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Modified hemp fibers as a novel and green adsorbent for organic dye adsorption: adsorption, kinetic studies and modeling

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Abstract

Synthetic dyes represent a serious hazard to aquatic environments. Many approaches for eliminating these contaminants have been devised and applied. This manuscript reports the production of a novel, low-cost and ecologically friendly bioad-sorbent based on hemp fibers that are functionalized with graphite oxide through bridging with an organosilane. Methylene blue was selected as a typical pollutant to be removed from wastewaters. The adsorbent was characterized through scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and Fourier-transform infrared (FTIR) analysis. An investigation of the effects of pH and temperature on the adsorption process was carried out. The adsorption capacity increased with increasing contact time as well as with the temperature, proving that the process shows endothermic behavior. Moreover, the process was found to be dependent on the pH level and, to corroborate the collected results, the point of zero charge was evaluated. The maximum adsorption capacity was found to be 57 mg/g, which was achieved with the following parameters: pH=7.5, T=80 °C and an initial dye concentration equal to 5 mg/L. Reusability studies showed a 15% decrease in adsorption capacity after 30 adsorption tests, proving the possibility of reusing the produced adsorbent without any great decay in performance. Finally, a potential adsorption mechanism is reported and discussed. The reported results prove that it is feasible to apply the designed adsorbent of organic dyes to the purification of wastewaters.

Graphical abstract



Keywords Hemp fiber · Water purification · Graphite oxide · Natural fiber · Adsorption · Advanced materials

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Introduction

Water is essential for the survival of life, but it has been polluted by dyes and fertilizer and through anthropogenic activities (Zafar et al. 2021), the depletion of crude oil resources (Sehar et al. 2020), rapid urbanization, individual mobility, increasing energy demands (Yin et al. 2020; Al-Rawi et al. 2020; Faridi et al. 2023), and incomplete combustion, which affects human health and the ecosystem (Rasheed et al. 2021). The presence of organic pollutants in the aquatic environment, which can cause adverse biological impacts, is leading to great concern over ecosystems. For example, traces of synthetic dyes in wastewaters represent a major issue due to their impact on ecosystems and their effect on the health of people (Tkaczyk et al. 2020; Viscusi et al. 2021a; Ma et al. 2022). Dyes are now used in different industrial fields, such as the textile industry, paper production, food technology, photochemical cells, agricultural research and hair coloring (Crini et al. 2019; Molla and Youk 2022; Shi et al. 2022). Different methodologies have been applied to remove pollutants, such as solvent extraction, flocculation, chemical oxidation, coagulation and adsorption (Hao et al. 2000; Forgacs et al. 2004; Zhang et al. 2016; Thong et al. 2018; Varghese et al. 2019; Kong and Wilson 2020), microbial fuel cells (Mohyudin et al. 2022), and catalysis (Al-Rawi et al. 2021). Adsorption is considered the methodology most commonly used to remove organic dyes, since this technology is quite simple and cheap (Wang et al. 2020; Viscusi et al. 2021b; Sağlam et al. 2023). Moreover, the use of common adsorbents can make the adsorption process quite expensive (Viscusi et al. 2022). So, the scientific community is focusing on the use of novel and sustainable low-cost adsorbents (Kong and Wilson 2020; Abbaz et al. 2023). Different natural materials have been used to remove pollutants from wastewaters, such as apricot seed shell (Hashem et al. 2022), aloe vera leaf waste (Khaniabadi et al. 2016), kapok fibers (Futalan et al. 2022), modified cotton fibers (Yang et al. 2022), almond peel waste (Al-Musawi et al. 2023), pineapple peels (Widiartyasari Prihatdini et al. 2023), orange peels (Eddy et al. 2023), date seed (Ali et al. 2017), clam shell (Qu et al. 2022), sesame hull (Feng et al. 2011), pomegranate peels (Abbaz et al. 2023), sugarcane bagasse ash (Garg et al. 2023) and an algae-based composite (Smječanin et al. 2022). One of the most interesting types of agro-waste materials is natural fibers. These materials are emerging mainly due to their advantageous properties such as low cost, availability and biodegradability (Faruk et al. 2012; Liu et al. 2017; Sanjay et al. 2019; Viscusi et al. 2020, 2021d). Among natural fibers, hemp fibers (Cannabis sativa L.) are attracting the interest of the scientific community because of their features: thermal insulation, low cost, no irritation, and a rapid growing cycle (Morin-Crini et al. 2018; Viscusi et al. 2020, 2021c; Viscusi and Gorrasi 2021). However, hemp fibers cannot be used as a highly effective adsorbent without modifying or treating them. So, this work proposes a sustainable approach to improve the adsorption properties of hemp fibers by modifying them with graphite oxide through chemical modification with a common organosilane, 3-aminopropyl triethoxysilane (OS). The use of carbon and carbon-derived materials for wastewater remediation has been widely explored. Sher et al. applied an electrochemical technique in combination with powdered activated carbon for the removal of micropollutants by adsorption (Sher et al. 2021). Rashtbari et al. developed zerovalent iron nanoparticles incorporated on activated carbon from pomegranate peel extract as an efficient and inexpensive adsorbent to eliminate furfural (Rashtbari et al. 2022). Moreover, different carbon-based materials have been used for water remediation, such as activated carbon (Rosli et al. 2023), graphene oxide (Konicki et al. 2017), reduced graphene oxide (Gupta and Khatri 2017), multi-walled carbon nanotubes (MWCNTs) (Shirmardi et al. 2013), mesoporous carbon materials (Mohammadi et al. 2011) and biochar materials (Ouedrhiri et al. 2022). Notwithstanding, up to now, despite the wide use of carbon for adsorption processes, there have not been any deep studies of novel adsorbents based on hemp fibers modified with graphene oxide. To study the adsorption capacity of the adsorbent designed in the present work, batch adsorption studies were carried out to evaluate the sorption of methylene blue. The effects of temperature and pH on the adsorption performance were then considered. Finally, reusability studies were carried out. Since the use of a powder-form adsorbent can generate pollution, separation and regeneration processes are needed to limit the use of these materials. It follows that the use of hemp fiberboard will allow the easy handling of the adsorbent, facilitating desorption and reusability processes and thus limiting operating costs.

Experimental

Materials

Hemp fibers (HF) were provided by Nafco Company. The organosilane [3-aminopropyl)triethoxysilane (OS)] and NaOH in pellet form were purchased from Sigma–Aldrich, while HCl solution 37% v/v and NaCl were purchased from Carlo Erba Reagents. Graphite oxide was received from Qingdao Tianhe Graphite Co. Ltd. Methylene blue was purchased from Panreac AppliChem ITW Reagents.

Surface modification

OS (5% wt) was hydrolyzed in water at 50 °C for 2.5 h (pH=3). After removing impurities, the HFs were modified with OS solution (T=25 °C; solid/liquid ratio equal to 0.03 g/mL) for 1.5 h. Due to the self-condensation of OS, siloxane oligomers with Si-OH groups can be formed (Raji et al. 2016). They are able to form hydrogen bonds with the hydroxyl groups of the HF (Kale et al. 2019). Graphite oxide (GO) in aqueous solution (0.2% w/w) was prepared by dissolving GO in water and using ultrasonication to make the dispersion homogeneous. The silane-modified HFs were soaked in the GO/water mixture for 48 h at 90 °C. Finally, the HF/GO samples were dried in an oven at 150 °C for 24 h. The functionalization of GO with OS-modified HF is based on either the reaction of the OH groups of GO with the Si-OH groups through the formation of Si-O-C bonds or the reaction of epoxy groups with the amino groups of the OS, leading to the formation of secondary amines (Li et al. 2016; Serodre et al. 2019). After that, the modified HF were washed and dried.

Methods

Scanning electron microscopy (SEM) was used to study the material's morphology. A Quanta 200 F microscope was used to acquire SEM images. Before the analysis, the samples were coated with a thin film of gold through sputtering.

Fourier transform infrared (FTIR) analysis was performed using a Bruker spectrometer (model Vertex 70; average of 64 scans, resolution of 4 cm⁻¹). This technique allows the changes and shifts in functional groups due to functionalization to be evaluated. The specimens were ground in KBr powder before they were dried under vacuum at room temperature.

Each spectrum was recorded 64 times with a resolution of 4 cm^{-1} . The blank spectrum was recorded under the same conditions by using a pure KBr sample.

The point of zero charge (pH_{PZC}) was evaluated by adopting a titration-based procedure (Viscusi et al. 2021a). A set amount of adsorbent was added to the NaCl solution to achieve equilibration before drops of HCl solution were added for titration. The pH was analyzed and Δ pH (final pH – initial pH) was plotted. The point where the curve intersected the *x* axis was identified as pH_{pzc}.

By monitoring volumetric N_2 adsorption on the samples at – 196 °C with the Costech Sorptometer 1042 analyzer, the specific surface area values of the samples were determined.

Batch adsorption tests were carried out as follows. Methylene blue (MB) solutions were prepared in distilled water (5 mg/L). The pH of the MB solution was varied (from 3 to 12) by adding drops of NaOH or HCl solution (1 M). The concentration of MB in the solution was evaluated using the UV–Vis technique (absorbance at $\lambda = 664$ nm). The adsorption capacity (q_t) was evaluated through Eq. 1:

$$q_{\rm t} = \frac{(c_0 - c_{\rm eq}) \times V}{m},\tag{1}$$

where c_0 is the initial dye concentration, c_{eq} is the equilibrium dye concentration, *V* is the volume of the solution and *m* is the mass of the membrane (Mohammad and Atassi 2020). Various kinetic models have been used to model adsorption data, such as Lagergren's pseudo-first-order model (Eq. 2), a pseudo-second-order model (Eq. 3) an intra-particle diffusion model (Eq. 4) (Slatni et al. 2022) and Elovich's model (Eq. 5) (Zhou et al. 2014; Largitte and Pasquier 2016):

$$\log(q_{\rm e} - q_{\rm t}) = \log(q_{e}) - \frac{k_{\rm 1}}{2.303} \times t$$
(2)

$$\frac{t}{q_{\rm t}} = \frac{1}{k_2 \times q_{\rm e}^2} + \frac{t}{q_{\rm e}} \tag{3}$$

$$q_{\rm t} = k_{\rm id} \times \sqrt{t} + C \tag{4}$$

$$q_t = \frac{1}{\beta} \ln\left(\alpha\beta\right) + \frac{1}{\beta} \ln\left(t + t_0\right),\tag{5}$$

where k_1 (1/min) and k_2 (mg/g min) are the rate constants of the first- and second-order models, respectively; q_e (mg/g) is the equilibrium amount of dye adsorbed per gram of adsorbent; *C* is the intercept of the intraparticle diffusion model, k_{id} is the intraparticle diffusion constant; α (mg/g min) is the initial adsorption rate; and β (g/mg) is related to the surface coverage and the activation energy. Desorption studies were then performed by washing the used HF/GO adsorbent with ethanol. The adsorbent was then dried and reused for further adsorption tests.

Computational work

Computation analysis was performed using Materials Studio 8.0 software. The structures of GO and MB were geometrically optimized using the Dmol3 module. The GO-dye system was analyzed using the Amorphous Cell option and optimized using the Forcite module (Task=Geometry Optimization; Forcefield=COMPASS).

Results and discussion

Morphological and spectroscopic analyses

Fig. 1 shows the SEM images of (a) untreated HF and (b) graphite-oxide-functionalized HF.

The SEM image of pristine hemp fibers showed the typical roughened surfaces of natural fibers. Even after being modified with graphite oxide, the hemp fiber surface preserved its morphology. The EDX maps confirmed the atomic weight distribution of Si and N due to organosilane grafting. Figure 1c reports the FTIR spectra of GO, HF and GO/HF. The peak located at about 3400 cm⁻¹ is related to OH groups of polysaccharides (Terpáková et al. 2012; Khanjanzadeh et al. 2018). The peaks at about 2910 cm^{-1} and 1736 cm⁻¹ concern CH stretching (Agarwal et al. 2010; Terpáková et al. 2012) and C=O stretching (Rachini et al. 2009) vibrations, while the peaks at 1454, 1373, 1314 and 1254 cm⁻¹ can be related to CH₂ bending, OH bending of carboxylic acids, C-O groups of polysaccharides and C-O stretching of acetyl groups (Sawpan et al. 2011; Kargarzadeh et al. 2015). The peaks in the range 1162-1030 cm⁻¹ concern C-O stretching and C-H rocking vibrations of the pyranose ring skeleton (Kargarzadeh et al. 2012). The OS modification provided new peaks: an N–H bending vibration at 1550 cm^{-1} (Robles et al. 2015; Khanjanzadeh et al. 2018); Si-O-Si and Si-O-C peaks at about 1135 and 1150 cm⁻¹, respectively; and Si–O–C and Si–O stretching vibrations and Si–H bond vibrations at 1040 cm⁻¹, 471 cm⁻¹ and 780 cm⁻¹, respectively (Allahbakhsh et al. 2017; Maleki and Karimi-Jashni 2020). In the GO spectrum, the peaks at 2927 and 2868 cm⁻¹ are associated with OH groups (Szabó et al. 2005; Jeong et al. 2009; Yan et al. 2017). The C=O carbonyl stretching at 1728 cm⁻¹ and the C–O epoxide group stretching at 1229, 1061 and 1036 cm⁻¹ are also observed in the FTIR spectrum of modified HF (Loryuenyong et al. 2013; Javed and Hussain 2015; Chong et al. 2018). Finally, the peak at 1625 cm⁻¹ is associated with the *sp*² character of C=C groups (Chong et al. 2018).

Kinetic studies

Adsorption capacities of GO/HF and HF

Before evaluating the effects of some experimental parameters on the adsorption capacity of modified HF, raw HF and GO-modified HF were tested to estimate their adsorption capacities. The initial MB concentration was set at 5 mg/l (T=20 °C and pH=7.5). Adsorption curves are reported in Fig. 2.

The amount of GO on the HF surface was evaluated through gravimetric analysis. The measurements provided a value of 62 ± 2 mg GO/g HF. According to the profiles reported in Fig. 2, GO modification increased the MB



Fig. 1 Top: SEM micrographs of a HF and b GO-functionalized HF. c FTIR spectra. Bottom: energy-dispersive X-ray spectroscopy (EDX) maps of GO-functionalized HF



Fig.2 q_t versus *t* for the adsorption of MB on raw hemp fibers and GO/HF



Fig.3 Adsorption capacity of GO/HF evaluated at pH=7.5 and $T\!=\!20~^\circ\mathrm{C},\,50~^\circ\mathrm{C}$ and $80~^\circ\mathrm{C}$

adsorption capacity of HF from 36.7 mg/g for raw HF to 53.86 mg/g for GO/HF: an increase of roughly 32%. The noticeable enhancement of the adsorption capacity after GO modification is attributed to the increase in specific surface area due to the intrinsically high surface area of GO. The specific surface areas are 45 and 82 m²/g for raw HF and GO/HF, respectively. These data support the increase in the adsorption capacity after the GO modification.

Effect of temperature

The adsorption kinetics were investigated to better understand the mechanism of adsorption. Figure 3 shows the kinetic curves for adsorbed MB versus contact time (pH=7.5) obtained at various temperatures (T=20 °C, 50 °C and 80 °C). The inset shows the adsorption profiles up to 20 min. The process can be studied by considering two steps:

- i) The fast adsorption of MB (t < 20 min) caused by the binding between the cationic dye and the vacant active adsorption sites. For short times, the concentration difference between the liquid and the solid phases is so high that MB adsorption is favored (Kavitha and Namasivayam 2007);
- ii) The slow diffusion of the dye molecules due to the fact that adsorption sites have been saturated, before a plateau regime is attained (Li et al. 2013).

As reported in Fig. 3, the adsorption capacity slightly increases upon increasing the temperature, proving the endothermic nature of the adsorption process. As the temperature rises, the rate of diffusion of the dye molecules across the external boundary layer and the internal pores of the adsorbent increases due to the decrease in viscosity (Sajab et al. 2011). Moreover, the increase in temperature affects different parameters such as the free volume, the mobility of the solute, the solubility, the chemical potential of dye molecules (Ho and McKay 1998; Kuang et al. 2020) and the surface activity (Oladipo and Ifebajo 2018). The adsorption data were modeled using the previously reported kinetic models. The fitting curves are depicted in Fig. 4.

The parameters of the kinetic models, as listed in Table 1, were easily evaluated by analyzing the plotted data.

Upon studying the data reported in Table 1, it appears that correlation coefficients were not significant for the pseudo-first-order model. A deviation from the straight line is observed, signifying that this model is not applicable. So, the sorption of methylene blue cannot be considered to be diffusion controlled. Concerning the intraparticle diffusion model, it appears that there could be a mathematical dependence of q_t on the square root of time. As seen in Fig. 4c, the plot of q_t against $t^{1/2}$ gives two straight lines with different slopes and intercepts. The initial linear part of the graph can be attributed to the boundary-layer diffusion of dye molecules, where the adsorption rate is high (Lorenc-Grabowska and Gryglewicz 2007), while the second step concerns the diffusion of dye from the external surface into the pores of the adsorbent followed by adsorption at the active sites of the internal surface. The slope of the linear part is k_{id} and is representative of the rate of the adsorption. Lower values mean a slower adsorption process. Based on the k_{id} values, the rate constants related to the diffusion into pores and adsorption were the highest, showing that the pore diffusion resistance is lower than the diffusion resistance of the boundary layer. Moreover, since the lines have nonzero intercepts (Fig. 4b), it can be claimed that the coexistence of an external film and intraparticle diffusion occurs during the adsorption process (Phuong and Loc 2022).



Fig. 4 Comparison of the **a** pseudo-first-order, **b** pseudo-second-order, **c** intra-particle diffusion and **d** Elovich kinetic models for GO/HF at different temperatures (pH=7.5)

Table 1 Parameters of the kinetic models for MB dye adsorption

	$T = 20 \ ^{\circ}\text{C}$	$T = 50 \ ^{\circ}\mathrm{C}$	$T = 80 \ ^{\circ}\mathrm{C}$
Pseudo-first-order model			
<i>k</i> ₁ (1/min)	0.0036	0.040	0.0033
$q_{\rm e} ({\rm mg/g})$	7.64	3.85	7.58
R^2	0.612	0.504	0.700
Pseudo-second-order model			
$q_{\rm e} ({\rm mg/g})$	54.05	55.86	59.03
$k_2 (\text{mg/g min})$	0.0041	0.0092	0.0043
R^2	0.999	0.999	0.999
Intraparticle diffusion step 1			
$k_{\rm id} ({\rm mg/g}{\rm min}^{0.5})$	8.73	10.09	10.65
C (mg/g)	0.48	1.56	2.17
R^2	0.992	0.945	0.907
Intraparticle diffusion step 2			
$k_{\rm id} ({\rm mg/g}{\rm min}^{0.5})$	0.086	0.048	0.092
C (mg/g)	51.25	54.35	55.84
R^2	0.45	0.29	0.64
Elovich model			
β (g/mg)	0.29	0.58	0.65
α (mg/g min)	7.5×10^4	4.1×10^{11}	7.3×10^{13}
<i>R</i> ²	0.609	0.543	0.761

Meanwhile, the intercept (*C*) concerns the boundary layer effect, and it is directly correlated to the mechanism of sorption at the surface in the rate-controlling step (Ahmad et al. 2015). Finally, the adsorption process can be considered to be perfectly modeled by the pseudo-second-order kinetic model ($R^2 > 0.99$), since the calculated adsorption capacities (q_e) were very similar to the experimental ones. Since the best fit was obtained by using pseudo-secondorder kinetics, the chemisorption phenomenon can be considered the main diffusion-rate-limiting step among the different interactions between the dye and adsorbent functional groups (Vimonses et al. 2009). The Elovich model was found to fit the experimental data in an unacceptable way considering the resulting low R^2 coefficients.

Mathematical expressions for the constants k_2 and q_e were therefore obtained by interpolating the data reported in the Table 1 as a function of temperature, allowing Eqs. 6 and 7 to be obtained:

$$k_2 = \frac{0.00235}{1 - 0.029 \times T(^{\circ}\text{C}) + 0.0003 \times T^2(^{\circ}\text{C})}$$
(6)

$$q_{\rm e} = 0.083T(^{\circ}{\rm C}) + 52.16. \tag{7}$$

Equation 7 indicates that the equilibrium amount of dye sorbed is linearly dependent on T and it is shown to increase as T increases, while a nonlinear dependency of

$$\frac{t}{q_t} = \frac{425.53 - 12.34 \times T(^{\circ}\text{C}) + 0.127 \times T^2(^{\circ}\text{C})}{(0.083 \times T(^{\circ}\text{C}) + 52.16)^2} + \frac{t}{0.083 \times T(^{\circ}\text{C}) + 52.16}.$$
(8)

The equation reported above allows q_t to be estimated for any contact time at each temperature.

Effect of pH

pH is a fundamental parameter that is known to affect adsorption processes by changing either the surface of the adsorbent or the adsorbate's properties. Figure 5 reports the adsorption capacities of the adsorbent for MB at pH = 3 and pH = 12 at different temperatures.

As *T* rises, the increased surface activity and kinetic energy of the adsorbate lead to an increase in the removal efficiency (Oladipo and Ifebajo 2018), as previously demonstrated. At low pH, H_3O^+ ions can compete with cationic MB ions, so a reduction in adsorption capacity was observed. Moreover, it is known that the competition between the MB cation and hydrogen ions to form electrostatic interactions with the functional groups of the adsorbent reduces as the pH increases (Shaiful Sajab et al. 2011). Since the point of zero charge (pH_{PZC}) is a key point when investigating the surface charge (Bingol et al. 2010), it was calculated through a titration procedure to deeply study the effect of pH on the adsorption data (Fig. 6).

The pH_{PZC} value is about 6.35. When $pH > pH_{PZC}$, an excess of negative charge is present on the surface adsorbent, which increases the adsorption capacity due to the presence of cationic MB in solution, favoring the formation



Fig.6 ΔpH versus pH plot for the evaluation of the point of zero charge

of electrostatic interactions between the oppositely charged groups: the cationic MB and the negative electron-rich sites on the adsorbent surface. When pH < pH_{PZC}, an excess of positive charge is present, so repulsive forces should limit the MB adsorption (Li et al. 2020); however, there is still a high adsorption capacity. Focusing on the equilibrium adsorption capacity, Fig. 7 reports the effects of *T* and pH on the adsorbed dye amount at equilibrium. Figure 7b shows a contour plot of q_e values which clearly shows the dependency of the equilibrium adsorption capacity on the pH and *T*.

Figure 7 clearly shows the effects of the two investigated parameters on adsorption performance. Temperature seems to have a slight effect on the adsorption capacity, but increasing it leads to higher q_e values, demonstrating the endothermic nature of the process. The effect of pH seems to be nonlinear. At low pH values, repulsive forces are responsible for decreasing the q_e value, as previously





Fig. 7 Effects of pH and T on the equilibrium adsorption capacity: a scatter data and b a 2D contour plot

Table 2 Empirical mathematical models of k_2 , q_e and t/q_t as functions of the pH at different temperatures	<i>T</i> =20 °C	$\begin{aligned} k_2 &= -0.004 + 0.00188 \times \text{pH} - 0.000105 \times \text{pH}^2 \\ q_e &= 12 + 10.55 \times \text{pH} - 0.65 \times \text{pH}^2 \\ \frac{t}{q_t} &= \frac{1}{\left(-0.004 + 0.00188 \times \text{pH} - 0.000105 \times \text{pH}^2\right) \times \left(12 + 10.55 \times \text{pH} - 0.65 \times \text{pH}^2\right)^2} \\ &+ \frac{t}{12 + 10.55 \times \text{pH} - 0.65 \times \text{pH}^2} \end{aligned}$
	<i>T</i> =50 °C	$k_{2} = -0.0032 + 0.00244 \times \text{pH} - 0.00022 \times \text{pH}^{2}$ $q_{e} = 32 + 6.13 \times \text{pH} - 0.39 \times \text{pH}^{2}$ $\frac{t}{q_{i}} = \frac{1}{(-0.0032 + 0.00244 \times \text{pH} - 0.00022 \times \text{pH}^{2}) \times (32 + 6.13 \times \text{pH} - 0.39 \times \text{pH}^{2})^{2}}$ $+ \frac{t}{100000000000000000000000000000000000$
	<i>T</i> =80 °C	$k_{2} = -0.006 + 0.0026 \times pH - 0.00016 \times pH^{2}$ $k_{2} = -0.006 + 0.0026 \times pH - 0.00016 \times pH^{2}$ $q_{e} = 26 + 8.45 \times pH - 0.54 \times pH^{2}$ $\frac{t}{q_{t}} = \frac{1}{(-0.006+0.0026 \times pH - 0.00016 \times pH^{2}) \times (26+8.45 \times pH - 0.54 \times pH^{2})^{2}}$ $+ \frac{t}{26+8.45 \times pH - 0.54 \times pH^{2}}$

discussed. However, at pH = 12, lower values of q_t were recorded respect to pH = 7 due to the potential demethylation of MB (Fa and Dk 2007).

As previously reported, fitting the adsorption data using the pseudo-second-order model allowed the values of k_2 and q_e to be calculated. Mathematical expressions were then used to modify the pseudo-second-order model by highlighting the effect of pH on the adsorption performance (Table 2).

These equations can then be used to derive the amount of MB adsorbed at any given initial pH, T and time.

Desorption studies and reusability

In order to fully study the adsorption performance and to evaluate the sustainability of the adsorption process, regeneration studies were carried out. Regeneration of the GO-modified HF adsorbent paves the way to affordable water remediation processes. The recovery (%) of the organic dye was evaluated as function of the number of adsorption tests (Fig. 8). It can be observed that there is a 15% drop in the adsorption performance after 30 regeneration cycles. The results show that the adsorbent could be continuously used for MB removal without noticeably affecting the adsorption performance.

Leaching

The GO can be released from the adsorbent through leaching, causing secondary pollution, which could be hard to control (Malhotra et al. 2020). Figure 9 reports the GO leaching (μ g/L) as a function of adsorption time (h).

It appears that after 240 h, only 0.15 μ g/L of GO was leached, making it possible to still guarantee high adsorption capacity despite the leached GO. So, the GO/HF can





be used, recovered, and reused without any noticeable loss of performance. This finding could be associated with the covalent binding of GO to the OS-modified HF.



Fig. 9 GO leaching as a function of time (h)

Adsorption mechanism

The adsorption mechanism can provide more insight into the phenomena involved in the adsorption process. Considering the collected data, this paper proposes a potential adsorption mechanism based on (i) electrostatic interactions, (ii) hydrogen bonding, (iii) π - π interactions and (iv) van der Waals forces (Fig. 10).

The dye adsorption could occur due to the electrostatic forces between the cationic MB ions and negatively charged OH and COO⁻ groups on the basal planes and edges of GO sheets. Also, π - π coupling could exist between the C=C of MB and delocalized π electrons in the benzene rings. It follows that the presence of GO contributes to increasing the density of epoxide, hydroxyl and carboxyl groups, leading to the generation of strong electrostatic interactions and π - π electron coupling. The sorption of methylene blue could occur due to the ability of the MB to form micelles (monomeric or dimeric) in aqueous solution. So, the following possible mechanism could be considered (Ofomaja 2008):



Fig. 10 a Adsorption mechanism of MB on GO/HF and b molecular modeling of the GO–MB interaction

Table 3Comparison of the
adsorption capacities (q_i) of
natural adsorbents for MB
removal

Adsorbent	q_t , mg/g	Reference	
Magnetite geopolymer composite	76.34	Al-husseiny and Ebrahim (2022)	
Konjac glucomannan-based magnetic carbon aerogels	9.37	Ye et al. (2016)	
Fallen leaf biochar	101.27	Ji et al. (2019)	
Luffa cylindrica fibers	49	Demir et al. (2008)	
Biochar from seaweed	512.67	Ahmed et al. (2019)	
Raspberry leaves	244.6	Mosoarca et al. (2022)	
Fruit-peel-derived activated carbon	142.86	Gupta et al. (2022)	
Turmeric/PVA/CMC	6.27	Radoor et al. (2022)	
Moroccan clay	456.62	Loutfi et al. (2023)	
Silica-coated soy waste	90	Batool and Valiyaveettil (2021)	
Pseudo-stem banana fibers	42.28	Rahman et al. (2022)	
Fly-ash-based spheres	79.7	Novais et al. (2019)	
Papaya bark fibers	66.67	Nipa et al. (2023)	
Cellulose-chitosan beads	55	Al-Ghamdi (2022)	
Typha latifolia	54.73	El Amri et al. (2022)	
Activated carbon/zeolite	51	Mohamed et al. (2022)	
Chitosan lignin membrane	241.62	Vedula and Yadav (2022)	

$$\begin{split} \mathsf{MB}^+ + \mathsf{GO} - \mathsf{HF}^- &\leftrightarrow \mathsf{MB}(\mathsf{GO} - \mathsf{HF}) \\ \mathsf{MB}_2^{2+} + 2\mathsf{GO} - \mathsf{HF}^- &\leftrightarrow \mathsf{MB}_2(\mathsf{GO} - \mathsf{HF})_2 + \ 2 \ \mathsf{H}^+ \end{split}$$

The interaction of MB with GO was proven through computational analysis. The geometrically optimized structures of GO and MB as well as the amorphous cell containing the studied compounds are reported in Fig. 10b. The analysis proved that the total energy of the system is 546.88 kcal/mol, the van der Waals energy is 38.13 kcal/mol, while the electrostatic energy is – 371.77 kcal/mol.

Comparison with other natural adsorbents

Table 3 reports the adsorption capacities of some natural adsorbents. The adsorption capacity of the designed GO/HF adsorbent was comparable to those of other bioadsorbents (Santoso et al. 2020), suggesting that it is a promising green adsorbent for wastewater remediation.

Concluding remarks

The production of environmentally friendly sorbents is considered one of the most promising techniques in water remediation. This manuscript focused on the use of hemp fibers, the least valuable part of the *Cannabis sativa* plant, as a support for producing a green adsorbent based on carbon-modified HF. A novel adsorbent for methylene blue removal from wastewaters was fabricated and characterized. The adsorbent was tested in batch conditions. The effects of the pH regime and temperature were correlated to the adsorption performance. The adsorption process appeared to be dependent on the pH and slightly affected by the temperature. The pH level greatly affects the adsorption process since electrostatic interactions can be generated between cationic MB molecules and electron-rich groups on the surface. The adsorption capacity at T = 20 °C changed from 37 to 54 mg/g upon increasing the pH from 3 to 7.5, while it decreased to 44.5 mg/g upon further increasing the pH to 12, due to the demethylation of MB. Also, when $T = 80 \,^{\circ}\text{C}$, q_t is 45.1, 57.8 and 48.9 mg/g at pH = 3, 7.5 and 12, respectively, proving the endothermic behavior of the process. Moreover, MB adsorption follows the pseudo-second-order model, proving that the adsorption process involves chemisorption: there is a surface complexation reaction between the MB and the negative charges present on the modified HF. The produced adsorbent is chemically stable, showing no noticeable leaching of GO over time. Reusability studies showed that q_t reduced by about 15% after 30 cycles. The presented data proved that hemp fibers modified with GO could potentially be used as novel and cheaper adsorbent materials in wastewater treatment processes. A low amount of the designed adsorbent is able to completely decolorize an aqueous solution of methylene blue within a short time. This research paves the way for the application of a novel bioadsorbent based on the use of an agro-waste resource. A further experimental campaign will aim to investigate the mineralization and the degradation of the adsorbent as the process conditions change. Also, a study of the economic aspects of the adsorbent is mandatory to facilitate the successful use of the material in water depollution and reuse processes.

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Data availability The data that used in this study is available on reasonable request.

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