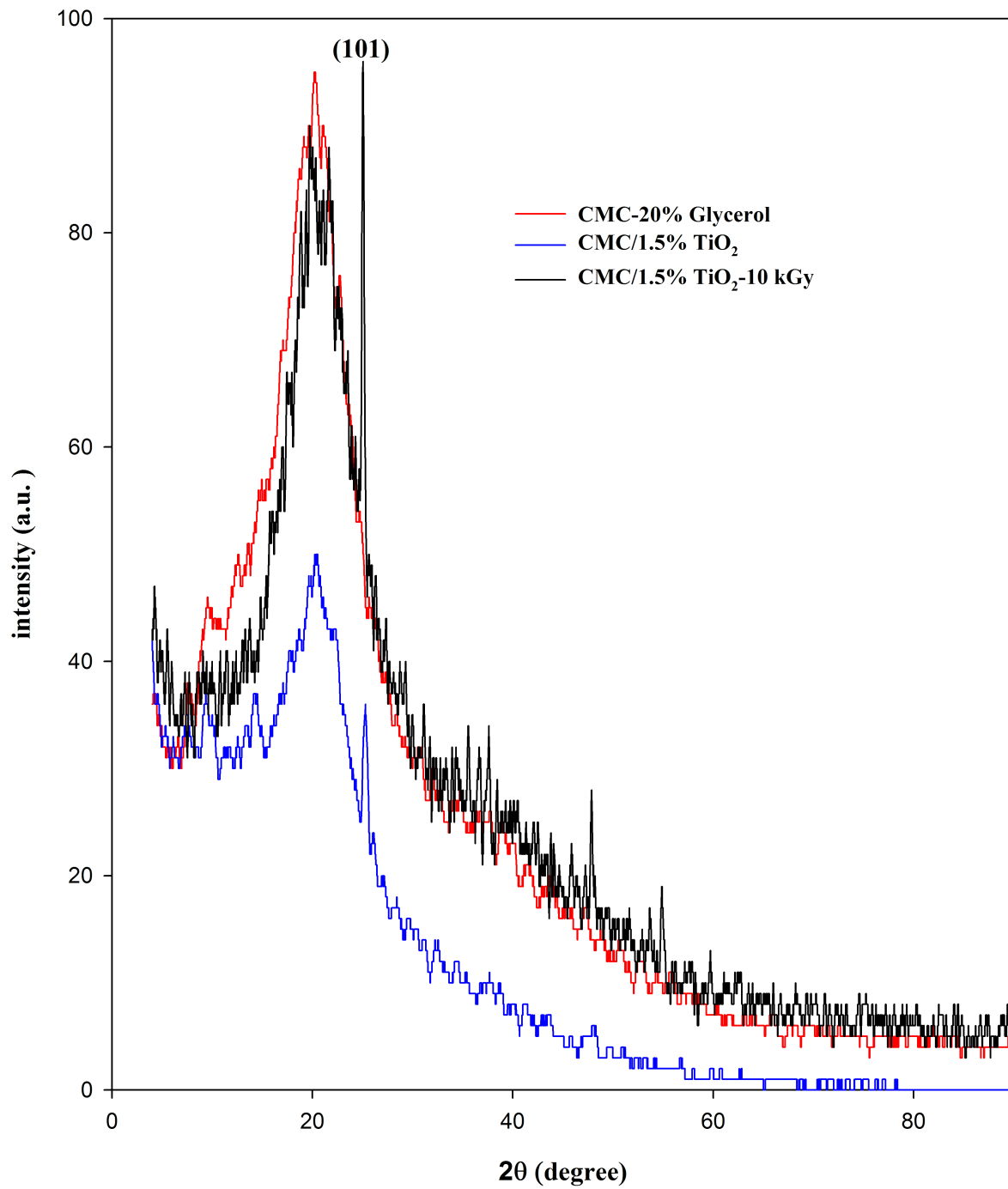


Figure 4

The X-ray diffraction patterns of CMC-20% Glycerol, CMC/1.5% TiO₂ and CMC/1.5%TiO₂-10kGy.

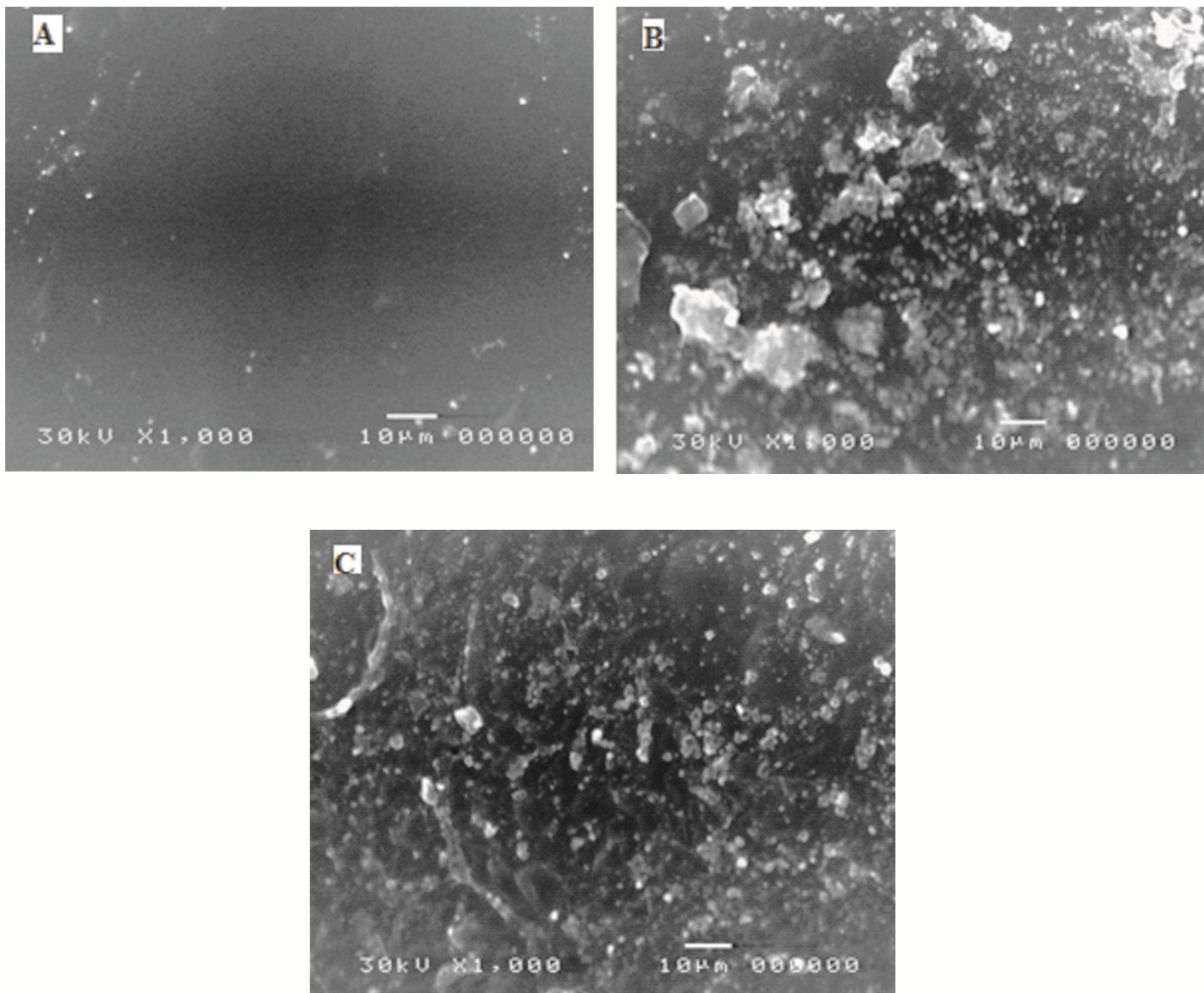


Figure 5

SEM of CMC films:(a) CMC-20% Glycerol, (b) CMC/1.5%TiO₂ and (c) CMC/1.5%TiO₂ - 10kGy.

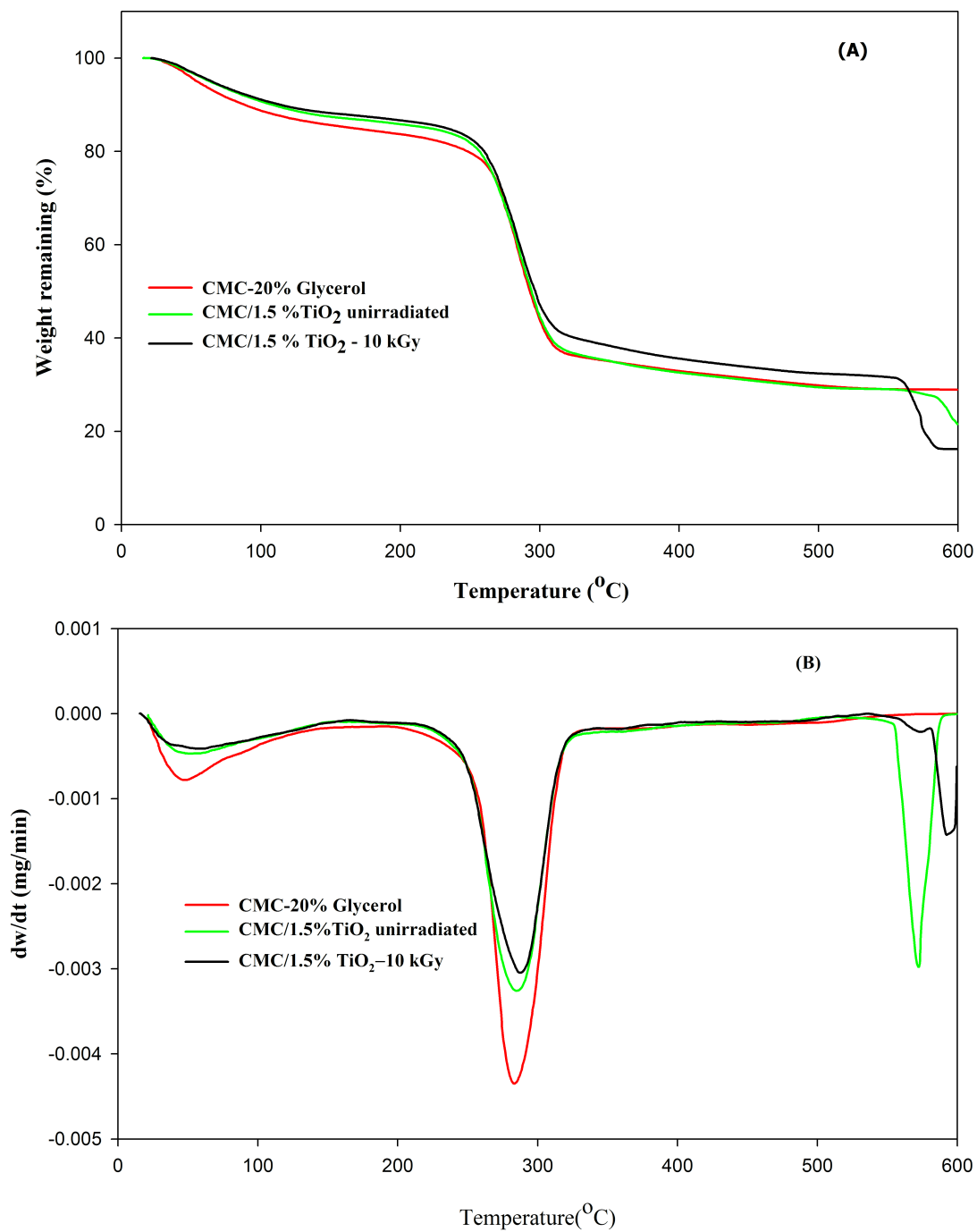
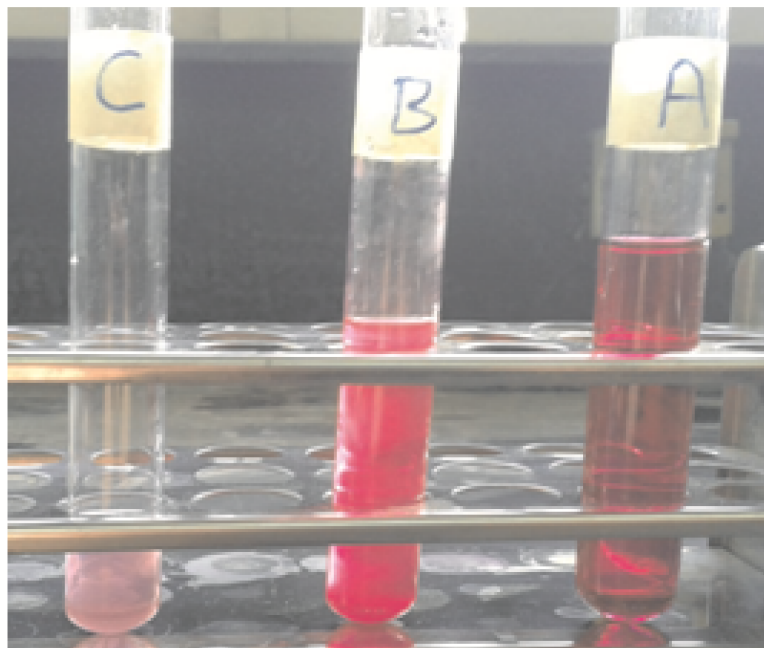
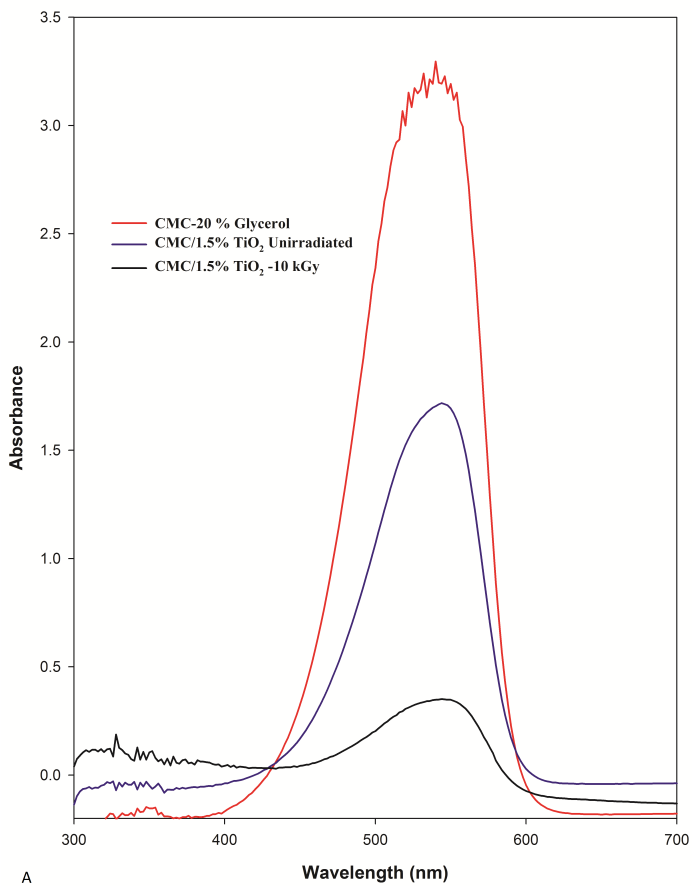


Figure 6

(A) TGA and (B) DTG thermograms of CMC-20%Glycerol, CMC/1.5%TiO₂ and CMC-1.5% TiO₂ at 10kGy.



B

Figure 7

A. shows the change in the absorbance of the basic violet 7 dye solutions onto blank CMC, irradiated and unirradiated CMC/TiO₂ composite after 24h. B. Effect of adsorbent type[(A) pure CMC, (B) Unirradiated CMC/TiO₂ and (C) CMC/1.5% TiO₂-10 kGy] on the removal of the basic violet dye after 24h.

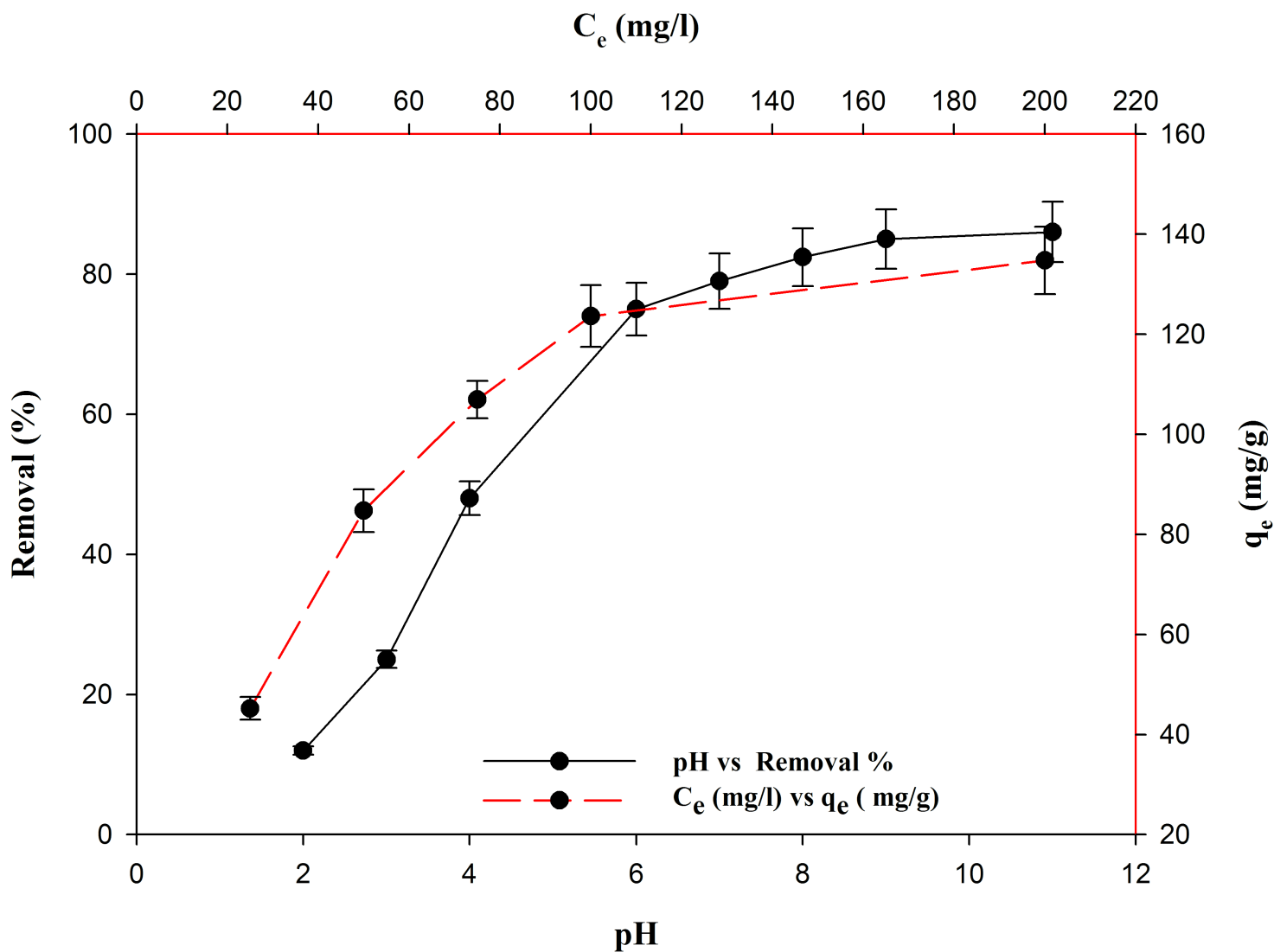


Figure 8

Effect of pH and initial concentration (mg/l) on the removal (%) and amount adsorbed (mg/g) of basic Violet 7 dye onto CMC/1.5 TiO₂- 10 kGy at conditions; adsorbent dosage = 0.2 g and contact time = 420 min at room temperature = 298 oK.

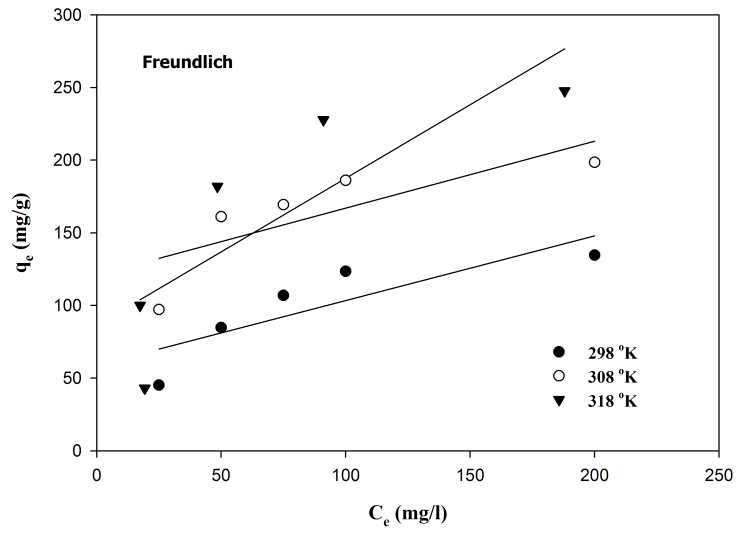
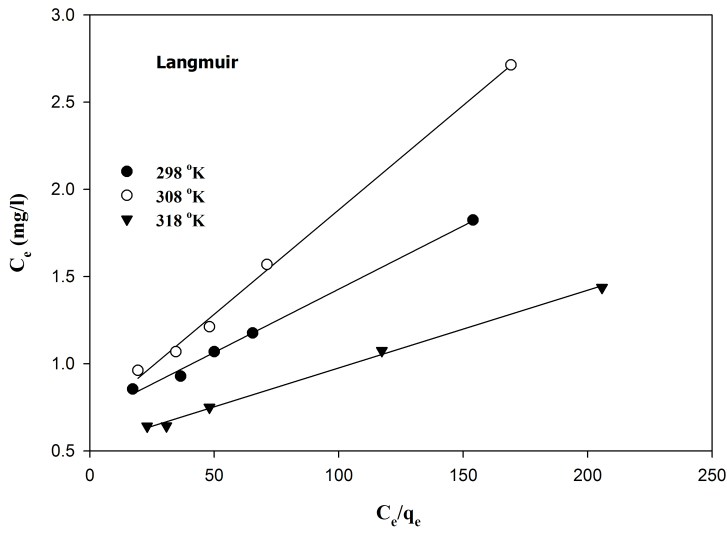


Figure 9

Effect of contact time (min.) and temperature (oK) on the amount adsorbed (q_t)(mg/g) of Basic Violet 7 dye onto CMC/1.5 % TiO₂- 10 kGy composite film at the conditions; initial concentration = 100 mg/l, adsorbent dose = 0.02 g, solution volume 50 ml and pH = 8.

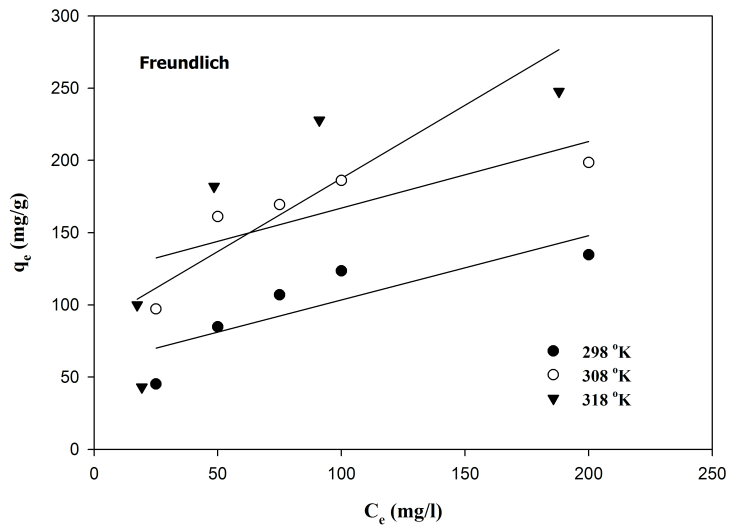
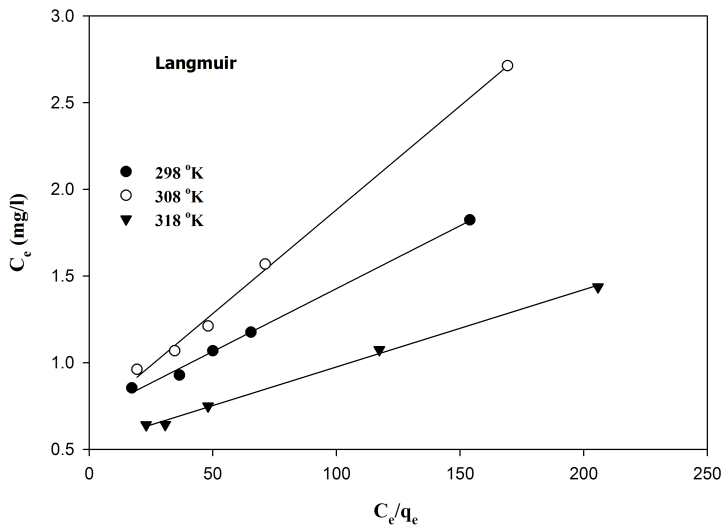


Figure 10

amount adsorbed of basic violet 7 dye fitted with the Langmuir model and Freundlich models.

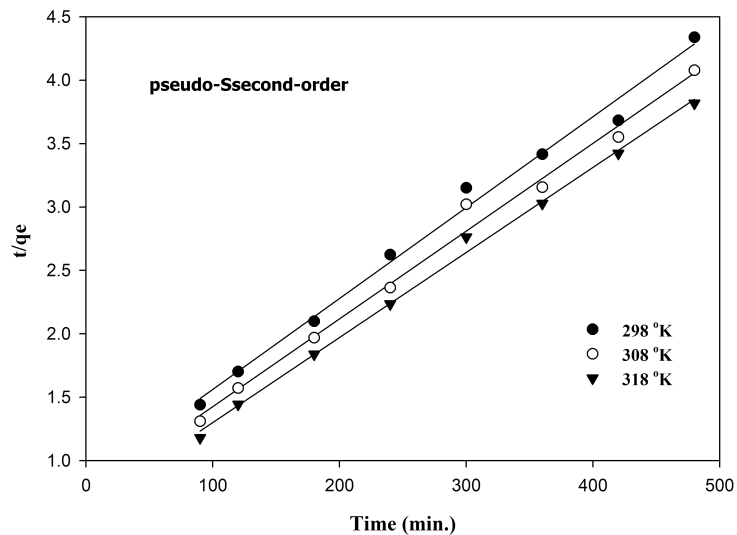
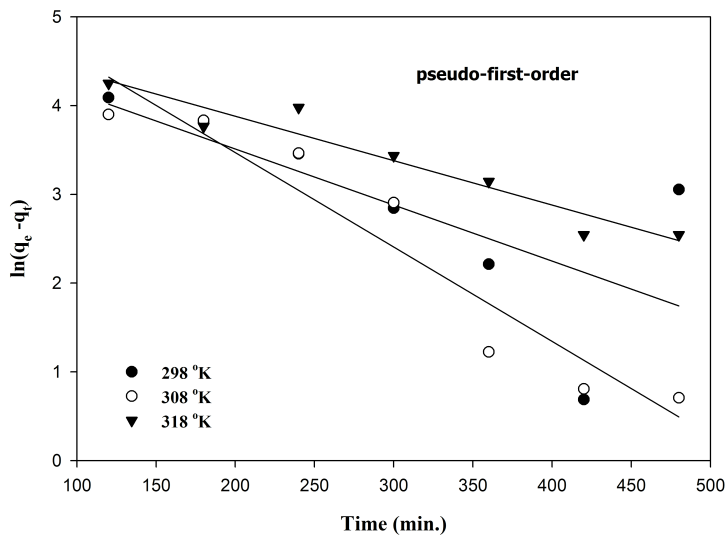


Figure 11

Fitted plots of the pseudo-first-order and pseudo-second-order kinetics of adsorption for basic violet dye onto CMC/1.5% TiO₂- 10 kGy.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupplementaryMaterial.docx](#)