Hydrogels Based on Polyacrylamide and Functionalized Carbon Nanomaterials for Adsorption of a Cationic Dye

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Abstract
Malachite green (MG) is used for the dyeing of cotton, paper, and jute, among other materials, and presents acute toxicity to a wide range of aquatic and terrestrial animals. A polyacrylamide (PA) hydrogel modified with a low content of oxygenated and aminated carbon nanomaterials may be a suitable candidate to adsorb MG from wastewater. Herein, graphene oxide and carbon nanotubes (CNTs) were incorporated during the in situ polymerization of PA. The hydrogels were characterized through thermogravimetry, differential scanning calorimetry and infrared spectroscopy as well as imagined by scanning electron microscopy. The swelling and adsorption capacity were investigated to explore the influences of different carbon dimensionalities (1D and 2D), zeta potentials and nanofiller concentrations on the adsorption behavior of the hydrogel. There was an increase of approximately 1500% in the adsorption capacity after 24 h of exposure of a hydrogel with graphene oxide (GO) at 0.25 wt% with respect to the neat PA. Aminated graphene produced similar gains in the adsorption capacity of the GO-hydrogel, although it presents a positive zeta potential that is the opposite of that of GO. The modified CNTs showed smaller gains in the adsorption capacity, reaching a maximum 400% increase with respect to the PA hydrogel. The main factors that seem to affect the adsorption capacity were the dimensionality and degree of functionalization. The graphene oxide-based nanofillers were 3 to 4 times more functionalized than the nanotubes. The adsorption results were adjusted with a pseudo-second order kinetic model that allowed a complementary discussion about the nature of the physico-chemical effects on the process of MG adsorption in the hydrogel nanocomposites.

Keywords Malachite green adsorption · Polyacrylamide hydrogel · Graphene oxide · Carbon nanotube

Introduction
Human activities have contributed over the years to a high impact on water resources and aquatic environments [1–4]. Among the human activities that affect water, the contamination of rivers and effluents by synthetic dyes can be highlighted. The disposal of this contaminant in water is mainly due to the leather, paper and textile industries [5]. Techniques for removing dyes from wastewater can be divided into three broad groups: biological methods, chemical methods and physical methods. The third group of methods corresponds to the use of physical phenomena in the removal of dyes, such as filtration, coagulation, adsorption, and membrane use, among others [6]. Adsorption is one of the most effective processes of advanced water treatment, and Yagub et al. [7] broadly discussed the application of adsorbents to remove dyes, the factors that influence adsorption and the effectiveness of several adsorbents appearing in the literature.

Hydrogels are versatile materials that have a wide range of applications. They are present in the biological sciences, contributing to antibacterial, antioxidant and electroactive properties [8], glucose monitoring devices and drug delivery [9]. Conductive hydrogels acting as wearable electronic components have also been developed [10, 11]. The use of hydrogels in the removal of water pollutants is also widely studied in the literature, with polymeric hydrogels being the most frequently employed in this case [12–14]. Polymeric hydrogels can be composed of homopolymers and copolymers, which can be physically or chemically modified and
can incorporate various additives to customize the adsorption of specific contaminants [12–15].

Nanomaterials have been studied in the literature as a component of hydrogels used in the removal of synthetic dyes. A hydrogel based on polyacrylamide, graphene oxide and iron III oxide was developed for the removal of organic pollutants and metal ions through the Fenton reaction [11]. Polyvinyl alcohol/carboxymethylcellulose hydrogels enhanced with graphene oxide and bentonite also acted as adsorbents for the removal of methylene blue [16]. The chitin-based hydrogel with reduced graphene oxide modified with tannic acid showed good adsorption capacity for Congo red [17]. Other authors have applied carbon nanotube-based hydrogels to the adsorption of dyes [18–21].

Herein, polyacrylamide (PA) hydrogels with carbon nanomaterials (CNMs) were studied as potential adsorbents of cationic dyes. Among the CNMs used are graphene oxide and carbon nanotubes, both with functionalization groups of two types, the oxidized and the aminated ones. Therefore, four types of nanomaterials were compared to support a broad analysis of their influence correlated with the physical and chemical features of the nanofillers. The cationic dye studied was malachite green (MG) because it is used for the dyeing of cotton, paper, jute, silk, wool, leather products and acrylic and presents acute toxicity to a wide range of aquatic and terrestrial animals [22]. In all cases, the samples of the hydrogels containing carbon nanomaterials showed higher efficiency than the reference (neat hydrogel) in the adsorption of dye. The dimensionality and the degree of functionalization of the CNM seem to be the main factors affecting the adsorption capacity of the hydrogel nanocomposites.

**Materials and Methods**

**Material**

Acrylamide (98%) (MM = 71.08 g mol⁻¹) and ammonium persulfate [(NH₄)₂S₂O₈] ACS (98%) (MM = 228.19 g mol⁻¹) were purchased from Éxodo Científica - Brazil. N,N-Methylenbisacrylamide (99.5%) (MM = 154.17 g mol⁻¹) was acquired from Sigma Aldrich. Malachite green oxalate P.A. (MM = 927.03 g mol⁻¹) was obtained from Neon—Brazil. Deionized water was obtained using reverse osmosis equipment. All materials and reagents were used without prior treatment or purification.

Graphene oxide (GO), CNToxidized (CNTO), GO functionalized with triethylenetetramine (TETA) and CNTO functionalized with TETA (CNTOA) were obtained by previous routes [23, 24] and studied at the Center for Nanotechnology of Nanomaterials and Graphene (CTNano)—Brazil. Table 1 shows the main properties of the carbon nanomaterials produced at CTNano and fully characterized in our previous works [24, 25] and in this work.

**Methods**

**Hydrogel Synthesis**

Figure 1 presents, in schematic form, the mechanism of synthesis of the hydrogels studied in this work. There is a small difference in the synthesis routes between the hydrogels containing GO and CNTO, the hydrogels containing GOA, CNTOA and the reference hydrogel. This difference is because nanomaterials containing only oxygenated groups disperse in water, and nanomaterials containing amino groups do not.

A typical experiment for the synthesis of hydrogels starts with the dissolution of 2.4 g of acrylamide and 0.48 g of N,N-methylenbisacrylamide in 47.6 g of deionized water. The stages for preparing the materials are shown in Fig. 2. For the reference hydrogels (neat material), the following step is to add 0.48 g of ammonium persulfate (APS) and subsequent immersion of the tip ultrasound (Sonics Vibra-Cell VCX 130) at 30% amplitude for 10 to 15 min. As soon as the gelation starts, the ultrasound is turned off, and the system is taken to an oven at 70 °C to finish gelation. After cooling to room temperature, the hydrogel was immersed in a container with abundant deionized water to wash it and remove unreacted material. This water is changed until the

| Table 1 | Main properties of the carbon nanomaterials used in this work |
|---------|---------------------------------------------------------------|
| Properties | GO | GOA | CNTO | CNTOA |
| Carbon content/% | 43.5 ± 0.2 | 55.65 ± 0.11 | 81.18 ± 0.06 | 82.22 ± 0.00 |
| Hydrogen content/% | 2.4 ± 0.1 | 3.51 ± 0.13 | 0.59 ± 0.01 | 1.16 ± 0.10 |
| Nitrogen content/% | 0.0 ± 0.0 | 12.21 ± 0.00 | 0.21 ± 0.0 | 4.49 ± 0.54 |
| Functionalization (TG)/% | 39 | 29 | 8 | 11 |
| External diameter (TEM)/nm | – | – | 18.6 ± 1.0 | 28.0 ± 0.2 |
| Number of layers (TEM) | 5 to 6 | 6 to 7 | 15 | 18 |
| Lateral dimensions (TEM)/nm | 401 to 1084 | 137 to 455 | – | – |
| Zeta potential/mV | pH 3 | −19 | +33.5 | −30 | +30.7 |
| | pH 7 | −48 | +11.5 | −47 | −10.5 |
material is completely washed. Finally, the hydrogels were shredded and lyophilized for further characterization and adsorption tests.

For the synthesis of hydrogels containing GO and CNTO, the nanomaterials previously dispersed in bath ultrasound are mixed with half the volume of water used in the reference hydrogel synthesis before ammonium persulfate addition (Fig. 2). For the hydrogels containing GOA and CNTOA, before ammonium persulfate addition, the nanomaterials are dispersed in the solution containing acrylamide and N,N-methylenebisacrylamide in bath ultrasound since they do not present good dispersion in deionized water. The total amount of water is 47.6 g in both cases.

Table 2 lists the amount of nanomaterial used in each sample as well as its respective code used in this work. The amount of nanomaterial is presented with respect to the acrylamide mass used in the synthesis (2.4 g).
Physical and Chemical Characterizations

The hydrogels were characterized through thermal and spectroscopic analyses as well as imagined by scanning electron microscopy (SEM). For the characterizations, the hydrogels were lyophilized (LIOBRAS Liotop LP8200) and broken into millimeter pieces. For SEM, the hydrogels were frozen in liquid nitrogen and randomly fractured to obtain an analysis region.

Fourier transform infrared absorption spectroscopy (FTIR) was performed on a Perkin Elmer Frontier IR Spectrophotometer in the range of 4000 to 400 cm⁻¹ in ATR mode. Differential scanning calorimetry (DSC) curves were obtained on a PerkinElmer DSC 8000, and initially, the samples were cooled from room temperature to −50 °C and then heated to a temperature of 230 °C with nitrogen gas with a flow rate of 20 mL.min⁻¹. Thermogravimetry curves (TG) and their derivative (DTG) were obtained on a thermobalance TGA Q5000 Thermogravimetric Analyzer from the company TA Instruments in a synthetic air atmosphere at a heating rate of 5 °C.min⁻¹ from room temperature to 800 °C. SEM images were obtained with FEI Quanta 3D FEG equipment; frozen pieces of the samples were placed on a metallic support and coated with carbon.

Measurements of pH and Zeta Potential

The pH of the samples was measured using a Kasvi benchtop pH meter. The pH values of the following systems were measured: (i) deionized water after contact with the hydrogel; (ii) water after 24 h of contact with the hydrogel; (iii) MG solution at 120 ppm and of the same solution after contact with the hydrogel at intervals of 1, 2, 3, 4, 6 and 24 h. The zeta potentials were measured using an Anton Paar Litesizer 500 particle analyzer. The MG solution was measured at 120 ppm. The carbon nanomaterials were measured at pH 4.5 to support the discussion of the adsorption mechanism because this is the pH of the MG solution. Each measurement was made in 5 runs, each run having at least 100 accumulations.

Swelling Test

The swelling test was performed by immersing 50 mg of hydrogel in deionized water. The mass of the sample was measured until it stabilized. To determine the swelling ratio, the following equation was used:

\[ W = \frac{w_f - w_i}{w_i} \times 100 \] (1)

where \( w_i \) is the initial weight of the hydrogel and \( w_f \) is the final weight of the hydrogel in the measured time interval.

Adsorption Studies

A total of 0.05 g of each hydrogel sample was immersed in 150 mL of 120 ppm MG solution. The systems were kept under gentle agitation, and the study was carried out over a period of 24 h. At intervals of 1, 2, 3, 4, 6 and 24 h, aliquots of the solution were collected to determine the concentration of dye remaining after each interval. The concentrations were determined with the aid of a UV–VIS Perkin Elmer spectrophotometer Lambda 35 at the maximum wavelength of 620 nm for MG using the Beer–Lambert law [26]. A previously made calibration curve was used to determine concentrations after each interval. The reference sample was performed in triplicate, and the mean values are presented with error bars.

The removal dosage \( q \) was obtained through Eq. 2:

\[ q(\text{mg g}^{-1}) = \frac{(C_i - C_f)V}{w_h} \] (2)

where \( C_i \) is the initial concentration, \( C_f \) is the final concentration (for each interval), \( V \) is the total volume of the dye solution, and \( w_h \) is the weight of the hydrogel.

The removal percentage was calculated by subtracting the initial concentration \( C_i \) of the dye from the final concentration \( C_f \) and dividing by the initial concentration \( C_i \) as described in Eq. 3 [26]:

\[ \%\text{Removal} = \frac{C_i - C_f}{C_i} \times 100 \] (3)

| Code of the hydrogel | CNM   | m_{CNS}/mg | %m/m of CNM |
|----------------------|-------|------------|-------------|
| PA                   | –     | 0          | 0           |
| GO-0.10              | GO    | 2.4        | 0.1         |
| GO-0.25              | 6     | 0.25       |
| GO-0.50              | 12    | 0.5        |
| GA-0.10              | GOA   | 2.4        | 0.1         |
| GA-0.25              | 6     | 0.25       |
| GA-0.50              | 12    | 0.5        |
| NO-0.10              | CNTO  | 2.4        | 0.1         |
| NO-0.25              | 6     | 0.25       |
| NO-0.50              | 12    | 0.5        |
| NA-0.10              | CNTOA | 2.4        | 0.1         |
| NA-0.25              | 6     | 0.25       |
| NA-0.50              | 12    | 0.5        |

Table 2 Coding and quantity of carbon nanomaterial (CNM) presented in each sample of PA hydrogel investigated

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Kinetic Study of Adsorption

The data obtained in the adsorption study were used to evaluate whether the adsorption kinetics approximate a pseudo-second order model, which is described by Eq. 4:

\[
\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e}
\]

where \( q_t \) and \( q_e \) are the amount of dye adsorbed (mg g\(^{-1}\)) as a function of contact time and at equilibrium, respectively, and \( t \) is the time and \( k \) adsorption rate constant. The data obtained in \( t/q_t \) format are plotted as a function of \( t \). The \( R^2 \) coefficient obtained in the linear regression allows us to evaluate whether the adsorption approaches pseudo-second-order kinetics [27].

Results and Discussion

Physicochemical Characterization of Solutions and Nanomaterials

Table 3 presents the pH values of the systems in contact with the reference hydrogel PA as well as the zeta potential value of the MG solution. The MG solution does not influence the pH value after contact with the hydrogel for 24 h. The stability of the hydrogel is also observed when measuring the pH values of the deionized water when in contact with the material, with the value varying from 6.30 to 6.25. The zeta potential value measured from the MG solution confirms the presence of malachite green cation since it presented a positive value of +9.85 ± 2.95 mV. The zeta potential values for the carbon nanomaterials at pH 4.5 show negative and positive values that are intermediate between those at pH 6 and 3, as shown in Table 3.

| System                     | pH*  | Zeta potential/mV |
|----------------------------|------|-------------------|
| Hydrogel/deionized water   | 6.30 | –                 |
| MG solution                | 4.51 | +9.85 ± 2.95      |
| GO                         | –    | –34.99 ± 0.27     |
| GOA                        | –    | +28.08 ± 0.90     |
| CNTO                       | –    | –39.43 ± 0.74     |
| CNTOA                      | –    | +17.89 ± 0.19     |

* Measurements of pH gave similar results after initial contact with hydrogel and after 24 h of contact with hydrogel

Physicochemical Characterization of Polyacrylamide Hydrogels

TG/DTG, DSC, FTIR and SEM were performed in samples of hydrogel with 0.5% of the various nanomaterials, in addition to the reference, to access a general understanding of structure and morphology, which may help to explain the adsorption of the dye.

Figure 3a shows the FTIR spectra for samples PA, GO-0.50, GA-0.50, NO-0.50 and NA-0.50. All spectra are similar, indicating that the content of nanomaterial used in the hydrogel nanocomposites did not provoke changes associated with interactions that can be probed by the FTIR-ATR measurement. As highlighted in the figure, the broad band centered at 3335 cm\(^{-1}\) refers to the stretching of the N–H bond from the crosslinking bridges [28], which are in the same region of the strong O–H stretching vibration [29]. The band observed at 2935 cm\(^{-1}\) is assigned to the asymmetric vibration of the CH bond, both in the crosslinking bridges and in the macromolecular chain. The absorption bands observed at 1654 cm\(^{-1}\) and 1535 cm\(^{-1}\) are assigned to C=O stretching and NH deformation from the crosslinking amidic group [28, 30]. Finally, the band observed at 1416 cm\(^{-1}\) is assigned to C–N bond stretching [31, 32].

In the TG and DTG curves presented in Fig. 3b–c, as well as in the other characterizations, there is no significant difference between the analyzed samples. Hydrogels are fully degraded at a temperature of approximately 600 °C. The DTG curves presented in Fig. 2c present three peaks at approximately 280, 370 and 520 °C that can indicate the temperatures at which loss or degradation in the maximum intensity of the different functional groups present in the hydrogels occurs. Taking these peaks into account, the TG curves can be divided into four temperature ranges: from room temperature to 200 °C, from 200 to 305 °C, from 305 to 420 °C and from 420 to 800 °C. The first interval, which shows a 12% decrease in mass, is associated with water loss; the second and third intervals show a mass loss of 12% and 29%, respectively, which may be associated with the loss of ammonia and water by the imidization and dehydration reactions, respectively; the last interval presents the mass loss of the last 47%, related to the degradation of the main carbon chain of the hydrogels [33, 34].

Figure 4 shows SEM micrographs for the PA, GO-0.50, GA-0.50, NO-0.50 and NA-0.50 samples. In general, hydrogels have pores with similar shapes and orientations, differing in terms of diameter and distribution. Pores have a wide range of diameters, from hundreds of nm to dozens of µm [35, 36].

The reference sample (PA) has well-distributed pores with an intermediate spacing between them when compared to the other samples. The pores of this hydrogel are the largest in diameter, with values ranging from 3 to 34 µm and
an average value of \((14.2 \pm 5.2) \text{ µm}\). The GO-0.50 sample presents pores with a less regular distribution compared to the reference sample, with regions of higher concentration of pores. The pores of this hydrogel have a diameter smaller than the reference, with values ranging from 1 to 29 µm and an average value of \((7.3 \pm 3.7) \text{ µm}\). The GA-0.50 sample is

**Fig. 3** Neat hydrogel and nanocomposites characterization: a FTIR spectra, b TG curves and c DTG of samples PA, GO-0.50, GA-0.50, NO-0.50 and NA-0.50.

**Fig. 4** SEM micrographs of samples PA, GO-0.50, GA-0.50, NO-0.50 and NA-0.50 at two different magnifications.
the one with the best distributed pores and the smallest spacing between them. The pores of this sample are the smallest in diameter, with values ranging from 0.1 to 6.1 μm and an average value of (1.6 ± 0.8) μm. The NO-0.50 sample also has well-distributed and closely spaced pores. The pore diameter varies from 0.9 to 10.3 μm, with an average value of (4.3 ± 1.8) μm. Finally, sample NA-0.50 has a less regular pore distribution. The pore diameters present values slightly larger than those of the NO-0.50 sample, ranging from 0.9 to 21.2 μm, with an average value of 4.5 ± 2.4 μm.

Swelling Test

Figure 5 presents the swelling data for all samples. It is possible to note that, in general, the values of swelling ratios are similar for all hydrogels. After 34 h of contact, the highest swelling ratio values are those for samples NO-0.10 and GO-0.25, which are 1172 and 1162%, respectively. The lowest values are those of the GO-0.10 and GA-0.25 samples, which are 1016 and 1033%, respectively.

The obtained swelling values are within the common range found in the literature. Ismail and Kocabay [37] showed 850% swelling for a polyacrylamide hydrogel crosslinked by poly(ethylene glycol) dimethacrylate. Yürüksoy [38] obtained a swelling of 1122% for acrylamide-based hydrogels. Onder et al. [39] obtained a swelling of approximately 500% for a crosslinked hydroxyethyl starch hydrogel with GO.

The results of structural and thermal characterization of the hydrogels Fig. 3 shows that the hydrogels are all very similar. The same is true for the results of swelling, all very similar. Therefore, the differences observed in the pore size (Fig. 4) were not determinant of the swelling behavior. One may affirm that the existing porosity allowed similar access of water to the entire material in all hydrogels.

Study of Adsorption Capacity

Removal efficiency and adsorption capacity with respect to contact time for the MG dye were investigated for all synthesized hydrogels. Figure 6 shows the MG removal efficiency data after 24 h of contact. The reference sample of neat PA showed a small removal efficiency, (5 ± 1) %, and samples of hydrogel with GO-0.25 and GA-0.10 showed the highest

Fig. 5  Swelling ratio as a function of time for samples a PA, GO-0.10, GO-0.25, GO-0.50, b PA, GA-0.10, GA-0.25, GA-0.50, c PA, NO-0.10, NO-0.25, NO -0.50, d PA, NA-0.10, NA-0.25 and NA-0.50.
removal rates: 76 and 71%, respectively. The samples containing GO and CNTO do not follow a tendency with respect to the nanomaterial content. The hydrogel with GA is the best adsorbent with the lowest concentration of 0.10%. It is worth noting that the removal efficiency obtained by the GO-0.25 and GA-0.10 samples are lower than the rates observed in other works in the literature that contain similar adsorbents, as shown in Table 4. However, the adsorption capacity of MG in this work is very competitive with the literature, as will be reported below.

Figure 7 shows the adsorption capacity with respect to contact time of the hydrogels for the MG dye. All hydrogels showed superior performance compared to the reference. It is possible to observe that most of the dye is removed in the first 6 h of contact, as seen in the curves. The amount of dye removed increases until it stabilizes, with values in the range from 17 to 274 mg g⁻¹ after 24 h of contact. The largest adsorption capacity is for the GO-0.25 hydrogel, and the smallest is for the reference sample. The GA-0.10 sample also presented a high value of adsorption capacity when compared to the other samples, i.e., 257 mg g⁻¹. Importantly, there was an increase...
of approximately 1500% in the adsorption capacity for GO-0.25 in comparison with the reference PA hydrogel.

Figure 8 presents the results of the adsorption capacity of hydrogels with greater efficiency for each nanomaterial. It should be noted that the GO-0.25 and GA-0.10 samples have considerably higher adsorption capacities than the other hydrogels. The physico-chemical properties of the carbon-based nanomaterials are reported in Tables 1 and 3. Figure 8b shows simplified schemes of the functionalized nanomaterials, indicating only one typical functional group. It is possible to affirm that the chemical groups with heteroatoms (O and N) are an important factor in favoring the adsorption mechanism. MG is a cationic aromatic dye that can adsorb to anionic functional groups by hydrogen bonding, ion-dipole interactions and π−π interactions of the aromatic ring. GO and GOA present degrees of functionalization of 39% and 29%, respectively, while CNTO and CNTOA present 3 to 4 times lower levels of oxygenated and amino groups.

Zeta potential is frequently considered to understand the adsorption mechanism of ionic dyes. However, the fact that the oxidized nanomaterials present a negative zeta potential and the aminated nanomaterials present a positive zeta potential (Fig. 8) does not correlate with the adsorption behavior observed in the results. Both GO- and GOA-based hydrogels showed high values of adsorption, which demonstrates that the charges present in the nanomaterials are not an influential factor for the adsorption efficiency. Furthermore, the swelling behavior was similar for all hydrogels (Fig. 5), and it is not a determinant factor in the adsorption behavior.

Therefore, it is possible to affirm that the factors with the greatest impact on the adsorption efficiency of MG for the studied systems are the dimensionality of the nanomaterials (layer 2D or tube 1D) and the percentage of functionalization. Most likely, the hydrogen bond, ion-dipole and π−π interactions through the aromatic structures are the relevant interactions that drive the adsorption of MG on the nanocomposite hydrogels.

Table 4 gathers some data on the adsorption capacity of different adsorbents with systems similar to those studied in this work. The results obtained herein approach or even surpass those obtained in other works. The adsorption capacity obtained by the GO-0.25 hydrogel is 274 mg g⁻¹, which is a value greater than double or even quadruple the values obtained by the nanocomposites of poly(acrylic acid), graphene oxide and monoacryloyl tetramonium tialcalix [4] arene [26] and by graphene oxide and aminated lignin aerogels [40]. The adsorption capacities of 289.10 and 265.87 mg g⁻¹ obtained in the works of Zhang et al. [41]and Chen et al. [42] are values closer to those obtained in this work.

**Study of Dye Adsorption Kinetics**

Raval et al. [22] reviewed a wide variety of adsorbents used in various works for the removal of malachite green (MG) dye. In this review, several optimal experimental conditions were evaluated, such as solution pH,
equilibrium contact time, amount of adsorbent and temperature, as well as adsorption isotherms and kinetic and thermodynamic data, which were analyzed and tabulated. In these tables, it is possible to observe that the great majority of the studied adsorbents show adsorption behavior that follows a kinetics adjusted to a pseudo-second-order model, mainly the systems containing nanomaterials. Thus, the kinetic study of the current work was focused on the adjustment to a pseudo-second-order kinetic model. The pseudo-first-order kinetic model was also tested, but the adjustments for the PA hydrogel and two of the nanocomposites were not possible, and for others, the fitting quality was not satisfactory.

Figure 9 presents the graphs of t/qi as a function of t, as proposed by Eq. 4 for pseudo-second-order kinetics. The linear adjustments provided the kinetic parameters shown in Table 5.

As seen in Table 5: Fig. 9, the values of R² indicate that the adsorption kinetics of the hydrogels studied for the MG dye approach a pseudo-second-order kinetic model. Only for the reference sample, whose R² value was 0.89244, was the fit not a perfect match. However, as this model was very well adjusted for all nanocomposite hydrogels, it was decided to work with it in this discussion. The values of qe, i.e., the adsorption capacity at equilibrium, did not follow the same order as the experimental data at 24 h. Sample GO-0.50 has the highest value, 384.6 mg g⁻¹, while sample GO-0.25 comes in second with 336.7 mg g⁻¹. The adsorption rate constant (k) values indicate that the adsorption processes of MG in the GO and GOA hydrogels are slower than those in the CTNT and CNTOA hydrogels. Moreover, the much higher adsorption capacity of graphene oxide-modified hydrogels indicates that the high content of functional groups probably acts as active sites for adsorption in this case. Therefore, a slower but more extensive mechanism of adsorption occurs in the layered highly functionalized structure.

**Conclusion**

This study reports the synthesis of nanocomposite hydrogels by an in situ polymerization method. Polyacrylamide-based hydrogels were synthesized using functionalized carbon nanomaterials GO, GOA, CTNT and CNTOA as additives at three different concentrations. Malachite green dye adsorption studies were carried out, and the removal efficiency and adsorption capacity of the synthesized hydrogels were evaluated. These studies showed that the addition of carbon nanomaterials to the polyacrylamide hydrogel significantly improved the adsorption properties of malachite green dye with respect to the reference. All hydrogels showed similar features in the FTIR and thermal characterization, and differences in porous sizes were observed but did not influence the swelling behavior, which was also similar for all hydrogels. The hydrogels containing GO and GOA presented adsorption values considerably higher than those of the other samples. The GO-0.25 hydrogel presented a removal efficiency and an adsorption capacity of 76% and 274 mg g⁻¹, respectively, against (5 ± 1)% and 17 mg g⁻¹ of the reference sample (PA). This represents a 71% increase in removal efficiency and an increase of approximately 1500% in the adsorption capacity of the MG dye. A complementary study of the adsorption kinetics was also carried out, and it was found that the adsorption of MG with the hydrogels studied fit the pseudo-second-order kinetic model. Finally, it is proposed that the addition of the carbon nanomaterials to the polyacrylamide hydrogel improves the adsorption of MG through the establishment of hydrogen bonding, ion-dipole and π—π interactions. In particular, the 2D highly
Fig. 9 Adjustments of the adsorption data to the pseudo-second-order kinetic model of the samples for the first 400 min: a PA, b GO-0.50, GA-0.50, NO-0.50 and NA-0.50, c GA-0.10, GA-0.25, GA-0.50, d NO-0.10, NO-0.25, NO-0.50, e NA-0.10, NA-0.25 and NA-0.50
Table 5 Kinetic parameters for MG adsorption for adjustment of pseudo-second-order adsorption kinetics of the hydrogels studied (experimental data from Fig. 7)

| Samples | k/g min⁻¹ mg⁻¹ | q/mg g⁻¹ | R² |
|---------|----------------|---------|-----|
| PA      | 0.00144739     | 19.72   | 0.89244 |
| GO-0.10 | 0.00000872     | 334.4   | 0.99818 |
| GO-0.25 | 0.00001499     | 336.7   | 0.98932 |
| GO-0.50 | 0.00000781     | 384.6   | 0.98737 |
| GA-0.10 | 0.00001473     | 314.5   | 0.99088 |
| GA-0.25 | 0.00001572     | 257.1   | 0.96262 |
| GA-0.50 | 0.00004333     | 157.7   | 0.95408 |
| NO-0.10 | 0.00048986     | 50.5    | 0.99411 |
| NO-0.25 | 0.00084966     | 39.9    | 0.99438 |
| NO-0.50 | 0.00040822     | 54.3    | 0.98189 |
| NA-0.10 | 0.00081944     | 85.0    | 0.99251 |
| NA-0.25 | 0.00639478     | 80.4    | 0.99999 |
| NA-0.50 | 0.00156401     | 81.0    | 0.9707 |

functionalized GO showed the best performance, which can support future applications.

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Declarations

Conflict of interest They have no competing interest as defined by Springer or other interests that might be perceived to influence the results and/or discussion reported in this paper.

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