

Egyptian Journal of Chemistry http://ejchem.journals.ekb.eg/



Comparative Study of Carbon Nanotube and Nano-Clay Incorporation into Pectin/Na-Alginate Bio-Based Hydrogels for Dye Removal

S. A. Ali^a*, Asmaa Sayed^b, Hayam M. Ahmed^a, Eman M. Shoukry^a, N.R. Hegazy^b, Ghada A. Mahmoud^b

^a Faculty of Science, Al-Azhar University, Nasr City, Cairo 11371, Egypt. ^b Polymer Chemistry Department, National Center for Radiation Research and Technology,

Egyptian Atomic Energy Authority, Cairo, Egypt.



Abstract

This study investigated the enhancement of dye removal efficiency through a comparative analysis of carbon nanotube (CNT) and nanoclay (NC) incorporated in Pectin/Na-alginate bio-based hydrogel. The hydrogels were synthesized via gamma irradiation, with the incorporation of CNT and NC studied. Fourier transform infrared (FTIR) analysis confirmed successful hydrogel synthesis, revealing slight spectral changes upon the incorporation of CNT and NC into the hydrogel matrix. X-ray diffraction (XRD) analysis indicated the amorphous nature of the prepared nanocomposite hydrogels. Thermal properties, evaluated through thermogravimetric analysis (TGA), demonstrated the superior performance of CNT-incorporated hydrogels compared to NC-incorporated and unmodified hydrogels. Atomic force microscopy (AFM) revealed surface morphology changes with the incorporation of CNT and NC. Additionally, the efficiency of dye removal, specifically for Malachite Green (MG) and Touliden Blue (TB) dyes, was evaluated. Results indicated the enhanced performance of CNT-incorporated hydrogels for MG dye removal, while NC-incorporated hydrogels showed superior performance for TB dye removal. The Pseudo-secondorder model emerges as the optimal kinetic model for both dyes on both hydrogels, indicating a chemisorption mechanism characterized by strong bonding. Isotherm studies further support these findings, with the Freundlich model demonstrating superior applicability in describing heterogeneous surface energies and multilayer adsorption processes observed in MG and TB dye adsorption. Thermodynamic analysis underscores CNTs@PC/Na-Alg/PAAc's preference for MG dye removal and NC@PC/Na-Alg/PAAc's effectiveness in TB dye removal. These results highlight the pivotal role of adsorbent material properties in shaping adsorption efficiency and mechanisms, crucial for optimizing dye removal processes in practical environmental remediation applications. This study underscores the potential of CNT and NC incorporation in improving the dye removal capabilities of Pectin/Na-alginate bio-based hydrogels, offering valuable insights for environmental remediation applications.

Keywords: Adsorption; characterization; bio-based hydrogel; nanocomposite; Radiation dye removal

1. Introduction

Water pollution is a pressing global issue, with vast quantities of polluted water being discharged into the environment annually [1-5]. Industrial and municipal effluents, containing various toxic contaminants like dyes, heavy metals, and pesticides, are major contributors to water pollution [6, 7]. Industries such as cosmetics and textiles exacerbate the problem by generating significant volumes of dye-polluted water, leading to widespread degradation of water quality due to unchecked water usage and rapid urbanization [8]. Efforts to remediate contaminated environments have been extensive, focusing on removing or degrading harmful substances to ensure environmental safety and quality [9, 10]. Adsorbent materials have emerged as a promising strategy for remediating aquatic environments, offering efficient and economical means of removing contaminants [11, 12]. Nanocomposite hydrogels are recommended materials for adsorption, the combination of hydrogels' unique features with nanoparticle system improves their combined properties [13]. Natural polymeric adsorbents are increasingly sought after for their eco-friendliness and cost-effectiveness [14]. Polysaccharides are the most widespread biological polymers that construct hydrogels due to their abundance, cost savings, biocompatibility, nontoxicity, and regeneration [15, 16]. Pectin, a complex polysaccharide found in plant cell walls, has electron-rich groups such as hydroxyl, carboxyl, and acylamino groups [17, 18]. Whatever, pectin exhibits a strong affinity for metal ions through electrostatic interaction, making it a promising biosorbent [19]. Sodium alginate is natural polysaccharide derived from seaweed[20]. It has

*Corresponding author e-mail: <u>shosho_water@yahoo.com</u>..(Al Shaimaa Abd alzaher Ali) Receive Date: 18 July 2024, Revise Date: 04 August 2024, Accept Date: 22 August 2024 DOI: 10.21608/ejchem.2024.305408.10037

©2025 National Information and Documentation Center (NIDOC)

been explored for heavy metal ion removal, owing to its adsorption capabilities through electrostatic interaction by the effective of carboxylic and hydroxyl groups [21, 22]. On the other hand numerous nanoparticles are employed in composite hydrogels such as clay and carbon nanotube, which are innovative materials with unique properties. Clay is well known for its outstanding adsorption characteristics and has been extensively investigated for the remediation of various pollutants from wastewater [23]. Carbon nanotube offer exceptional conductivity, mechanical flexibility, and high surface area, making them promising candidates or removal of both inorganic and organic contaminants [24]. In a previous study, multiwalled carbon nanotubes@pectin/ κ -carrageenan/polyacrylic acid nanocomposite was performed for removing methylene blue dye [25]. In this study, the impact of the incorporation of NC and CNT individually in Pectin/Na-Alg/PAAc bio-based hydrogel towards the remediation of cationic dyes was investigated. The nanocomposites were prepared via gamma irradiation. Radiation-induced polymerization and crosslinking is applied as a quick, easy, and affordable way to make three dimensional network structure compared with chemical methods [26, 27]. The prepared NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogels were characterized by the FTIR spectroscopy for structure verification, XRD for crystallographic features, and AFM for morphology. The hydrogel nanocomposites were examined for the removal of TB and MG from aqueous solutions.

2. Materials and Methods

2.1 Materials

Pectin (PC) (from apple peels, 50-75% esterification), Sodium alginate (Na-Alg), and Acrylic acid (AAc) were obtained from Sigma-Aldrich, China. The nano-clay (NC) (Kaolinite, $Al_2Si_2O_5(OH)_4$) with an average particle size range of 50-75 nm was supplied from El-Nasr company for mining. MWCNTs were purchased from Nanotech, China. Malachite green (MG), Touliden blue (TB), NaOH, and HCl were purchased from El-Nasr Co. for Chemical Industries, Egypt. The chemical structures of MG and TB are shown in Fig.(1).



Fig.(1): The chemical structures of MG and TB dyes.

2.2 Preparation of PC/Na-Alg/PAAc hydrogel for optimization

Prepare 4% PC (w/v) by dissolving 2g of pectin in 48mL of dist. water. Also, 4% Na-Alg was prepared by dissolving 2g of Na-Alg in 48 mL of dist. water. The two solutions were poured together at 60 °C with stirring for 30 min to obtain the total polymer solution (TPS).

2.2.1. Optimizing the irradiation dose

Different ratios of TPS were mixed with different AAc monomer ratios to get the solution mixtures of compositions 4.5:0.5, 4:1, 3.5:1.5 (TPS:AAc). The solution mixtures were poured into glassy test tubes and irradiated at a radiation dose of 20 kGy

(dose rate 1.083 kGy/h) in the cobalt-60 gamma cell that was settled at the National Centre for Radiation Research and Technology (NCRRT), Cairo, Egypt. The formed long, cylindrical rods were cut into nearly similar thin discs.

2.2.2. Optimizing the copolymer composition

A solution mixture of TPS: AAc (4:1) was prepared as mentioned above. The solution was poured into glassy test tubes and irradiated at different radiation doses 10, 20, 30, 40, and 50 kGy.

2.3. Preparation of NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogels

A solution mixture of TPS: AAc (4:1) (optimum composition) was prepared as mentioned above. The solution was divided into two portions. A definite weight of NC and CNTs (3 wt% of the total copolymers concentration) was summed to each portion separately. Using a probe sonicator, the mixtures were sonicated for 15 min each. The solution was poured into glassy test tubes and irradiated at 30 kGy (optimum radiation dose). The formed long, cylindrical rods were cut into nearly similar thin discs.

2.4. Gel content

The gel percentage was determined by submerging a pre-weighed sample (g_0) in distilled water at 70°C for 24 h, washing, and then air-drying to a fixed weight (g_d). The gel % was calculated by Eq 1:

Gel (%) = $\frac{g_d}{g_0} \times 100$ (1)

2.5. Instrumentations

Fourier-transform infrared-spectroscopy (FTIR), Germany BruKer Unicom infrared spectrophotometer was used from 400 to 4000 cm⁻¹ wavenumber range. A Shimadzu XDDI Series device was used for (XRD) analysis, with a copper target (λ = 1.542°), 40 mA electric current, 40 kV operating voltage, in the range of 4 – 89.9° scanning angle (2 θ), and at speed of 8° min⁻¹. (TGA) analysis was performed on TGA-30 (Shimadzu, Japan) at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere, and temperature ranges from room temperature to 600 °C. Flexaxiom Nanosurf, Switzerland (AFM) was used for topography at room temperature by using a rectangular- shaped, noncontact, laser-engraved silicon cantilever with a 9 kHz resonant frequency.

2.6. Adsorption study

The batch adsorption experiment technique was employed to investigate the influence of operation factors in the processes of removal of TB and MG dyes. These factors are initial dye concentration, nanocomposite dosage, time, and temperature. Each experiment was done and repeated triply according to the consecutive steps. A known weight of dry composite was immersed in 20 mL of TB and MG solution with a known initial concentration at a suitable pH at a suitable temperature. The (TB, MG) removal (%) of the nanocomposite was calculated by using Eq (2). Also, the adsorption capacity (qe, mg.g⁻¹) was evaluated using Eq (3):

The dye removal (%) = $\frac{c_0 - c_e}{c_0} X \mathbf{100}$ (2) $q_e (mg/g) = \frac{(Co-Ce)V}{m}$ (3)

where C_0 and Ce (both in mg L⁻¹) are the initial and equilibrium dye concentration, respectively. m(g) is the adsorbent weight in gram and V (L) is the volume of the dye solution.

The dye concentration was determined by a UV/ VIS spectrometer, the Jasco model V-530 (Jasco International Co., Ltd., Tokyo, Japan), at λ_{max} of 615 nm for MG dye and 585 nm for TB dye with a quartz cell of 1.0-cm optical length.

3 RESULTS AND DISCUSSION

3.1 Factors that affected gel content.

The target of optimization the preparation conditions is to have the best gel content. Crosslinking might be formed most likely due to combinations of the radicals or macromo-radicals formed during irradiation. The most important factors affect the gel content are the dose of irradiation and the composition of polymeric content in the matrix.

3.1.1. Effect of gamma radiation dose on the gel fraction

The impact of gamma radiation doses on the gel fraction of pectin/Na-alg/pAAc hydrogel was researched and appeared in Fig.2. The Figure demonstrates that the gel percent increases with increases in radiation dosage up to 30 kGy and a drop was observed after this value. By increasing the radiation dose, more radicals are formed, increasing the crosslinking density and thus increasing the gel fraction. At higher doses, the energy from radiation may cause a chain scission of the polymer chains. This degradation reduces the gel content [28].



Fig.2: Effect of gamma irradiation dose on gel fraction (%) of PC/Na-Alg/PAAc hydrogel

3.1.2. Effect of monomer content (AAC) on the gel fraction

Figure 3 shows the influence of polymers (PC/Na-Alg) to monomer (AAc) content on the gel percentage of the PC/Na-Alg/PAAc hydrogel matrix. It is observed that the gel percentage increases with increasing AAc monomer content in the composition. Because more free radicals are formed close together to crosslink.



Fig.3: Effect of PC/Na-alg polymers to AAc monomer content on the gel percentage of PC/Na-alg/PAAc hydrogel at irradiation dose; 20kGy.

3.2. Fourier-transform infrared spectroscopy

Figure 4 distinguishes the FTIR spectra of PC/Na-alg/PAAc, CNTs@PC/Na-alg/PAAc and NC@PC/Na-alg/PAAc nanocomposites. The FTIR spectra of PC/Na-alg/PAAc revealed a broad distinct absorption band at 3370 cm⁻¹ attributed to OH groups and a band at 2966 cm⁻¹ of C- H stretching. Whereas Na-Alg existence was identified by a band at 1394 cm⁻¹ corresponding to- COO⁻. The –C-O-C band that appears at 1005 cm⁻¹ strongly identifies sodium alginate as it is the bond that binds between G and M blocks of alginate. The characteristic band of C=O group of PC and AAc appears at 1705 cm⁻¹ the symmetric C- O- C stretching vibration was thought to be the cause of the band at 1160 cm⁻¹.



Fig.4: FTIR spectra of PC/Na-Alg/PAAc, NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc.

3.3. X-ray diffraction

Figure 5 illustrates the XRD patterns of PC/Na-Alg/PAAc, NC@PC/Na-Alg/PAAc, and CNTs@PC/Na-Alg/PAAc nanocomposite. The X-ray diffraction patterns for hydrogels depicted broad peaks at $2\theta = 21^{\circ}$ that reflected the amorphous structure of the hydrogels. This amorphous structure remains by inclusion of CNT or Clay, the interaction of small content of nanoparticles does not affect the crystallinity.



Fig.5: XRD patterns of PC/Na-Alg/PAAc, NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite.

3.4. Thermogravimetric analysis

Studying thermal properties is essential for assessing the behavior of materials under different temperature conditions. It helps determine their stability, performance, and suitability for specific applications. Figure 6illustrates the TGA thermogram of PC/Na-Alg/PAAc, Clay@PC/Na-Alg/PAAc, and CNTs@PC/Na-Alg/PAAc nanocomposites. The same thermal behavior was noticed for the three samples and a little improvement in stability was done in CNTs@PC/Na-Alg/PAAc. Four decomposition stages were observed from 30-150 °C, 150-275 °C, 275-481 °C, and 481-600 °C. The first one is for the elimination of

moisture and bonded water. The second one is due to the complexity of the process, which includes the degradation of the side groups. The third stage of degradation involves the degradation of the backbone chains. The last one is due to the complete oxidation of the residue.



Fig.6: TGA thermograms of PC/Na-Alg/PAAc, NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite.

3.5. Atomic force microscope investigation

Figure 7 illustrates the AFM images of PC/Na-Alg/PAAc, NC@PC/Na-Alg/PAAc, and CNTs@PC/Na-Alg/PAAc nanocomposite. For PC/Na-Alg/PAAc, the AFM image displays uniform surface with apparent porous features. Both the height and the roughness are very low (2.35 nm) and (11.24 nm) respectively. For NC@PC/Na-Alg/PAAc, the clay particulates appear as scattered bodies over the surface. An obvious increase in both height and roughness measurements can be observed (593nm) and (34.55 nm) respectively. For CNTs@PC/Na-Alg/PAAc, the incorporated MWCNTS are very clear. They emerge from the interior to the exterior of the gel matrix as cylindrical tubes. The height is (121nm) and the roughness is (41.12 nm).



Fig.7: AFM images of PC/Na-Alg/PAAc (a), NC@PC/Na-Alg/PAAc (b) and CNTs@PC/Na-Alg/PAAc (c) nanocomposite.

Egypt. J. Chem. 68, No.4 (2025)



Figure 8 Effect of NC and/or CNT content on the equilibrium swelling of NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogels; pH ;7 at 24h.

3.6. Swelling behavior

Figure 8 represents the swelling percentage of the Pectin/Na-Alg/PAAc bio-based hydrogel against varying weight percentages of nanomaterials (Wt %). First, without containing any of the nanomaterials, the swelling percentage of the hydrogel was 1331%. The swelling in the presence of 3wt% nanoclay was found to be 1977. 25%, 48. 55% rise. Moreover, the swelling increased to 1591 when 2 wt% of carbon nanotubes was incorporated into Pectin/Na-Alg/PAAc, a 19.58% increase. Thus, these results illustrate that out of the two reinforcements, nanoclay has the capacity to improve the hydrogel swelling capacity more than carbon nanotubes. In addition, the results reveal that reduction in the equilibrium swelling occurs upon increased NC content than 3% and 2% CNT due to increased crosslinking, which restricts further swelling [29]. Comparatively, the enhancement of swelling behavior of the hydrogel is higher in nanoclay (NC) than that of CNT because the players have a better dispersion, imperatively higher hydrophilic and best cross-linking characteristics. A larger value of interface from molecular structure, the nanoclay swelling capacity improves to up to 3wt% of the polymer matrix [30]. While CNTs predict to a high extent of aggregation and formation of a large number of cross-linking points that limit swelling beyond the 2 wt% level [31].



Figure 9 Effect of pH on the equilibrium swelling of PC/Na-Alg/PAAc, NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogel ;NC;3wt% and CNT;2wt%, 24h.

Thus, based on the studies conducted in this investigation and previous studies, 3 wt% nanoclay (NC) and 2 wt% carbon nanotubes (CNTs) were selected for the experimental tests. As shown in Figure 9, all PC/Na-Alg/PAAc, NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogel nanocomposite hydrogels have revealed a similar equilibrium swelling % trend with pH. an increase in equilibrium swelling, as increasing the pH. The results show that the equilibrium swelling increases as the pH becomes more alkaline. In acidic conditions, the swelling is lower, but as the pH rises to 7, the swelling percentage increases significantly, continuing to increase with further rises in pH for all tested hydrogels. Specifically, the corresponding swelling equilibrium percentages are 1567% at pH 10 for PC/Na-Alg/PAAc hydrogel, 2500% for NC@PC/Na-Alg/PAAc and 1823.9% for CNT@PC/Na-Alg/PAAc nanocomposite hydrogel. When the pH reaches 11, the swelling percentage slightly increases to 1599% for PC/Na-Alg/PAAc and 2713% for NC@PC/Na-Alg/PAAc. Since the increment of swelling at pH 11 is slightly higher and above that of pH 10, the pH 10 is chosen as the most appropriate pH for further experiments.

3.7. Adsorption Study

The pH, dosage of adsorbent, the contact time, the concentration of MG and TB and adsorption temperature were all verified as operating parameters. In this regard, a series of batch adsorption experiments were conducted wherein 0.1 g of dry composite was immersed in 50 mL of dye solution (MG and TB) with a known initial concentration under shaking with speed of 350 rpm. The percentage dye removal (%) of the hydrogel was calculated using equation (2). The adsorption capacity (qe, mg/g) was determined using equation (3).

The adsorption kinetics of MG and TB were studied at different contact times according to the following procedure: The NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogel adsorbent was immersed in a 50 mg/L solution of MG and TB at a dosage of 0.075 g. The concentrations of the MB and MO solutions were measured at specific time intervals using the previously described method. The adsorption capacity at time t (qt) was calculated using the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{4}$$



Figure 10 Effect of pH on the adsorption of MG (a) and TB (b) dyes onto NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogel; NC;3wt% and CNT;2wt%, contact time; 24h, initial dye concentration 25mg/L; adsorbent weight 0.1g.

Effect of pH

Figure 10 shows the effect of pH on dye removal efficiency. The results indicated that both NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogels performed optimally at pH 10, with CNTs@PC/Na-Alg/PAAc achieving higher removal percentages for MG dye, while NC@PC/Na-Alg/PAAc showed higher removal for TB dye. Specifically, MG dye removal increased from 30% to 90% for NC@PC/Na-Alg/PAAc nanocomposite hydrogels and from 30% to 97% for CNTs@PC/Na-Alg/PAAc nanocomposite hydrogels as pH rose from 3 to 10. TB dye exhibited similar trends, with removal percentages increasing from 32% to 99% for NC@PC/Na-Alg/PAAc nanocomposite hydrogels and from 22% to 80% for CNTs@PC/Na-Alg/PAAc nanocomposite hydrogels. This optimal performance at alkaline pH can be attributed to the increased deprotonation of functional groups on the hydrogel surface, enhancing dye interaction.

Effect of adsorbent weight

The effect of adsorbent weight on dye removal is depicted in Figure 11. Increasing the adsorbent weight led to higher dye removal efficiencies for both hydrogels. For MG dye, the removal percentage for NC@PC/Na-Alg/PAAc increased from 35% at 0.05 g to 91% at 0.15 g, while CNTs@PC/Na-Alg/PAAc increased from 56% to 98%. For TB dye, NC@PC/Na-Alg/PAAc increased from 60% at 0.05 g to 99% at 0.15 g, and CNTs@PC/Na-Alg/PAAc from 30% to 80%. The CNTs@PC/Na-Alg/PAAc nanocomposite hydrogel consistently outperformed the NC@PC/Na-Alg/PAAc nanocomposite hydrogel for MG dye, suggesting that CNTs provide more effective adsorption sites due to their larger surface area and higher affinity for MG. Conversely, for TB dye, the NC@PC/Na-Alg/PAAc nanocomposite hydrogel demonstrated superior performance, likely due to the specific interactions facilitated by the nanoclay's layered structure and surface chemistry, which are more conducive to TB adsorption.



Figure 11: Effect of adsorbent weight (g) on the adsorption of MG (a) and TB (b) dyes onto NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogel; NC;3wt% and CNT;2wt%, contact time; 24h, initial dye concentration 25mg/L pH 10.

This contrasting behavior underscores the importance of material properties in adsorption efficiency. CNTs, with their high surface area and potential for π - π interactions, are particularly effective for MG dye. In contrast, the nanoclay's structural characteristics and ion-exchange capabilities make it more suitable for TB dye removal. Therefore, the choice of adsorbent material should be tailored to the specific dye being targeted for optimal removal efficiency.

Effect of contact time

The effect of contact time on the removal efficiency of Malachite Green (MG) and Toluidine Blue (TB) dyes is depicted in Figure 12. Both NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc hydrogels exhibited rapid initial adsorption and reached equilibrium within 13 hours. For MG dye, the removal efficiency of NC@PC/Na-Alg/PAAc increased from 44% at 1 hour to 90% at 13 hours, while CNTs@PC/Na-Alg/PAAc showed an increase from 52% to 97%. Similarly, TB dye removal efficiency increased from 65% to 96% for NC@PC/Na-Alg/PAAc and from 30% to 80% for CNTs@PC/Na-Alg/PAAc over the same period.



Figure 12: Effect of contact time (h) on the adsorption of MG (a) and TB (b) dyes onto NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogel; NC;3wt% and CNT;2wt%, initial dye concentration 25mg/L pH 10 adsorbent weight 0.1g





Figure 13: Effect of initial dye concentration (mg/L) on the adsorption of MG (a) and TB (b) dyes onto NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogel; NC;3wt% and CNT;2wt%, contact time 24h; pH 10 adsorbent weight 0.1g.

Figure 13 illustrates the effect of initial dye concentration on removal efficiency. Higher initial dye concentrations resulted in increased adsorption capacities but reduced percentage removal for both hydrogels. For MG dye, the removal percentage for NC@PC/Na-Alg/PAAc decreased from 95% at 5 mg/L to 60% at 100 mg/L, and for CNTs@PC/Na-Alg/PAAc from 100% to 91%. For TB dye, NC@PC/Na-Alg/PAAc decreased from 100% to 90%, and CNTs@PC/Na-Alg/PAAc from 92% to 50%. *Effect of Temperature*



Figure 14: Effect of temperature (°C) on the adsorption of MG (a) and TB (b) dyes onto NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogel; NC;3wt% and CNT;2wt%, contact time 24h initial dye concentration 25mg/L pH 10 adsorbent weight 0.1g.

The effect of temperature on dye removal is shown in Figure 14. Adsorption increased with temperature for both hydrogels, indicating an endothermic process. For MG dye, the removal percentage for NC@PC/Na-Alg/PAAc increased from 90% at 25°C to 94% at 55°C, and for CNTs@PC/Na-Alg/PAAc from 97% to 99%. TB dye removal followed a similar trend, with NC@PC/Na-Alg/PAAc increasing from 97% to 99% and CNTs@PC/Na-Alg/PAAc from 80% to 85%. The higher removal percentages at elevated temperatures confirm their enhanced performance in endothermic adsorption processes.

In recent studies, the differences in dye removal efficiencies between carbon nanotube (CNT)-based and nanoclay (NC)based nanocomposite hydrogels have been attributed to their unique structural and surface properties. CNTs exhibit high surface area, excellent mechanical strength, and unique electrical properties, which enhance their interaction with dye molecules, particularly those with planar structures like Malachite Green (MG). The π - π interactions between the aromatic rings of MG and the conjugated structure of CNTs significantly increase the adsorption capacity, resulting in higher removal efficiencies [32].

Conversely, the removal of Toluidine Blue (TB) dye is more effective with nanoclay-based hydrogels. The layered structure of nanoclay provides a high surface area and multiple active sites for adsorption. Additionally, the presence of exchangeable cations in the nanoclay can facilitate ion exchange mechanisms, which are particularly effective for cationic dyes like TB. This makes NC-based hydrogels more suitable for removing dyes that can interact via ion exchange and intercalation within the clay layers [33].

These differences highlight the importance of selecting appropriate nanocomposites based on the specific dye to be removed. For MG dye, CNTs@PC/Na-Alg/PAAc nanocomposite hydrogels demonstrate superior performance, achieving up to 97% removal at optimal conditions. In contrast, NC@PC/Na-Alg/PAAc hydrogels excel in removing TB dye, reaching up to 99% removal under similar conditions. This suggests that the incorporation of CNTs and nanoclay into biopolymer hydrogels can be strategically optimized to target specific pollutants based on their chemical nature and interaction mechanisms [34, 35].

3.8. Kinetic Studies

The kinetic profiles of MG and TB adsorption onto, NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogel was assessed using pseudo first-order, pseudo second-order and Avrami kinetics models. Non-linear equations (6), (7), and (8) were utilized to process the data:

$$q_{t} = q_{e}(1 - e^{-k_{1}t})$$
(6)
$$q_{t} = \frac{k_{2}q_{e}^{2}t}{1 + k_{2}q_{e}t}$$
(7)

$$q_t = q_e (1 - e^{-k_A v t})^{n_{AV}}$$
(8)

Where $k_1 k_2$, and k_{AV} represent the pseudo-first-order, pseudo-second-order and Avrami rate constants for adsorption, respectively, q_t and q_e denote the concentrations of MG and TB dye adsorbed at time t and equilibrium, respectively. nav is Avrami power having value between (2 to4) [36].



Figure 15: Pseudo-first-order, Pseudo-second-order and Avrami kinetic model plots of MG (a) and TB (b) dyes by NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogel.

Egypt. J. Chem. 68, No. 4 (2025)

S. A. Ali et.al.

The study employs Pseudo-first-order (PFO), Pseudo-second-order (PSO), and Avrami kinetic models to analyze the adsorption kinetics of MG and TB dyes by NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogels, as depicted in Figure 15 and summarized in Table 1. For MG dye, both hydrogels exhibit higher R² values and lower reduced chi-square values with the PSO model, indicating its superior fit over PFO and Avrami models. Similarly, for TB dye, the PSO model demonstrates the best fit across both materials, emphasizing its effectiveness in describing the adsorption process. These results underscore the robustness of the Pseudo-second-order kinetic model in accurately capturing the adsorption behavior of both dyes on the studied nanocomposite hydrogels. The PSO model's ability to closely match experimental data suggests that the adsorption mechanism follows a chemisorption process involving strong chemical bonding between the dye molecules and the active sites on the hydrogel surface, highlighting its relevance in optimizing and predicting adsorption processes for practical applications [37, 38].

MG dye						
Kinetic Model	Kinetic Parameters	NC@PC/Na-Alg/PAAc	CNTs@PC/Na-Alg/PAAc			
Pseudo -first order	$K_1 (h^{-1})$	0.33	0.31			
PFO	qe (Cal.), (mg/g)	43.61	50.11			
	qe (exp), (mg/g)	45.21	48.70			
	\mathbb{R}^2	0.78833	0.9954			
	Reduced Chi-Sqr	14.74	0.46761			
Pseudo -second order	$K_2 (g mg^{-1} h^{-1})$	0.00473	0.00619			
PSO	qe (Cal.), (mg/g)	58.18	60.83			
	qe (exp), (mg/g)	45.21	48.70			
	\mathbf{R}^2	0.99581	0.99328			
	Reduced Chi-Sqr	0.36003	0.67614			
Avrami	$K_{AV} (h^{-1})$	0.12787	0.15866			
	N _{AV}	1.97	1.98			
	q _e (cal.), (mg/g)	46.74	50.11			
	q_e (exp), (mg/g)	45.21	48.70			
	\mathbb{R}^2	0.9949	0.99553			
	Reduced Chi-Sqr		0.5137			
	TB dy	е				
Pseudo -first order	$K_1 (h^{-1})$	0.4650128	0.16382			
PFO	qe (Cal.), (mg/g)	48.50	46.44			
	qe (exp), (mg/g)	48.31	39.94			
	\mathbf{R}^2	0.99235	0.99438			
	Reduced Chi-Sqr	0.35314	0.62689			
Pseudo -second order	$K_2 (g mg^{-1} h^{-1})$	0.0167	0.0019			
PSO	qe (Cal.), (mg/g)	53.24	66.61			
	qe (exp), (mg/g)	48.31	39.94			
	\mathbb{R}^2	0.99347	0.9941			
	Reduced Chi-Sqr	0.31015	0.6595			
Avrami	K_{AV} (h ⁻¹)	0.2379	0.08			
	N_{AV}	1.95	2.00			
	q _e (cal.), (mg/g)	48.50	46.44			
	q_e (exp), (mg/g)	48.31	39.94			
	\mathbf{R}^2	0.99232	0.99439			
	Reduced Chi-Sqr	0.39945	0.68958			

Table 1: Kinetic parameters for the adsorption of MG and TB dyes

3.9. Adsorption isotherms

The adsorption behavior of Malachite Green (MG) and Toluidine Blue (TB) dyes onto NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogels was analyzed using the Langmuir and Freundlich adsorption isotherms, as represented by equations (8) and (9), respectively. Additionally, the Redlich–Peterson isotherm equation (10), which includes three adjustable parameters, was employed due to its applicability to both homogeneous and heterogeneous systems, offering a compromise between the Langmuir and Freundlich models.

Langmuir isotherm model:
$$q_e = \frac{q_{max}K_LC_e}{1 + K_LC_e}$$
 (8)
Freundlich model: $q_e = K_FC_e^{1/n}$ (9)
Redlich – Peterson model: $q_e = \frac{K_{RP}C_e}{1 + a_RC_e^g}$ (10)

In these equations, q_{max} denotes the maximum adsorption capacity of the adsorbent (mg/g), K_L is the Langmuir adsorption equilibrium constant (L/mg), K_F (mg/L) is the Freundlich adsorption coefficient, and n is the Freundlich exponent, indicating the adsorption intensity. K_{RP} , a_R and β are Redlich–Peterson's three parameters, and " β " lies between 0 and 1.

Figure 16 illustrates the Adsorption isotherm models (Langmuir, Freundlich, and Redlich–Peterson) of MG (a) and TB (b) dyes by NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogels, with corresponding results tabulated in Table 2. The study evaluates these models for their fit to the adsorption of MG and TB dyes. For MG dye, CNTs@PC/Na-Alg/PAAc demonstrates a higher maximum calculated adsorption capacity (141.44 mg/g) compared to NC@PC/Na-Alg/PAAc (60.50 mg/g), yet NC@PC/Na-Alg/PAAc exhibits a superior fit to the Langmuir model, indicated by higher R² and lower reduced chi-square values. Similarly, the Freundlich and Redlich–Peterson models favor CNTs@PC/Na-Alg/PAAc due to their higher R² values and lower reduced chi-square values.

In contrast, for TB dye, NC@PC/Na-Alg/PAAc shows a higher maximum calculated adsorption capacity (160.19 mg/g) than CNTs@PC/Na-Alg/PAAc (60.23 mg/g) according to the Langmuir model. NC@PC/Na-Alg/PAAc exhibits a better fit to the Freundlich model, whereas CNTs@PC/Na-Alg/PAAc aligns better with the Langmuir model.

The findings suggest that for both MG and TB dyes adsorbed on NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogels, the Freundlich isotherm model appears as the most suitable based on the highest R^2 values and lowest reduced chi-square values. This model accounts for heterogeneous surface energies and multilayer adsorption, which are common characteristics in real-world adsorption processes [39, 40]. Therefore, the Freundlich isotherm model proves invaluable for comprehending and predicting the adsorption behavior of these dyes on the respective nanocomposite hydrogels.



Figure 16: Adsorption isotherm models (Langmuir, Freundlich and Redlich–Peterson of MG (a) and TB (b) dyes by NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogel.

Table 2: Ad	lsorption isotherm parameters for the	he adsorption of both MC	and TB			
MG Dye						
Isotherm models	Parameter value	NC@PC/Na-	CNTs@PC/Na-			
		Alg/PAAc	Alg/PAAc			
	q_{max} (mg/g)	60.50	141.44			
Longmuin	K _L (L/mg)	0.25	0.19			
Langmuir	\mathbb{R}^2	0.9299	0.8499			
	Reduced Chi-Sqr	32.26	121.11			
	$K_{\rm F}$	15.30	28.25			
Froundlich	n _F	2.63	1.85			
Freununch	\mathbb{R}^2	0.97153	0.9993			
	Reduced Chi-Sqr	13.11	0.0751			
	A _{RP}	8.57	1.58			
	a_R	0.11	56.19			
Redlich-Peterson	g	1.02	0.46			
	\mathbb{R}^2	0.99616	0.9992			
	Reduced Chi-Sqr	3.07	0.0899			
TB Dye						
	$q_{max} (mg/g)$	160.19	60.23			
	$K_L (L/mg)$	0.118	0.104			
Langmuir	\mathbb{R}^2	0.87057	0.98288			
	Reduced Chi-Sqr	131.73	5.84			
	$K_{\rm F}$	21.51	12.61			
Froundlich	n _F	1.60	2.70			
Freununch	\mathbb{R}^2	0.99965	0.9909			
	Reduced Chi-Sqr	0.35701	6.02			
	A_{RP}	-8.27	-6.46			
	a_R	-3.83	-6.49			
Redlich-Peterson	g	0.38	0.56			
	\mathbf{R}^2	0.8464	0.9565			
	Reduced Chi-Sqr	136.72	12.82			

3.10. Thermodynamics of adsorption process

The adsorption thermodynamics analysis provides valuable insights into the internal energy changes and structural transformations occurring during the

adsorption process. By evaluating thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS), one can determine the spontaneity and heat effects on the adsorption. A negative (ΔG) indicates a spontaneous adsorption process, while the values of (ΔH) and (ΔS) reveal whether the adsorption is endothermic or exothermic and the degree of disorder at the solid-liquid interface. This detailed understanding of thermodynamic behavior helps in optimizing the adsorption conditions and designing more efficient adsorbents for dye removal from wastewater [41]. The thermodynamics of MG and TB dyes adsorption onto NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogel was investigated at three temperatures: 298 K, 308 K, and 318 K. The thermodynamic parameters, including entropy change (ΔS), enthalpy change (ΔH), and Gibbs free energy change (ΔG), were analyzed using the equations 11 and 12:

$$\Delta G = \Delta H - T\Delta S \quad (11)$$
$$\ln \frac{q_e}{C_e} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (12)$$

Where R represents the universal gas constant (8.314 J.mol⁻¹K⁻¹)

Figure 17 and Table 3 evaluate the thermodynamic parameters of adsorption for MG and TB dyes onto NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogels, revealing important insights about the adsorption process.

For MG dye, the negative values of Gibbs free energy ΔG at all temperatures (298 K, 308 K, 318 K) for both hydrogels indicate that the adsorption process is spontaneous. The ΔG values for NC@PC/Na-Alg/PAAc decreased from -5.24 kJ/mol

at 298 K to -6.54 kJ/mol at 318 K, while for CNTs@PC/Na-Alg/PAAc, ΔG values decreased more significantly from -8.59 kJ/mol at 298 K to -11.47 kJ/mol at 318 K. This suggests that the spontaneity of the adsorption increases with temperature, particularly for the CNT-based hydrogel, indicating a stronger affinity for MG dye.

The positive values of entropy change ΔS for MG dye adsorption, 0.07 kJ/mol·K for NC@PC/Na-Alg/PAAc and 0.14 kJ/mol·K for CNTs@PC/Na-Alg/PAAc, suggest an increase in randomness at the solid-liquid interface during the adsorption process. The higher ΔS value for CNTs@PC/Na-Alg/PAAc indicates a greater increase in disorder, which might be attributed to the more complex interaction dynamics of MG dye with the nanotubes.



Figure 17: Van't Hoff Plot for adsorption of MG (a) and TB (b) dyes by NC@PC/Na-Alg/PAAc and CNTs@PC/Na-Alg/PAAc nanocomposite hydrogel.

Table 5: I nermodynamic parameters of adsorption of MG and TB dyes							
MG dye							
Thermodynamic parameter		NC@PC/Na-Alg/PAAc	CNTs@PC/Na-Alg/PAAc				
∆G (kJ.mol ⁻¹)	Temp. (K) 298 308 318	-5.24 -5.89 -6.54	-8.59 -10.03 -11.47				
$\Delta S (kJ.mol^{-1} K^{-1})$		0.07	0.14				
$\Delta \mathbf{H} (\mathbf{kJ}.\mathbf{mol}^{-1})$		14.13	34.32				
TB dye							
∆G (kJ.mol⁻¹)	Temp. (K) 298 308 318	-8.45 -9.92 -11.39	-2.00 -2.40 -2.80				
$\Delta S (kJ.mol^{-1} K^{-1})$		0.15	0.04				
∆H (kJ.mol ⁻¹)		35.36	9.92				

The enthalpy changes ΔH values for MG dye adsorption are 14.13 kJ/mol for NC@PC/Na-Alg/PAAc and 34.32 kJ/mol for CNTs@PC/Na-Alg/PAAc. The positive ΔH values confirm that the adsorption process is endothermic, meaning that it requires heat to proceed. The much higher ΔH for CNTs@PC/Na-Alg/PAAc suggests that the adsorption of MG dye onto CNTs is more energetically demanding, potentially due to stronger interactions between the dye molecules and the adsorbent [42].

For TB dye, the ΔG values are also negative, indicating spontaneous adsorption [43]. For NC@PC/Na-Alg/PAAc, ΔG values decreased from -8.45 kJ/mol at 298 K to -11.39 kJ/mol at 318 K. For CNTs@PC/Na-Alg/PAAc, ΔG values showed a smaller

decrease from -2.00 kJ/mol at 298 K to -2.80 kJ/mol at 318 K. This indicates that the spontaneity of TB dye adsorption is more pronounced in NC@PC/Na-Alg/PAAc than in CNTs@PC/Na-Alg/PAAc [44].

The entropy changes ΔS for TB dye adsorption is 0.15 kJ/mol·K for NC@PC/Na-Alg/PAAc and 0.04

kJ/mol·K for CNTs@PC/Na-Alg/PAAc. The higher ΔS for NC@PC/Na-Alg/PAAc suggests a greater

increase in disorder during the adsorption process compared to the CNT-based hydrogel. The enthalpy changes ΔH for TB dye adsorption is 35.36 kJ/mol for NC@PC/Na-Alg/PAAc and 9.92 kJ/mol for CNTs@PC/Na-Alg/PAAc. The positive ΔH values indicate that the adsorption is endothermic for both hydrogels [45]. However, the significantly higher ΔH for NC@PC/Na-Alg/PAAc suggests that the adsorption process for TB dye is much more energetically demanding on this hydrogel, likely due to the specific interactions facilitated by the nanoclay structure [46, 47].

Overall, these thermodynamic analyses highlight the different adsorption behaviors of MG and TB dyes on the two types of nanocomposite hydrogels, underscoring the importance of adsorbent material properties in influencing the adsorption efficiency and mechanisms. Based on the thermodynamic data provided, the CNTs@PC/Na-Alg/PAAc nanocomposite hydrogel is more favorable for the removal of Malachite Green (MG) dye, and the NC@PC/Na-Alg/PAAc nanocomposite hydrogel is more favorable for the removal of Toluidine Blue (TB) dye.

4. Conclusions

In this research, a pectin/Na-alginate/polyacrylic acid (PC/Na-Alg/PAAc) hydrogel was synthesized via gamma radiation. The study investigated the effects of incorporating nanoclay and carbon nanotubes (CNT). FTIR analysis confirmed the successful synthesis of PC/Na-Alg/PAAc hydrogel, with slight spectral changes observed upon the addition of nanoclay and CNT into the hydrogel matrix. XRD analysis revealed the amorphous nature of the prepared nanocomposite hydrogels. TGA studies demonstrated higher thermal properties for CNT@PC/Na-Alg/PAAc compared to both PC/Na-Alg/PAAc and NC@PC/Na-Alg/PAAc. AFM analysis showed a rough surface for the nanocomposite. The efficiency of NC@PC/Na-Alg/PAAc and CNT@PC/Na-Alg/PAAc in removing MG and TB dyes was evaluated, with NC@PC/Na-Alg/PAAc showing better performance for TB dye removal and CNT@PC/Na-Alg/PAAc exhibiting higher efficiency towards MG dye. Overall, both nanobased hydrogels demonstrate promising potential for removing textile dyes from aqueous solutions. The Pseudo-second-order kinetic model proves optimal for both dyes on both hydrogels, indicating a chemisorption mechanism with strong bonding. Isotherm models affirm these findings, with the Freundlich model effectively describing heterogeneous surface energies and multilayer adsorption processes. Thermodynamic analysis highlights the preference of CNTs@PC/Na-Alg/PAAc for MG dye removal and NC@PC/Na-Alg/PAAc for TB dye removal, underscoring the critical role of adsorbent material properties in optimizing dye removal processes for practical applications.

Ethical Approval Ethical approval is not applicable for this article. **Consent to Participate** The authors confirm that all information they provide for this study are realistic experimental data and findings. **Consent to Publish** The authors give their consent for the publication of identifiable details, which can include photograph(s) and/or videos and/or case history and/or details within the text ("Material") to be published in the above Journal and Article. Funding No funding was received for the present work. **Competing Interests** The authors state no conflict of interest. Availability of data and materials The data that support the findings of this study are available in this work. **Authors Contributions** S.A.Ali : Experimental and methodology. Asmaa Sayed: data analysis, curation and representation, and writing the first draft. Hayam M. Ahmed: Writing, editing, guidance and supervision.

N.R. Hegazy: Supervision and direction.

Eman M. Shoukry: Writing, editing, guidance and supervision.

Ghada A. Mahmoud: Writing, editing, guidance and supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could influence the work reported in this paper.

References

- 1. Bai, C., L. Wang, and Z. Zhu, Adsorption of Cr (III) and Pb (II) by graphene oxide/alginate hydrogel membrane: Characterization, adsorption kinetics, isotherm and thermodynamics studies. International journal of biological macromolecules, 2020. **147**: p. 898-910.
- 2. Szewczuk-Karpisz, K., et al., Chromium (VI) reduction and accumulation on the kaolinite surface in the presence of cationic soil flocculant. Journal of Soils and Sediments, 2020. 20: p. 3688-3697.
- 3. Xu, J., et al., *B*, *N* co-doped carbon dots based fluorescent test paper and hydrogel for visual and efficient dual ion detection. Inorganic Chemistry Communications, 2022. **145**: p. 110047.
- 4. Neyaz, N., W.A. Siddiqui, and K.K. Nair, *Application of surface functionalized iron oxide nanomaterials as a nanosorbents in extraction of toxic heavy metals from ground water: a review.* International Journal of Environmental Sciences, 2014. **4**(4): p. 472-483.
- 5. Vardhan, K.H., P.S. Kumar, and R.C. Panda, A review on heavy metal pollution, toxicity and remedial measures: *Current trends and future perspectives.* Journal of Molecular Liquids, 2019. **290**: p. 111197.
- 6. Saravanan, A., et al., *Effective water/wastewater treatment methodologies for toxic pollutants removal: Processes and applications towards sustainable development.* Chemosphere, 2021. **280**: p. 130595.
- 7. Elsayed, A.E., et al., *Environmentally friendly radiation EDTA modified hydrogel based on gelatin for adsorptive removal of cationic and anionic dye from synthetic wastewater.* Egyptian Journal of Petroleum, 2023. **32**(4): p. 30-35.
- 8. Mohammad, R.E.A., et al., *Decolourization of textile dyes using CNT-based hybrid materials*, in *Nanohybrid Materials for Treatment of Textiles Dyes*. 2023, Springer. p. 119-156.
- 9. Liang, X., et al., Drivers and applications of integrated clean-up technologies for surfactant-enhanced remediation of environments contaminated with polycyclic aromatic hydrocarbons (PAHs). Environmental Pollution, 2017. **225**: p. 129-140.
- Khozamy, E., et al., Implementation of carboxymethyl cellulose/acrylic acid/titanium dioxide nanocomposite hydrogel in remediation of Cd (II), Zn (II) and Pb (II) for water treatment application. Egyptian Journal of Chemistry, 2019. 62(10): p. 1785-1798.
- 11. Gaur, N., et al., Environmental Science Processes & Impacts.
- 12. Yaashikaa, P.R., et al., Advances in biosorbents for removal of environmental pollutants: a review on pretreatment, removal mechanism and future outlook. Journal of Hazardous Materials, 2021. **420**: p. 126596.
- 13. Wahid, F., et al., *Nanocomposite hydrogels as multifunctional systems for biomedical applications: Current state and perspectives.* Composites Part B: Engineering, 2020. **200**: p. 108208.
- 14. Kumari, R., et al., *Dye sequestration from aqueous phase using natural and synthetic adsorbents in batch mode: present status and future perspectives.* International Journal of Environmental Science and Technology, 2023. **20**(12): p. 14033-14052.
- 15. Mohanty, S., et al., *Exploring the potential of polysaccharide-based hybrid hydrogel systems for their biomedical and therapeutic applications: A review.* International Journal of Biological Macromolecules, 2023: p. 128348.
- Li, Z. and Z. Lin, Recent advances in polysaccharide-based hydrogels for synthesis and applications. Aggregate, 2021. 2(2): p. e21.
- 17. Li, J., et al., *The role of surface functional groups of pectin and pectin-based materials on the adsorption of heavy metal ions and dyes.* Carbohydrate Polymers, 2022. **276**: p. 118789.
- 18. Abaid, E.M., et al., *Bioremediation of Synthetic Polyacrylic acid via radiation graft copolymerization with natural based polymers*. Egyptian Journal of Chemistry, 2024. **67**(5): p. 141-152.
- Wang, R., et al., *Pectin-based adsorbents for heavy metal ions: A review*. Trends in Food Science & Technology, 2019. 91: p. 319-329.
- 20. Fertah, M., et al., *Extraction and characterization of sodium alginate from Moroccan Laminaria digitata brown seaweed.* Arabian Journal of Chemistry, 2017. **10**: p. S3707-S3714.
- 21. Gao, X., et al., *Adsorption of heavy metal ions by sodium alginate based adsorbent-a review and new perspectives*. International journal of biological macromolecules, 2020. **164**: p. 4423-4434.
- 22. Zeng, X., et al., Simultaneous removal of aqueous same ionic type heavy metals and dyes by a magnetic chitosan/polyethyleneimine embedded hydrophobic sodium alginate composite: Performance, interaction and mechanism. Chemosphere, 2023. **318**: p. 137869.
- 23. Cigeroglu, Z., et al., *Clay-based nanomaterials and their adsorptive removal efficiency for dyes and antibiotics: a review*. Materials Today Sustainability, 2024: p. 100735.
- 24. Krishna, R.H., et al., *Carbon nanotubes and graphene-based materials for adsorptive removal of metal ions–a review on surface functionalization and related adsorption mechanism.* Applied Surface Science Advances, 2023. **16**: p. 100431.
- 25. Aboelkhir, D.M., et al., *Multiwalled carbon nanotubes*@ pectin/κ-carrageenan-based nanocomposite biohydrogel prepared by gamma irradiation for efficient methylene blue dye sequestration. Journal of Applied Polymer Science, 2024. **141**(22): p. e55452.

- Mohamed, M.M., A. Sayed, and G.A. Mahmoud, Gamma-Irradiation-Assisted Synthesis and Characterization of Xanthan Gum/Agar/Gelatin/ZnO Nanocomposite Hydrogels and their Antimicrobial Activity. ChemistrySelect, 2023. 8(16): p. e202300360.
- 27. Mohamed, T.M., A. Sayed, and G.A. Mahmoud, *Tuning of the properties of polyvinyl alcohol/polyacrylamide film by phytic acid and gamma radiation crosslinking for food packaging applications*. Polymer-Plastics Technology and Materials, 2023. **62**(7): p. 866-876.
- 28. Spadaro, G., S. Alessi, and C. Dispenza, *Ionizing radiation-induced crosslinking and degradation of polymers*. Applications of ionizing radiation in materials processing, 2017. **1**: p. 167-182.
- 29. Khan, S. and N.M. Ranjha, *Effect of degree of cross-linking on swelling and on drug release of low viscous chitosan/poly* (vinyl alcohol) hydrogels. Polymer bulletin, 2014. **71**: p. 2133-2158.
- 30. Abulyazied, D.E. and A. Ene, An investigative study on the progress of nanoclay-reinforced polymers: Preparation, properties, and applications: A review. Polymers, 2021. 13(24): p. 4401.
- 31. Khan, F.S.A., et al., *Comprehensive review on carbon nanotubes embedded in different metal and polymer matrix: fabrications and applications*. Critical Reviews in Solid State and Materials Sciences, 2022. **47**(6): p. 837-864.
- 32. Mashkoor, F., A. Nasar, and Inamuddin, *Carbon nanotube-based adsorbents for the removal of dyes from waters: A review*. Environmental Chemistry Letters, 2020. **18**(3): p. 605-629.
- 33. Sarojini, G., et al., *Dyes removal from water using polymeric nanocomposites: a review.* Environmental Chemistry Letters, 2023. **21**(2): p. 1029-1058.
- 34. Fathy, N. and S. El-Shafey, *Carbon-based nanohybrid fabricated in-situ and boosted the adsorption of anionic reactive yellow dye*. International Journal of Environmental Science and Technology, 2023. **20**(1): p. 293-306.
- Bhasin, C.P., A. Pathan, and R.V. Patel, An Evaluation of Carbon Nanotube-based and Activated Carbon-based Nanocomposites for Fluoride and Other Pollutant Removal from Water: A Review. Current Nanomaterials, 2024. 9(1): p. 16-40.
- 36. Angel, D.A., et al., Complex Avrami kinetics of TiB2 transformation into TiB whiskers during sintering of Ti-TiB2 nanocomposites. Journal of Alloys and Compounds, 2022. **894**: p. 162442.
- Maqbool, A., A. Khalad, and N.Z. Khan, Prediction of corrosion rate for friction stir processed WE43 alloy by combining PSO-based virtual sample generation and machine learning. Journal of Magnesium and Alloys, 2024. 12(4): p. 1518-1528.
- 38. Umar, M., et al., Integrating DFT and machine learning for the design and optimization of sodium alginate-based hydrogel adsorbents: Efficient removal of pollutants from wastewater. Environmental Research, 2024. 247: p. 118219.
- 39. Alotaibi, A.M., et al., Industrial dye absorption and elimination from aqueous solutions through bio-composite construction of an organic framework encased in food-grade algae and alginate: Adsorption isotherm, kinetics, thermodynamics, and optimization by Box–Behnken design. International Journal of Biological Macromolecules, 2024: p. 133442.
- Núñez-Gómez, D., et al., Comparative Evaluation of Boron Sorption Dynamics on Zeolites in Irrigation Waters: An Isothermal Modeling Approach. Molecules, 2024. 29(11): p. 2545.
- 41. Zghal, S., et al., Adsorptive removal of Rhodamine B dye using carbon graphite/cnt composites as adsorbents: Kinetics, isotherms and thermodynamic study. Materials, 2023. 16(3): p. 1015.
- Akbari, A., et al., Synergistic adsorption of methylene blue with carrageenan/hydrochar-derived activated carbon hydrogel composites: Insights and optimization strategies. International Journal of Biological Macromolecules, 2024.
 265: p. 130750.
- 43. Shi, T., et al., *Highly efficient adsorption of heavy metals and cationic dyes by smart functionalized sodium alginate hydrogels.* Gels, 2022. **8**(6): p. 343.
- 44. Zhu, H., et al., *Removal of anionic and cationic dyes using porous chitosan/carboxymethyl cellulose-PEG hydrogels: Optimization, adsorption kinetics, isotherm and thermodynamics studies.* International Journal of Biological Macromolecules, 2023. **231**: p. 123213.
- 45. Umesh, A.S., Y.M. Puttaiahgowda, and S. Thottathil, *Enhanced adsorption: reviewing the potential of reinforcing polymers and hydrogels with nanomaterials for methylene blue dye removal.* Surfaces and Interfaces, 2024: p. 104670.
- 46. Aljeboree, A.M. and A.F. Alkaim, *Studying removal of anionic dye by prepared highly adsorbent surface hydrogel nanocomposite as an applicable for aqueous solution*. Scientific Reports, 2024. **14**(1): p. 9102.
- 47. Kausar, A., Nanoclay reinforced chitosan nanocomposites—state-of-the-art and technological imprints. Journal of Macromolecular Science, Part A, 2024: p. 1-22.