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Assessment of micro and nanosize C-based adsorbents for methylene blue uptake: A review

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HIGHLIGHTS

- Recently, MWCNTs and GO and related composites have received high attention as dye adsorbents.
- The overall performance of AC, MWCNTs, and GO toward methylene blue uptake is critically assessed.
- Binding capacity, uptake rate, and equilibrium time are the criteria for assessment purposes.
- Diethylenetriamine-GO composite is the winner: uptake capacity of 3036 mg g^{-1}, uptake rate of 3025 mg g^{-1} min^{-1}, and 5.0 min contact time.

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ABSTRACT

Carbon-based adsorbents, including activated carbon, multiwalled carbon nanotubes, and graphene oxide, have received great attention for removing pollutants, including dyes, from solution. In this review, the overall performance of high-grade C-based adsorbents for removing methylene blue was evaluated for the first time through three criteria: maximum uptake capacity, reaction rate, and equilibrium time of the process. For this, data on adsorption of methylene blue by thirty C-based adsorbents was collected from the literature and analyzed in the framework of the aforementioned criteria. The statistical analysis showed that the equilibrium time of methylene blue uptake on graphene oxide composites is much faster compared to other adsorbents (such as activated carbon and multiwalled carbon nanotubes). Among MWCNTs, Fe_3O_4-Alginate-MWCNTs is the most practical to remove methylene with an uptake capacity of 906 mg g^{-1}, equilibrium time of 60 minutes, and simple isolation from solution using an external magnet. Graphene oxide composites outperform other adsorbents, with an average adsorption capacity of 896 mg g^{-1}, a mean reaction rate of 870 mg g^{-1} min^{-1}, and a median equilibrium time of 50 minutes. Among these, diethylenetriamine-modified graphene oxide was found the best adsorbent with an uptake capacity of 3036 mg g^{-1}, a reaction rate of 3025 mg g^{-1} min^{-1}, and an equilibrium time of only five minutes. The outputs of the current work will be helpful when choosing the most practical adsorbent for dyes. Unfortunately, the performance of these adsorbents under continuous flow conditions has not been examined to date, which cannot permit a comprehensive practical assessment. The adopted selection strategy is applicable for other classes of adsorbents toward pollutants, especially non-conventional materials. The estimated cost index of C-adsorbent for removing 1.0 g MB was 0.003, 38.3, and 42.3 $ for AC, MWCNTs and GO, respectively. The high production costs of MWCNTs and GO-composites may reduce their utilization on a large scale.

1. Introduction

1.1. Limitations of current research

In the last few years, many review articles have been published dealing with different types of adsorbents for dye removal [1–7], in general addressing the importance of non-conventional adsorbents and nano-adsorbents as promising materials for removing methylene blue and other dyes from wastewater. In general, these reviews only consider one type of adsorbent, such as activated carbon or natural silicates, and

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for example the performance of micro- and nano-size C-based adsorbents has not been reviewed to date. Besides, the evaluation of adsorbent performance is often based only on the adsorption capacity, not including other parameters like reaction rate and equilibrium time. Thus, the adsorbent should manifest a high adsorption capacity, high adsorption rate, and a short equilibrium time. In order to contribute to overcome these current limitations, in this review we have assessed the removal efficiency of methylene blue by thirty C-based adsorbents, including activated carbons, multiwalled carbon nanotubes, and graphene oxide, in terms of uptake capacity, reaction rate, and equilibrium time. We believe that the proposed strategy is important for targeting the most effective adsorbents, specially taking into account the current context of growing number of adsorbents proposed for dye removal in the scientific literature.

1.2. Industrial and medical profile of methylene blue and treatment options

Methylene blue or Basic Blue 9, 3,7-bis(dimethylamino) phenothiazine chloride tetramethylthionine chloride, is an aromatic compound with a chemical formula $C_{16}H_{18}N_3S$ (Fig. 1). Methylene blue is a cationic and thiazine type of dye with many applications in textile industry as a fiber coloring agent [8], mostly used in the textile and apparel sectors to color different types of fabric including wool, silk, cotton, leather [9,10] and paper [10]. Moreover, it has many applications in the field of medicine as staining agent, and for therapeutic and prophylactic purposes [11]. Food, cosmetic, and pharmaceutical industries consume a significant amount of methylene blue in their manufacturing processes [12]. It is also used as an indirect food additive in the food sector and in aquaculture to cure a variety of illnesses in fish [10], and as a sensitizer in the photo-oxidation of organic molecules used in microbiology, medicine, and diagnostics [13].

Considering the aforementioned applications, methylene blue is unquestionably a useful dye. But because of its high toxicity [14] and persistent character [15], it has been shown to be hazardous to human health and the environment at certain concentrations [16]. Although it represents only a small amount of the discharged textile wastewater, its removal is an important issue for the textile industry due to its high tinctorial value, making water highly visible even at low amounts (1.0 mg L^{-1}). Due to limited light penetration, the dye has a substantial impact on the photosynthetic activity of aquatic life [10]. Therefore, removal of methylene blue from wastewater is environmentally important to avoid the toxic effects it poses to human health and the environment.

It is known that methylene blue is often tested as a model pollutant to assess the performance of any new adsorbent. Adsorption, coagulation, oxidation, ozonation, membrane filtration, ion exchange, and irradiation are among the treatment options taken into consideration for methylene blue removal from wastewater [10,17,18]. Each procedure has advantages and disadvantages, which are extensively covered in the literature, with adsorption being suggested as the most secure solution [19,20]. Recently, there has been an increase in the use of biological materials, mineral oxides, activated carbons, and polymer resins as sorbents for the removal of methylene blue [4,21]. Nano-size C materials like multiwalled carbon nanotubes and graphene oxides composites are able of removing pollutants at trace levels [22] and have unusual affinity for methylene blue in terms of uptake capacity, rate of uptake and equilibrium time, as will be discussed in this review.

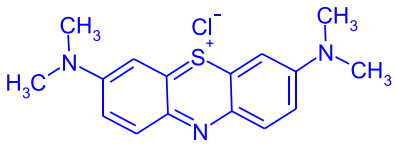

Fig. 1. Structural formula of cationic Methylene Blue (Basic Blue 9).

1.3. Classification of C-based adsorbents

Currently, several classifications exist for adsorbents, and because of their increasing number, it is important to have a widely accepted classification scheme for them. The one proposed by Crini [23] classifies adsorbents in two categories: (a) commercial activated carbon; (b) nonconventional adsorbents like waste materials from agriculture and industry, natural materials, biosorbents, and miscellaneous adsorbents. The author listed many materials from different classes and pointed out that biosorbents are effective to remove dyes from water, but nano-adsorbents and related composites were not included. A more comprehensive classification was proposed by Raval et al. [1] and Singh et al. [24], who clustered adsorbents into: (a) activated carbon adsorbents; (b) nonconventional adsorbents; (c) nanomaterial adsorbents; (d) composites and nanocomposites adsorbents; and (e) miscellaneous adsorbents. More recently, Dutta et al. [4] have proposed a general classification for all adsorbents into: (a) activated carbon; (b) nonconventional; (c) hybrid nanomaterials; (d) metal oxide hybrid materials; (e) metal-organic frameworks; and (f) polymers and polymer composites. Activated carbon is common to all previous classifications, as it was the first and most prevalent adsorbent used in water treatment.

Despite the comprehensiveness of the previous classification schemes, their application is challenging when conducting a comparative study among adsorbents toward a specific pollutant, due to the high variation in the physicochemical properties of the adsorbents and their increasing number, especially nanoadsorbents. In this sense, Sadegh et al. [22] have proposed a specific classification for C-based adsorbents, the number and types of which are increasing, including activated carbon, single-walled carbon nanotubes, multiwalled carbon nanotubes, fullerenes, carbon rods, carbon wires, and carbon dots adsorbents. The classification employed in this work (Fig. 2) is an extension of the classification proposed by Sadegh et al. [22] for activated carbon and C-based nano-adsorbents. As this work was limited to C-based adsorbents, activated carbon was added to the classification scheme. In the future, this classification can be extended to include new C-based adsorbents.

Prior to going into detail about the preparation and applications of various C-based adsorbents, it is crucial to review the most prevalent allotropic forms of the C atom. On an atomic scale, the majority of carbons exhibit the allotropic form of graphite i.e. a sp^2-based structure, while diamond has a sp^3-based structure [25]. On the other hand, C atom in fullerenes and other derivatives has mix hybridization between sp^2 and sp^3 often presented as $sp^{2+\varepsilon}$ [25]. However, depending on the degree of crystallographic order in the third direction (*c*-direction), carbons based on the allotropic form of graphite can be classified into graphitic carbons (which have a measurable crystallographic order in *c*-direction) and non-graphitic carbons (no measurable crystallographic order in *c*-direction) [25,26]. Non-graphitic carbons are further divided into graphitizable and non-graphitizable carbons. Thus, a graphitizable carbon is “a non-graphitic carbon which upon graphitization is converted into graphitic carbon”, while a non-graphitizable carbon is “a non-graphitic carbon which cannot be transformed into graphitic carbon even at high temperature and a lower pressure” [26].

1.3.1. Activated carbons

Moving up from nano to microscale, carbons exhibit very different structures. Some of these microstructures are arranged in preferential directions, like synthetic graphite or graphitized carbon fibers, while disordered microstructures are characteristic of chars or activated carbons. Such a wide variety of possible structures gives rise to a large amount of different types of carbons. These are non-graphitic, non-graphitizable carbons with a highly disordered microstructure and can be found as powder (particle size <100 μm) or granular (including extruded and pelletized) activated carbons (Sadegh et al., 2017). Activated carbon material, as it is known nowadays, was discovered by Raphael von Ostrejko. In 1901, he patented two different methods of

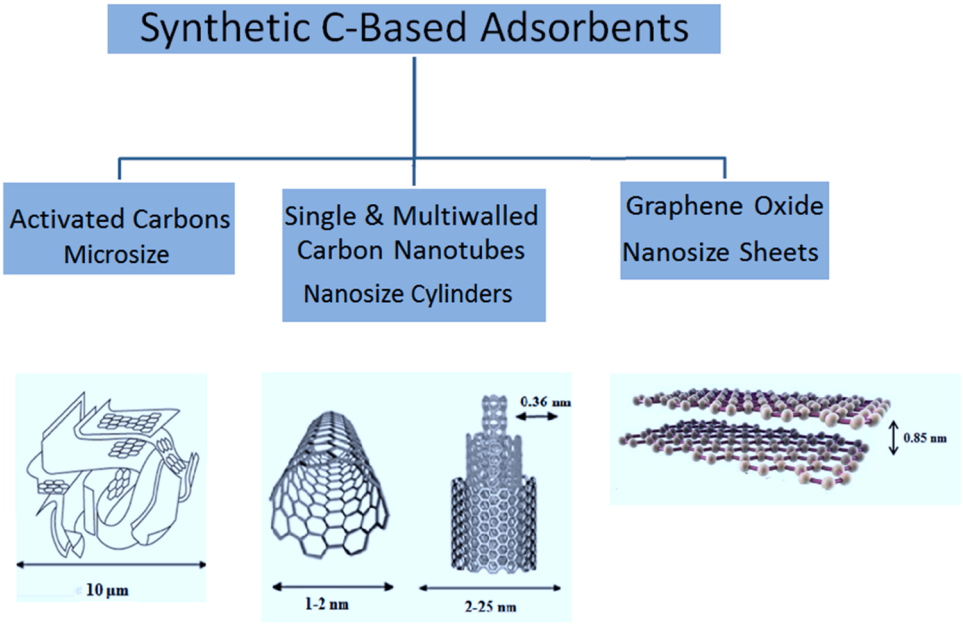

Fig. 2. Classification of synthetic C-based adsorbents used for MB uptake (modified from Sadegh et al. [22]).

producing activated carbons: (a) chemical activation: the carbonization of lignocellulosic materials with metal chlorides; and (b) physical activation: the gasification of chars with steam or carbon dioxide at high temperatures [25]. Other forms of carbon are also used as adsorbents, such as activated carbon fibers, fabrics, and felts. Chemical activation, also known as wet oxidation, for the preparation of activated carbon has received high attention from researchers and it is often applied for organic materials containing cellulose, such as sawdust, wood, and fruit pits [27]. In this process, organic precursors are activated in the presence of chemical agents and at high temperatures. First the raw material is saturated with a strong oxidizing agent and in the presence of highly dehydrated reagents. After impregnation, the mixture is then dried, and the remaining suspension mixture is gradually heated for a pre-selected time. Depending on the activating agent and the quality of the final product, the activation process can be performed over the range 400–900 °C where cellulose is degraded. Finally, activated carbon is obtained from the repetitive washing of the mixture. Chemical activation reagents are dehydrating agents that improve pyrolytic decomposition by inhibiting the formation of bitumen and increasing the content of porous activated carbon [27].

Activated carbon has excellent affinity for most pollutants due to its high porosity, high surface area and presence of many functional groups [17,28,29]. Activated carbons derived from chestnut shell, mango peel, syagrus oleracea, betel nut husk, and bamboo have been found efficient for methylene blue uptake with retention capacities over the range 714–1191 mg g^{-1} [30–32]. Generally, activated carbon can be used to remove dyes without embedding substrates to its surface as is the case with other nano C-adsorbents.

1.3.2. *Multiwalled carbon nanotubes and related composites*

Multiwalled carbon nanotubes (MWCNTs) can be prepared by three different methods at high temperature [33]: (a) catalytic chemical vapor deposition of hydrocarbon at 650 °C, which is the most common method; (b) arc discharge method, where a temperature higher than 3000 ºC is applied to evaporate carbon atoms into a plasma to finally form carbon nanotubes; and (c) laser ablation method, which involves the vaporization of graphite in an electrical furnace heated at 1200 ºC to generate carbon nanotubes.

Among the preparation methods, chemical vapor deposition (CVD) is the most often used to prepare single and multiwalled carbon nanotubes [34]. In CVD, a thin film is created on the substrate surface through the chemical reaction of vapor-phase precursors. A precursor should be of high chemical purity, adequate volatility, and high stability through evaporation. Moreover, its decomposition should not result in remaining impurities. For the production of carbon nanotubes by CVD, a substrate is located in an oven, heated to a high temperature and a carbon-containing gas is slowly introduced as a precursor. At high temperatures, the decomposition of the gas releases carbon atoms, which recombine to form carbon nanotubes on the substrate. In general, CVD technology is excellent for manufacturing high-quality multiwalled carbon nanotubes [34].

Multiwalled carbon nanotubes have a high surface area and can be embedded with many substrates, including sodium alginate [28,35], Fe_3O_4 [36], polyamine [19], or maghemite/alginate [37]. These nano-adsorbents are efficient for methylene blue adsorption, with uptake capacities 172–1596 mg g^{-1}. The previous literature survey indicated that multiwalled nanotubes are more efficient than single-walled carbon nanotubes, so the latter were excluded from this review.

1.3.3. *Graphene oxide and related composites*

Hummer`s and modified Hummer`s methods are the most adopted for producing large quantities of graphene oxide from graphite [38]. Initially, graphite is oxidized using $KMnO_4/H_2O_2$ to produce graphene nanosheets that can be fully delaminated into graphene oxide using liquid exfoliation techniques [39,40]. A brief summary of improved Hummer`s method is provided herein [41]. A 9:1 mixture of concentrated H_2SO_4/H_3PO_4 is added to a mixture of graphite powder and $KMnO_4$. The reaction is heated to 50 °C and stirred for few hours. After the oxidation step, the resulting mixture is added to a beaker containing H_2O_2 to quench the reaction. The mixture is filtered under vacuum. The resulting compact cake is washed with deionized water, HCl, and ethanol to clean the oxidized graphite. The obtained compact cake is slurred with dry diethyl ether, filtered, and dried at 100 °C. The produced graphite oxide is dispersed in deionized water and sonicated in an ultrasonication bath to obtain nano-sheets of graphene oxide in the solution. To reduce the high dispersion of graphene oxide in solution and improve dye uptake, different substrates are embedded in the graphene oxide matrix, including polysaccharides [42], Fe_3O_4 [43], glucose-ethylenediamine-rGO [44], and diethylenetriamine [45]. The examined graphene oxide composites are efficient toward methylene

blue with an uptake capacity over range 197–3036 mg g^{-1}.

A comparative summary of the main properties of activated carbon, multiwalled carbon nanotubes, and graphene oxide and their application as dye adsorbents are presented in Table 1.

2. Methodology

2.1. Literature survey and search approach

High-indexed research articles that listed in international databases like PubMed®, Web of Science®, and Scopus® were collected and analyzed in this review. The search was limited to literature published from 2013 to 2024, and the used keywords were “Methylene Blue," "Adsorbents," and "Adsorption." The suitability assessment of the research article was as follows: (a) articles addressing adsorbents other than activated carbon, multiwalled carbon nanotubes, and graphene oxide were excluded; (b) the maximum uptake capacity or Q_{max} under optimum conditions should be $>$ 150 mg g^{-1}; (c) the effect of mass, pH, contact time, temperature, and ionic strength on methylene blue uptake should be systematically examined; (d) kinetic and adsorption isotherm studies of the dye should be provided; (e) maximum adsorption capacity and reaction rate of methylene blue should be estimated from Langmuir isotherm and pseud-second order model, respectively; and (f) the main physicochemical parameters, including particle diameter, specific surface area, pore volume, pore diameter, and pH_{ZPC} were also collected. The details on the collected research studies along with adsorption parameters of methylene blue are provided in Tables 2 and 3.

As shown in Table 2, 30 research articles were selected within the above-mentioned requirements, with 10 adsorbents for each adsorbent sub-class with $Q_{max} > 150$ mg g^{-1}, as (Fig. 3). It is worth mentioning that fullerene and single-walled carbon nanotubes were excluded from the study as they receive limited attention compared to other adsorbents.

Table 1
Structural details and properties of activated carbon, multiwalled carbon nanotubes and graphene oxide as dye adsorbents [a].

C-adsorbent	C allotrope	Preparation method	Structure	Dye adsorbent	Separation from solution	Recycling	Commercial cost
Activated carbon AC	sp^2	Generally, AC is prepared by impregnating organic source like wood, coal, nutshell, and bamboo with HNO_3 or H_3PO_4 and heating the product under N_2 gas up to 800–1000 °C.	• Particle size 0.5–10 μm • Intense porous structure with surface area $>$ 1000 m^2/g • Surface functional groups COOH, OH and NH_2	• High capacity for cationic dyes. • Not effective for anionic dyes. • Not efficient for removing trace dye level. • Modifiable surface for improving its retention for dyes. • With a high mechanical strength, activated carbon is used as fixed bed adsorber	The large particles of activated carbon are easily separated from solution by simple filtration.	Poor recycling due to its high porosity.	Moderate cost 2.0$/kg
Multiwalled carbon nanotubes MWCNTs	$sp^{2+\varepsilon}$ (mix between sp^2 and sp^3)	Generally, MWCNTs prepared using chemical vapor deposition technology. In this process, thermal decomposition of a hydrocarbon vapour at 650 °C is achieved in the presence of a metal catalyst to prepare C-nanotubes	• Nano-tubes of diameter up to 25 nm and 10 μm length. • Moderate surface area compared to AC (700 m^2) • Should be oxidized by strong acid to generate acidic functional groups.	• Moderate capacity for cationic dyes. • Not effective for anionic dyes. -Efficient for removing dye even at trace level • Modifiable surface for improving its retention for dyes. • MWCNTs often applied as a nano-membrane for water treatment systems.	• Due to its nano-size, a high speed centrifugation often needed for its separation from solution. • Fe_3O_4- MWCNTs composite is easily separated using external magnet.	• Due to its high cost, MWCNTs should be recyclable • Recycling of MWCNTs and related composites is still a questionable issue.	High cost 100–300$/kg
Graphene oxide GO	$sp^{2+\varepsilon}$ (mix between sp^2 and sp^3)	Generally, GO is prepared from graphite by Hummer`s method. Graphite is extremely oxidized using $KMnO_4/H_2O_2$ to finally produce GO.	• Nano-sheets of 500 nm^2 size. • Moderate surface area compared to AC (900 m^2) • High dispersion in the solution with a swelling capacity 1000 gg−1.	• High capacity for cationic dyes. • Not effective for anionic dyes. V Efficient for removing dye even at trace level. • Modifiable surface for improving its retention for dyes. • GO often applied as a nano-membrane for water treatment systems.	• Due to its dispersion, a high speed centrifugation often needed for isolation from solution. • Fe_3O_4- GO composite is easily separated using external magnet.	• Due to its high production cost, GO should be recyclable • Recycling of GO and related composites is still a questionable issue.	High cost 200–500$/kg

[a] The collected information is available in the literature [25,34].

Table 2
Adsorption parameters of MB on different C-based adsorbents.

Class	Adsorbent	Optimum conditions				ΔH° (kJ/mol)	Adsorption rate h (mg g^{-1} min^{-1})[c]	Maximum adsorption Q_{max} (mg g^{-1})[d]	Reference
		S/L[a]	pH	T (°C)	Equilibrium time (min)[b]				
Activated Carbon	Shaddock Peel-AC	0.5		30	200	18.2	574	860	[32]
	Chestnut Shell-AC		12.0	25	600	139.9	260	1191	[31]
	Mango Peel-AC	0.9	8.7	25	180		26	233	[18]
	Syagrus oleracea-AC	2.0		25	120		3.6	680	[54]
	Commercial-AC			22	100	−2.4	435	400	[58]
	Dipterocarpus alatus-AC	0.2	6.5		240	10.3	1.0	269	[29]
	Betel nut husk-AC	1.0	10.0	30	300		2.0	381	[17]
	Edible fungus-AC	0.4	10.0	20	90		405	714	[30]
	Bamboo-AC	1.0	7.0	30	600		391	454	[59]
	Sewage sludge-AC	2.0	11.0		120		125	125	[47]
Multiwalled C-Nanotubes	MWCNTs			22	300	9.6	48	172	[58]
	Sodium alginate-MWCNTs	0.3	9.0	25	50		2035	1596	[35]
	Carrageenan-Fe_3O_4- MWCNTs	0.4		25	180	36.9	2.0	395	[60]
	Fe_3O_4-Alginate-MWCNTs	1.0	10.0	20	60		1642	906	[36]
	Alkali-Activated-MWCNTs	0.8	7.0	25	120	11.4	144	400	[61]
	Fe_3O_4-hydroxyapatite- MWCNTs	0.3	10.0	25	120	−20.0	938	211	[57]
	Fe_3O_4-MWCNTs	0.8	10.0	22	300	−9.0	98	204	[20]
	Polyamine-MWCNTs	0.8	10.0	25	30		844	800	[19]
	Calcium-alginate- MWCNTs	0.5		22	600		57	1189	[53]
	Maghemite/alginate –MWCNTs		10.0	25	20		17	905	[37]
Graphene Oxide	Fe_3O_4-Polypyrrole-GO	0.25	8.0	25	20	11.0	207	332	[48]
	Ni-rGO	0.02	10.0		60		12	946	[40]
	MgO-GO	1.0	11.0		20	−12.9	35	833	[39]
	Polysaccharides-GO	0.5	10.0	25	30		2624	769	[42]
	Sodium dodecyl sulfate-GO	0.05	9.0	25	50		30	833	[46]
	Methacryloyloxyethyl -Fe_3O_4-GO	1.5	11.0		50	28.6	1140	205	[43]
	Vinylimidazole-acrylic acid-Fe_3O_4-GO	1.0	12.0	40	80		65	625	[38]
	L-Lysine-GO	1.0		25	100		365	1634	[52]
	Glucose -Ethylenediamine-rGO	0.25		30	100	38.5	26	197	[44]
	MOF-UiO−66-carboxylated-GO	0.5	10.0	25	60	−150	2040	449	[49]
	Diethylenetriamine-GO	0.23	11.0	25	5		3025	3036	[45]

[a] solid to liquid ratio g/L.
[b] Equilibrium time obtained from the kinetic curve.
[c] Initial adsorption rate h estimated from pseudo-second order rate constant k_2 as: $h = k_2 q_e^2$. q_e is the equilibrium capacity estimated form the kinetic test [50].
[d] In all cases, Q_{max} was estimated from Langmuir isotherm.

2.2. Experimental factors

Many experimental factors can affect methylene blue adsorption from solution, including dosage of adsorbent, solution pH, contact time, ionic strength, particle size, and temperature, with adsorbent dosage, pH, and contact time as the most commonly examined factors (Table 2).

For different C-adsorbents, comparable doses are used for dye uptake: 0.2–2.0, 0.3–1.0, and 0.02–1.5 g L^{-1} for activated carbons, MWCNTs, and graphene oxide (GO), respectively. Due to the high capacity of GO-composites, some tests are operated at unusually low doses: 0.02 g L^{-1} [40] and 0.05 g L^{-1} [46]. The nanostructure of GO-composite, in addition to the high dispersion in solution, can explain the high uptake capacity even at low doses. Regarding solution pH, most tests are carried out at alkaline conditions (pH 8.0–12.0), what evidences that electrostatic attraction between the cationic dye and the negatively charged C-adsorbents controls the process [36,43,47]. Most adsorption tests are carried out over the temperature range of 20.0–30.0 °C, and studies on thermodynamics have shown that methylene blue uptake is endothermic with ΔH° range from + 9.0 to + 140.0 kJ/mol, i.e., physisorption process. Few cases reported exothermic uptake process: on Fe_3O_4-MWCNTs [20] and on diethylenetriamine-GO [45].

Unfortunately, recycling of adsorbents was only seldom investigated, which may limit a comprehensive practical evaluation of the adsorbents [30,36,42,48].

2.3. Adsorption models

In most of the reviewed articles, the commonly reported isotherms for dye uptake from solution belong to types L1, L2 and H2 [17,35,43]. In these cases, dye adsorption proceeds with low competition with solvent molecules until surface saturation. In most of the examined studies, methylene blue equilibrium adsorption curves were adequately presented by the Langmuir model, so the maximum adsorption capacity Q_{max} can be determined, allowing for comparison of the performance of different adsorbents. Langmuir model is defined as:

$$q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \quad (1)$$

where Q_{max} (mg g^{-1}) and K_L (L mg^{-1}) are the maximum adsorption capacity and the energy constant, respectively. The model assumes equal-energy active sites, no interaction with adsorbed solutes, and formation of one mono-layer. In few cases, Q_{max} was also estimated using Dubinin-Radushkevish model [19,20,30,36].

In addition to equilibrium uptake capacity, adsorption rate of methylene blue is also often investigated. The rate and mechanism of adsorption, as well as the potential rate-controlling processes, such as chemical reactions, diffusion, and mass transport processes, are investigated using kinetic tests [39,49]. In all works, study of the effect of contact time on dye uptake shows that methylene blue uptake rate is high initially and gradually decreases with time until reaching equilibrium [38,43]. The faster adsorption process in the initial stages is due to the presence of a large number of active sites in most adsorbents; later the dye uptake rate decreases and the process become less efficient due

Table 3
The main physicochemical parameters of the examined C-based adsorbents.

Class	Adsorbent	SSA[a], m^2/g	TPV[b], cm^3/g	MPD[c], nm	pH_{ZPC}[d]	Reference
Activated Carbon	Shaddock Peel-AC	2398	1.82	3.0		[32]
	Chestnut Shell-AC	1705	1.73	4.1		[31]
	Mango Peel-AC	1151	0.61	3.1	6.4	[18]
	Syagrus oleracea-AC	120				[54]
	Commercial-AC	835	0.54	1.4	5.4	[58]
	Dipterocarpus alatus-AC	517	0.3	2.3	6.5	[29]
	Betel nut husk-AC	82	0.7	3.5	7.9	[17]
	Edible fungus-AC	1070	0.7	2.5	6.9	[30]
	Bamboo-AC	1896	1.1	2.3		[59]
	Sewage sludge-AC	1412	0.7	9.9		[47]
Multiwalled C-Nanotubes	MWCNTs	358	0.6	3.4	4.2	[58]
	Sodium alginate-MWCNTs				2.2	[35]
	Carrageenan-Fe_3O_4- MWCNTs	142	0.9			[60]
	Fe_3O_4-Alginate-MWCNTs				8.2	[36]
	Alkali-Activated-MWCNTs	729	1.7	7.9	2.0	[61]
	Fe_3O_4-hydroxyapatite- MWCNTs	120				[57]
	Fe_3O_4-MWCNTs	646	2.8	17.1		[20]
	Polyamine-MWCNTs	30			3.8	[19]
	Calcium-alginate- MWCNTs	87				[53]
	Maghemite/alginate –MWCNTs				8.2	[37]
Graphene Oxide	Fe_3O_4-Polypyrrole-GO					[48]
	Ni-rGO				4.1	[40]
	MgO-GO				10.1	[39]
	Polysaccharides-GO					[42]
	Sodium dodecyl sulfate-GO					[46]
	Methacryloyloxyethyl -Fe_3O_4-GO				7.5	[43]
	Vinylimidazole-acrylic acid-Fe_3O_4-GO	14.0				[38]
	L-Lysine-GO					[52]
	Glucose-Ethylenediamine-rGO					[44]
	MOF-UiO−66-carboxylated-GO	917	0.12	1.2		[49]
	Diethylenetriamine-GO				8.2	[45]

[a] Specific surface area estimated using N_2-adsorption method.
[b] Total pore volume estimated using N_2-adsorption method.
[c] Mean pore diameter estimated using N_2-adsortpion method.
[d] Point of zero charge estimated using pH drift method.

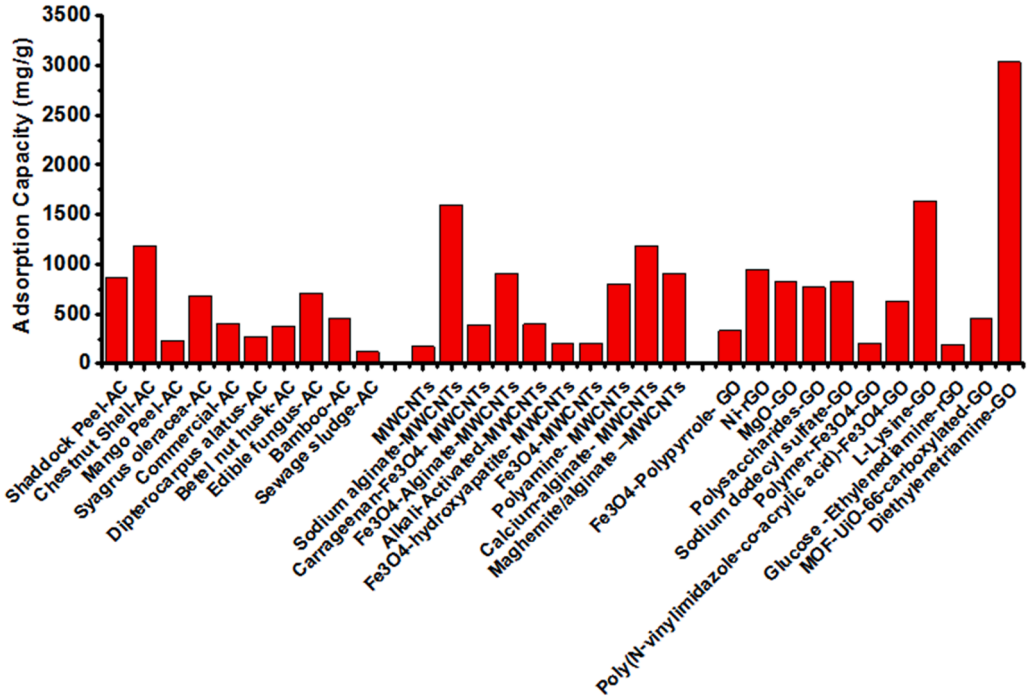

Fig. 3. Adsorption capacity of MB on different C-based adsorbents (Data collected from Table 2).

to more of these sites being occupied [49]. The optimum equilibrium times of methylene blue uptake by different C-based adsorbents estimated from kinetic profile are summarized in Table 2. In all examined studies, adsorption rate of the dye was adequately presented by pseudo-second order model, which would support that methylene blue removal is a fast process and proceed until surface saturation [50]. The

parameters of the kinetic models can be helpful for comparison of adsorption rates among adsorbents. Pseudo-second order model is defined as follows [50]:

$$q_t = \frac{tk_2q_e^{\,2}}{1 + tk_2q_e} \tag{2}$$

where q_t and q_e are the amounts of dye removed at time t and equilibrium time, respectively while k_2 (g mg^{-1}min^{-1}) is the second order rate constant. Higher values of k_2 reflect faster adsorption rate. Moreover, the initial adsorption rate h is estimated as:

$$h = k_2q_e^{\,2} \tag{3}$$

The success of this model for presenting the kinetics of dye uptake makes it possible to compare adsorption rates on different C-based adsorbents.

2.4. Statistical analysis of adsorption parameters

Initially, to identify the variations between the adsorption parameters (Q_{max}, adsorption rate h, and equilibrium time) of methylene blue uptake by different adsorbents, the results were explored using box-whisker plots. These plots allow the visual inspection of entire data, dispersion in the results, and detection of outliers. The collected data are presented in Fig. 4, where the minimum, first quartile, median, third quartile, and maximum values of Q_{max}, reaction rate, and equilibrium time are provided for different C-adsorbents. Besides, the Shapiro-Wilk test at 95 % confidence level was applied to assess the normality in the collected results of the three parameters. When the adsorption results are normally distributed then both mean and median values can be used for comparison purposes [51]. In turn, median values are more convenient for comparison between adsorption parameters of methylene blue when data are skewed or not normally distributed, because the mean will be distorted by outliers. To verify the existence of significant differences in the parameters (Q_{max}, adsorption rate h, and equilibrium time) for methylene uptake by different adsorbents, a two-sample z-test at 95 % confidence level was applied.

3. Performance of C-based adsorbents for methylene blue uptake: micro- against nano-sized adsorbents

3.1. Equilibrium adsorption capacity of different adsorbents

Compared to many non-carbonaceous adsorbents, uptake of methylene blue and other organic dyes by C-based adsorbents is much higher, what is likely due to the high surface area and porosity of the latter [23]. Regarding the examined adsorption parameters, Q_{max} is considered the most significant, as it largely reflects the high performance of the adsorbent for wastewater treatment. As explained above, statistical comparison was performed between the adsorption capacity of methylene dye on activated carbons $Q_{max\text{-}AC}$, on MWCNTs $Q_{max\text{-}MWCNTS}$, and on graphene oxide $Q_{max\text{-}GO}$.

As shown in Fig. 4A, $Q_{max\text{-}AC}$ values indicate a positive skew and interquartile range of 270–714 mg g^{-1}, and a high difference in the mean and median, while no outliers were detected. For $Q_{max\text{-}MWCNTs}$, the results show a negative skewness, high dispersion, and IQR 211–906 mg g^{-1}. No outliers were detected but a significant difference was found between mean and median of $Q_{max\text{-}MWCNTs}$ values, 600 and 678 mg g^{-1}, respectively. The results for $Q_{max\text{-}GO}$ present a serious negative skew, high dispersion, IQR 333–946 mg g^{-1}, and an outlier at 3036 mg g^{-1}. Indeed, the reported adsorption value for diethylenetriamine-GO is unusual and not reported for other C-adsorbents [45]. A significant difference between median and mean was also observed $Q_{max\text{-}GO}$ values, 769 and 896 mg g^{-1} respectively.

Regarding mean values, uptake capacity of methylene blue increases in the trend: AC-adsorbents (531 mg g^{-1}) < MWCNTs-adsorbents (678 mg g^{-1}) << GO-adsorbents (896 mg g^{-1}), whereas for the median values, uptake capacity of methylene blue increases as: AC-adsorbents (427 mg g^{-1}) < MWCNTs-adsorbents (600 mg g^{-1}) << GO-adsorbents (769 mg g^{-1}). The outputs of the normality test should be considered taking into account the high dispersion in the Q_{max} values for the adsorbents. As shown in Fig. 4A, the collected results for $Q_{max\text{-}AC}$ were not normally distributed (P 0.007) while normally distributed for $Q_{max\text{-}MWCNTs}$ (P 0.09) and $Q_{max\text{-}GO}$ (P 0.52). Hence, it is more convenient to adopt median value for $Q_{max\text{-}AC}$ and mean values for $Q_{max\text{-}MWCNTs}$ and $Q_{max\text{-}GO}$ for comparison purposes. Results of the z-test (Table 4) indicated that the means of Q_{max} of methylene blue uptake by different C-adsorbents was not significant as estimated z values (0.50–1.36) were lower than critical value 1.96.

Two GO composites were the most efficient for methylene blue

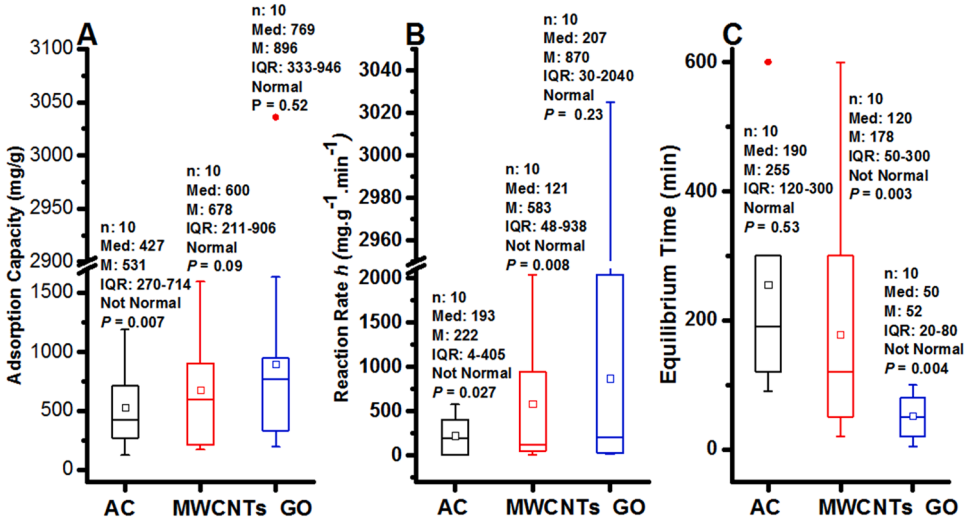

Fig. 4. Box-Whisker plots of MB adsorption parameters on different C-based adsorbents. The box stretches from the lower hinge (25th percentile) to the upper hinge (75th percentile). The median value is indicated as a line across the box, the mean value is presented by as empty square, and outliers presented by a red circle (data taken from Table 2). Shapiro-Wilk test was used to check normality in the results ($P > 0.05$).

Table 4
Significance of difference ($P < 0.05$) in the means of Q_{max}, reaction rate h, and equilibrium time for MB uptake by different C-adsorbents.

Adsorbents[a]	*z-estimated*		
	Q_{max}	Reaction Rate h	Equilibrium Time
AC/MWCNs	0.80(1.96)[b]	1.46(1.96)	0.92(1.96)
AC/GO composites	1.36(1.96)	**2.76**(1.96)	**3.27**(1.96)
MWCNTs/ GO composites	0.50(1.96)	**2.10**(1.96)	**2.17**(1.96)

[a] 10 adsorbent of each subclass was collected as shown in Table 2
[b] Values between brackets are critical z, the difference is significant when estimated-z > critical-z.

uptake among adsorbents with Q_{max} of 1634 and 3036 mg g^{-1} which reported for Lysine-GO and diethylenetriamine-GO, respectively [45, 52]. The performance of many GO-composites toward methylene blue was excellent and this expected due to the high surface area of nano-sheets of GO. For instance, the affinity of Ni-GO was outstanding for MB uptake with Q_{max} of 946 mg g^{-1} [40]. Moreover, lysine-GO also exhibited unusual affinity with Q_{max} 1634 mg g^{-1} [52].

Regarding MWCNTs, both calcium-alginate-MWCNTs and sodium alginate-MWCNTs were the most effective with Q_{max} of 1189 and 1596 mg g^{-1}, respectively [35,53]. Three other adsorbents were outstanding with uptake capacity higher than the mean of $Q_{max\text{-}MWCNTs}$ values: Fe_3O_4-alginate-MWCNTs (906 mg g^{-1}), polyamine-MWCNTs (800 mg g^{-1}), and maghemite/alginate–MWCNTs (906 mg g^{-1}). For AC, adsorbents with uptake capacity higher than the mean of $Q_{max\text{-}AC}$ values, syagrus oleracea-AC and edible fungus-AC are considered the best, with uptake values of 680 and 714 mg g^{-1}, respectively [30,54].

Many organic substrates like alginate, hydroxyapatite, Fe_3O_4, and polyamine are added to MWCNTs to improve dye retention from solution, as shown in Table 2. In fact, GO is rich with modifiable functional groups like -OH and -COOH which can interact with certain substrates including Fe_3O_4, polysaccharides, sodium dodecyl sulfate, lysine, ethylenediamine, and diethylenetriamine as shown in Table 2. GO-composites received more attention compared to GO itself as the later adsorbent has unusual swelling capacity > 1000 g g^{-1} in solution and hard recovery from water [55]. Hence, GO-composites are ideal adsorbents due to: (a) high uptake capacity for the cationic dye 3000 mg g^{-1} [45]; (b) short equilibrium time [48], and (c) with high swelling ratios 500–1000 g g^{-1}, GO-composites can improve dyes diffusion inside their hydrogel matrix [55,56].

3.2. Reaction rate of methylene blue on different adsorbents

The adsorption rates were examined as they give a good idea of the feasibility of adsorption treatment in real conditions. Statistical comparisons were focused on the initial adsorption rate on activated carbons $h_{\text{-AC}}$, on MWCNTs $h_{\text{-MWCNTS}}$, and on graphene oxide $h_{\text{-GO}}$. Box-whisker plot, z-test and normality tests were used for better assessment of the results as explained above. As shown in Fig. 4B, the shape of boxes obtained for reaction rates indicated a high dispersion, longer upper whiskers and higher positive skew for the results obtained for GO and MWCNTs than for AC adsorbents. No outliers were detected in the reaction rates for any adsorbent. As shown in Fig. 4B, the collected results for $h_{\text{-}AC}$ and $h_{\text{-MWCNTs}}$ were not normally distributed with P values of 0.027 and 0.008, respectively, while normally distributed for $h_{\text{-GO}}$ (P 0.23). Hence, it is more suitable to adopt median values for $h_{\text{-}AC}$ and $h_{\text{-MWCNTs}}$ and mean value for $h_{\text{-}GO}$ for comparison purposes.

Initial reaction rates increased in the order: AC < MWCNTs < < GO, with mean h values of 222, 583 and 870 mg g^{-1} min^{-1}, respectively. The z-test indicated significant differences in the means of h for methylene blue uptake on different C-adsorbents. Based on the statistical analysis, the highest uptake rate of methylene blue was reported for GO adsorbents. Dye uptake by GO composites was 2.6 and 3.9 times faster than on MWCNTs and AC adsorbents, respectively, with no significant differences between MWCNTs and AC adsorbents (Table 4). The results obtained from box-whisker plot agree with the outputs of z-test as the rate of methylene blue uptake on GO composites is significantly higher when compared with AC and MWCNTs adsorbents (Table 4). The maximum adsorption rate of methylene blue was very high with values of 2040 and 3025 mg g^{-1} min^{-1} reported for MOF-UiO-66-carboxylated-GO and diethylenetriamine-GO, respectively [45,49].

Based on the box-whisker plots, the adsorbents with the ideal Q_{max} and reaction rate are easy to pick. For AC adsorbents, these should be above the means of each parameter, i.e. Q_{max} over 531 mg g^{-1} and h above 222 mg g^{-1} min^{-1}. The best cases reported are chestnut shell-AC and shaddock peel-AC with Q_{max} values of 1191 and 860 mg g^{-1} respectively, and h values of 260 and 574 mg g^{-1} min^{-1}, respectively [31,32]. The performance of edible fungus-AC was also high with Q_{max} of 714 mg g^{-1} and h of 405 mg g^{-1} min^{-1} [30]. Despite the high dye uptake by syagrus oleracea-AC (680 mg g^{-1}), the uptake rate was very low 3.6 mg g^{-1} min^{-1}, which may impair the practical application of this material [54].

In the case of MWCNTs, the most efficient adsorbent should have Q_{max} higher than 678 mg g^{-1} and h higher than 583 mg g^{-1} min^{-1}. Based on this, sodium alginate-MWCNTs and Fe_3O_4-alginate-MWCNTs are the best adsorbents with Q_{max} 1596, 906 mg g^{-1} and h 2035, 1642 mg g^{-1} min^{-1}, respectively [35,36]. The performance of polyamine-MWCNTs is also promising with Q_{max} of 800 mg g^{-1} and uptake rate 844 mg g^{-1} min^{-1} [19]. Fe_3O_4-hydroxyapatite-MWCNTs show very high reaction rate for methylene blue 938 mg g^{-1} min^{-1} but with a low Q_{max} 211 mg g^{-1} [57]. Despite the high uptake of methylene blue on calcium-alginate-MWCNTs and maghemite/alginate-MWCNTs (906–1189 mg g^{-1}), they present a low uptake rate of 17–57 mg g^{-1} min^{-1}, which can reduce their practical application for water treatment [37,53].

In the case of GO composites, the most efficient one should have Q_{max} above 896 mg g^{-1} and h above 870 mg g^{-1} min^{-1}. The best GO adsorbent would be diethylenetriamine-GO with unusual Q_{max} and h of 3036 mg g^{-1} and 3025 mg g^{-1} min^{-1}, respectively [45]. In addition, the performance of lysine-GO and polysaccharides-GO is also high with Q_{max} values of 1634, 769 mg g^{-1} and h of 365, 2624 mg g^{-1} min^{-1}, respectively [42,52]. Even though methylene blue uptake by Ni-rGO, sodium dodecyl sulfate-GO, and poly(n-vinylimidazole-acrylic acid)-Fe_3O_4-GO is high (625–946 mg g^{-1}), low adsorption rates are reported in these cases (12–65 mg g^{-1} min^{-1}), so their practical application could not be feasible [38,40,46]. On the other hand, the rates of methylene blue uptake by MOF-UiO-66-carboxylated-GO and Fe_3O_4-GO are very high 1140–2024 mg g^{-1} min^{-1} although their uptake capacities are not very, 205–449 mg g^{-1} [43,49].

3.3. Equilibrium time for different adsorbents

In addition to high Q_{max} and h, uptake process should be accomplished within a short time, since long processes consume extra energy with an impact on the overall cost of the treatment. Statistical comparisons were made between the equilibrium time ET for methylene blue uptake on activated carbons, $ET_{\text{-AC}}$, on MWCNTs, $ET_{\text{-MWCNTS}}$, and on graphene oxide, $ET_{\text{-GO}}$. Fig. 4C displays the box-whisker plots of the equilibrium time of dye uptake on different C-based adsorbents. For AC adsorbents, the box indicated a positive skew and presence of two outliers at 600 min. For MWCNTs, the box indicated positive skew and no outliers were detected. For GO composites, no skewness and no outliers in the results as seen in Fig. 4C. The results of the normality test indicate that data for AC are normally distributed (P 0.53), but not for MWCNTs (P 0.003) or GO adsorbents (P 0.004). Hence, it is convenient to use mean values for AC and median values for MWCNTs and GO adsorbents. Accordingly, the equilibrium time for dye uptake increases in the sequence: GO (median 50 min), MWCNTs (median 120 min), and AC (mean 255 min). Differences for equilibrium time on GO composites compared to AC and MWCNTs were statistically significant (Table 4).

Overall, the equilibrium time of methylene blue uptake by GO composites is very short compared to other adsorbents.

3.4. Influence of physicochemical properties of C-based adsorbents on dye uptake

Many of the examined research studies reported physicochemical parameters of the adsorbents including specific surface area, pore volume, pore diameter and pH_{ZPC} (Table 3). The nature of dye-adsorbent interaction can be elucidated from these parameters.

As summarized in Table 3, a large number of studies reported the main physicochemical properties of AC and MWCNTs, which may allow correlating their uptake behavior within their intrinsic properties. Unfortunately, very few studies reported the physicochemical properties of GO adsorbents. For AC adsorbents, the mean specific surface area is 1119 $m^2\ g^{-1}$ ($n = 10$), the mean pore volume 0.9 $cm^3\ g^{-1}$ ($n = 9$), and the mean pH_{ZPC} 6.6 ($n = 6$). MWCNTs adsorbents present a mean specific surface area of 302 $m^2\ g^{-1}$ ($n = 7$), mean pore volume of 1.5 $cm^3\ g^{-1}$ ($n = 4$), and pH_{ZPC} of 4.8 ($n = 6$). Despite the very high surface area of AC adsorbents, 3.7 times higher than MWCNTS, the latter are more effective in removing methylene blue, which may imply that the uptake mechanism is of a chemical nature and not a physical one.

Based on the results collected, the maximum retention of methylene blue and on most adsorbents happens at mean pH 9.3 ($n = 7$) and 9.2 ($n = 7$) for AC and MWCNTs, respectively. Under alkaline conditions, the net surface charge of AC (mean pH_{ZPC} 6.6) and MWCNTs (mean pH_{ZPC} 4.8) is negative, and this improves cationic dye uptake via electrostatic attractions.

3.5. Overall performance of C-based adsorbents

At this point, the best adsorbents in each subclass would be selected while considering the following three criteria at the same time: (a) maximum uptake: capacity of the adsorbent should be above 427, 678, and 896 mg g^{-1} for AC, MWCNTs, and GO composites, respectively; (b) reaction rate: the adsorption rate should be higher than 193, 583, and 870 mg g^{-1} min^{-1} for AC, MWCNTs, and GO composites, respectively; and (c) equilibrium time of the process should be shorter than 255, 120, and 50 min for AC, MWCNTs, and GO composites, respectively.

For AC adsorbents, only two adsorbents fulfill the earlier criteria. AC derived from edible fungus outperformed other AC adsorbents with a high uptake capacity of 714 mg g^{-1}, a high reaction rate of 405 mg g^{-1} min^{-1} and a short equilibrium time of 90 min [30]. Moreover, a commercial activated carbon was also effective with Q_{max} 400 mg g^{-1}, and contact time 100 min [58]. Other AC adsorbents have a high uptake capacity 454–1191 mg g^{-1} and a high h 260–574 mg g^{-1} min^{-1}, but long contact times to reach equilibrium of 200–600 min [31,32,59].

Three modified MWCNTs adsorbents also fulfilled the three conditions above. Sodium alginate-MWCNTs and Fe_3O_4-alginate-MWCNTs were the best with uptake capacity 906–1596 mg g^{-1}, uptake rate 1642–2035 mg g^{-1} min^{-1} and a short contact time of 50–60 min [35,36]. Moreover, the performance of polyamine-MWCNTs was also high with Q_{max} 800 mg g^{-1}, h 844 mg g^{-1} min^{-1}, and very short contact time 30 min [19]. Although calcium-alginate-MWCNTs has a high uptake capacity for MB 1189 mg g^{-1}, it may not be suitable for practical applications due to its low uptake rate of 57 mg g^{-1} min^{-1} and very long contact time of 600 min [53]. Despite having a high adsorption capacity of 906 mg g^{-1} min^{-1} and a short contact time of 20 min, maghemite/alginate–MWCNTs is not advised for practical purposes because of its poor uptake rate of 17 mg g^{-1} min^{-1} [37].

Four GO adsorbents: polysaccharides-GO, lysine-GO, and MOF-UiO-66-carboxylated-GO, are excellent for methylene blue removal, with uptake capacity 449–1634 mg g^{-1}, uptake rate 365–2624 mg g^{-1} min^{-1}, and contact time 30–100 min [42,49,52]. Among all examined adsorbents, diethylenetriamine-GO was the best with Q_{max} 3036 mg g^{-1}, uptake rate 3025 mg g^{-1} min^{-1}, and contact time down to 5 min only [45]. Although a very short contact time was reported for a number of GO composites 20–60 min, however, their practical use is not recommended for two reasons: a low uptake rate as in the case of Ni-rGO and MgO-GO 12–35 mg g^{-1} min^{-1} [39,40], and a low Q_{max} (205 mg g^{-1}) as in the case of methacryloyloxyethyl-Fe_3O_4-GO [43].

The high reaction rate and retention capacity of GO composites and MWCNTs is mainly attributed to the large surface area stemming from their nano-structure and high intensity of surface functional groups of these adsorbents compared with activated carbon [22,34]. In fact, the efficiency of adsorbents is frequently assessed only on the basis of their adsorption capacity. This study provides more than one criterion for a more comprehensive evaluation of the efficiency of C-based dye adsorbents. The first requirement is the reaction rate, while the second is the equilibrium time, which was not investigated in the literature. The researchers believe that Fig. 4, which compares the performance of C-based adsorbents, provides a more complete picture, as the adsorption capacity, reaction rate, and equilibrium time were used to determine the efficient C-based adsorbents for methylene blue. It should be recalled here that there are important factors that should be further verified, such as adsorbent recycling, separation method from solution, uptake performance under dynamic condition, and production/modification costs.

4. ECONOMICAL EVALUATIONS OF DIFFERENT C-BASED ADSORBENTS

The cost of C-adsorbent preparation and usage should also be evaluated from an economic point of view. Hence, it is vital to consider the economic feasibility of using different C-adsorbents for treating textile wastewater, considering the high variations in their production costs. It is also critical to examine the cost of utilizing C-adsorbents for wastewater treatment, as this is one of the principal considerations and obstacles to commercializing adsorption technology, i.e., scaling up adsorption technologies from pilot to industrial scale. In this section, the cost of utilizing different C-adsorbents to remove methylene blue based solely on their production costs will be addressed. The expenses of the adsorption process itself, such as heating, stirring, filtration, and the additional costs of running fixed bed technology, will not be considered. Researchers rarely refer to the production cost of C-adsorbents, as well as the additional costs of the treatment process, and this was attributed to the lack of a unified or standardized procedure to estimate these expenses [62].

Few research studies have presented adequate models to estimate the cost of adsorbents. For instance, the net production cost of an adsorbent can be estimated from the following : cost of raw materials, cost of raw materials transportation, cost of the chemicals consumed, cost of the energy consumed, cost of mixing, cost of heating, cost of filtration, and cost grinding [62]. Based on our extensive search, there is no comprehensive review related to the production and utilization costs of C-based-adsorbents for removing pollutants from water, despite the decades of intensive research in this field. However, a few studies reported approximate production costs of activated carbon [63], multi-walled carbon tubes [64], and graphene oxide [65]. The average production costs of C-based adsorbents are provided in Table 5.

As shown in Table 5, MWCNTs, GO and related composites have a much higher production cost than AC due to the usage of expensive chemicals as well as the use of high energy expenditures during the manufacturing process [62]. The substantial cost disparity within the prices of MWCNTs and GO can be traced back to differences in the cost of electricity, chemicals, the value of manufacturing taxes, and labor wage in the countries that produce these nano-adsorbents [62]. Although GO and GO-composites outperformed other C-adsorbents for removing MB, their application on a large scale is a questionable issue considering the high production costs.

However, comparing the production costs of C-adsorbents based on their unit mass would be misleading considering the high variations in their uptake capacities. As a result, the estimated costs of adsorbents

Table 5
Average production cost and cost index of C-based adsorbents for removing 1.0 g of methylene blue.

C-adsorbent	Range of production cost (US$/g)[a]	Average production cost (US$/g)	Maximum adsorption capacity, Q_{max} ($g_{MB}/g_{adsorbent}$)[b]	Cost index (US $/$g_{MB}$)[c]
Activated carbon	0.0005–0.002	0.00125	0.427	0.003
MWCNTs	1.0–45	23.0	0.600	38.3
GO	8.0–57.0	32.5	0.769	42.3

[a] Range of production cost of C-based adsorbents as reported in the recent literature [62–65].
[b] Maximum uptake capacity was collected from Fig. 4A. Median Q_{max} values were selected for comparison purposes.
[c] Estimated from Eq. 4.

should be normalized for comparison of adsorbents per adsorption capacity rather than per unit mass. This can be simply performed by dividing the cost per g adsorbent (e.g., USD/$g_{adsorbent}$) by the adsorption capacity of the adsorbent to obtain the cost in units of USD/$g_{adsorbate}$ [62]. Therefore, comparing C-adsorbents may require not only considering their production costs but by the adsorption capacity at optimum conditions . The cost of an adsorbent per gram of adsorbate, also known as cost index of adsorbent, can be used to determine the cost of the adsorption process and estimated as following [66]:

$$Adsorbent\ Cost\ Index\left(\frac{US\$}{g_{adsorbate}}\right) = \left[\frac{Production\ Cost\left(\frac{US\$}{g_{adsorbent}}\right)}{Qmax\left(\frac{mg_{adsorbate}}{g_{adsorbent}}\right) \times 10^{-3}\frac{g_{adsorbent}}{mg_{adsorbate}}}\right] \quad (4)$$

Table 5 shows the estimated cost index of C-adsorbents for the removal of one gram of methylene blue from water. As data show, using MWCNTs and GO would be quite expensive, with costs of 38.3 $ and 42.3 $, respectively, so using nano-adsorbents might not be commercially viable to remove methylene blue on a large scale. The high production cost of GO and MWCNTs, combined with their high affinity for methylene blue, would need of increased recycling efforts. The best adsorbent is activated carbon with a cost of 0.003 $/$g_{MB}$, but it should be remembered here that the production costs of C-based materials are high compared to those of many non-conventional adsorbents, such as natural clay, around 0.01–0.1 $/kg, or zeolites, around 0.03–0.12 $/kg [63].

5. Conclusions and perspectives

The results of this review indicate the availability of a large number of C-based adsorbents with a high performance for removing methylene blue, as a model pollutant, from solution. Many of the activated carbon adsorbents are derived from organic solid waste and examined for removing methylene blue. For MWCNTs adsorbents, which are often prepared using chemical vapor deposition for the hydrocarbon, were also found useful applications for removing organic dyes like methylene blue. In the recent decade, more applications of graphene oxide, prepared from graphite by Hummer`s methods, were reported for removing dyes from solutions. As known, these C-based materials manifested intense surface area, porosity, high swelling capacity, and a unique nanostructure. Three criteria were proposed to select the most efficient adsorbents from a practical point of view: (a) maximum uptake capacity Q_{max}; (b) rate of adsorption h; and (c) equilibration time for the uptake process. Based on the results collected from 30 research articles, these conditions are fully achieved by GO composites, which outperformed other C-adsorbents in removing methylene blue with mean adsorption capacity of 896 mg g^{-1}, mean uptake rate of 870 mg g^{-1} min^{-1}, and median contact time of 50 min. The next step or suggested future research is paying more attention to the type of chemical substrates that can be added to the surface of graphene oxide to improve its performance as a dye adsorbent. In fact, the surface of graphene oxide is very active and can interact with many substrates, including organic compounds, polymers, and inorganic compounds. the most important substrate added to graphene oxide was Fe_3O_4, which highly improved its separation from solution by an external magnet. Even though MWCNTs, GO, and related composites manifested excellent performance for removing methylene blue, the extensive use of chemicals and energy for their synthesis leads to a high estimated cost for their production per unit mass. On the other hand, activated carbon with simpler synthesis procedures may be more profitable from an economic point of view for removing dyes on a large scale.

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Khaled Al-Zawahreh: Writing – review & editing, Writing – original draft, Visualization, Validation, Project administration, Methodology, Formal analysis, Data curation. **Remigio Paradelo Nuñez:** Writing – review & editing, Visualization, Validation, Project administration, Methodology, Conceptualization.

Declaration of Competing Interest

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

Data Availability

No data was used for the research described in the article.

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