Jurnal Presipitasi
Media Komunikasi dan Pengembangan Teknik Lingkungan
e-ISSN: 2550-0023

Vol 19, No 2, 2022, 384-397
Article available at homepage presipitasi

Review Article

Adsorption of Dyes Using Graphene Oxide-Based Nano-Adsorbent: A Review

Danar Arifka Rahman[1*], Qomarudin Helmy[2], Mindriany Syafila[3], Andri Gumilar[2,3]

[1]Environmental Engineering Study Program, Faculty of Civil and Environmental Engineering, Bandung Institute of Technology, Bandung, Indonesia
[2]Bioscience and Biotechnology Research Center, Bandung Institute of Technology, Indonesia
[3]Water and Wastewater Engineering Expertise Group, Bandung Institute of Technology, Indonesia
*Corresponding author, e-mail: rahmandanar@gmail.com

Abstract

Graphene Oxide (GO) based adsorbents have attracted much attention from researchers because there have been many reports that they are effective for removing dyes from aqueous environments. That is because GO has good mechanical, electrical, optical and chemical properties, so graphene and its derivatives, such as graphene oxide, have been used in various applications in the field of environmental management. Modifying GO into nano size is an effort to improve its performance in removing dyes. This review uses a database from Science Direct, Google Scholar and Springer, which was screened using graphene oxide, pigments, adsorption and nano adsorbent. The performance of the nano adsorbent showed quite good results in the removal of dyes. The isotherm model suitable for adsorption varies between Langmuir, Freundlich and Redlich-Peterson isotherms. Pseudo-second-order (PSO) is the best model to explain the adsorption process kinetics. Nano-adsorbent modification can be reused at least five times with a reduced adsorption capacity of 4-8%. Studies related to adsorption with GO-based nano adsorbents show promising results in pollutant removal. Still, aspects such as synthesis method, surface functional groups interaction and dye ions and the stability of synthesis products need to be investigated further.

Keywords: Dye; graphene oxide; modification; nano adsorbents

1. Introduction

Rapid economic development in recent decades has increased water pollution, especially in the industry sector. The textile industry's effective use of different synthetic dyes (Congo red, crystal violet, methylene blue, and so on) has become one of the leading pollutants in water (Calza et al., 2016). Every year large amounts of dye-contaminated wastewater are discharged into water bodies without prior treatment, with dire consequences for living things, including humans. In addition, coloured compounds affect wastewater's transparency and inhibit aquatic organisms' photosynthetic capacity (Rahim Pouran et al., 2014; Sharma et al., 2018). The Ministry of Environment and Forestry 2019 set the textile industry effluent dye quality standard of 200 PtCo. Due to their synthetic composition and intricate aromatic structure, dyes have poor biodegradability and excellent chemical stability in water. Because of these properties, the dye is resistant to degradation by physical and chemical treatments. As a result, the handling of dye-containing waste has been a critical environmental problem. Therefore,

mitigating dyes emerging in wastewater using high-efficiency techniques is a significant challenge (Dehghani et al., 2020; Wu and Andrews, 2020).

Adsorption-based treatment systems have shown excellent performance and feasibility in recent literature. Indeed, this method's significant advantage is efficiently absorbing various toxic dyes from the aqueous phase at an affordable operating cost, while no complicated facilities are required. In addition, large amounts of adsorbent are easy to obtain. This adsorption process is also cheaper and environmentally friendly than removing dyes (Majhi and Patra, 2020; Wang et al., 2018). Therefore, developing more advanced and profitable techniques for removing stains from wastewater is necessary. Nanomaterials as if metal oxides, graphene and organic sources have provided new prospects for pollutant treatment. Due to its outstanding electrical, physical, structural and chemical characteristics, graphene, a single-layer carbon allotrope with sp2 hybridized carbon, is one of the most intensely investigated materials. Graphene is a useful nano adsorbent for dealing with environmental pollutants because of its high surface area (Khurana et al., 2017). One of graphene product derivatives, Graphene Oxide (GO), has attracted much deliberation as a promising dye adsorbent due to its excellent conjugated formation, which gives a higher adsorption capacity for dye particles with π-π bonds (Guo et al., 2015).

GO, a chemically oxidized form of graphene material, comprises many functional groups, such as epoxy, hydroxyl and carboxyl. The functional groups promote the firmness and negative surface charge and can also associate via hydrogen and π bonds. As a result, GO may be an excellent constituent for efficient nanocomposites in pollutant remediation (Xing et al., 2017; Zhao et al., 2015). Because GO can absorb colours and metals from industrial waste, it has garnered much attention. Different dyes and other pollutants can be adsorbent and degraded using GO and its polymer nanocomposites (Jiao et al., 2015).

Many studies have revealed that GO-based composites have been used to remove cationic and anionic dyes in aquatic environments. Some composites are metal oxides, carbon transcription, and metal or polymer hybrids created using solvothermal synthesis, hydrothermal processes, microwave-assisted composites, one-step sonochemical routes, coprecipitation, and ultrasonication routes (Khurana et al., 2017). The purpose of GO composites is to improve the adsorbent's performance in removing pollutants by increasing the porosity and surface area. Therefore, this study will discuss studies related to dye removal from the waters with GO-based nanomaterials.

2. Methodology

This literature review aims to provide the latest data regarding the dye adsorption process by graphene oxide-based nano adsorbents. For this, a scan of the literature in the year interval from 2012 to 2022 is shown. The databases used in collecting data and information are Science Direct, Springer and Google Scholar. Meanwhile, the keywords used are graphene oxide, dyes, adsorption and nano adsorbent.

The inclusion criteria in this literature study were articles from quantitative research results published in 2012-2022 and fully accessible articles. Meanwhile, the exclusion criteria in this study were not to discuss the adsorption process of dyestuffs with graphene oxide-based adsorbents that are not nanomaterials and not to discuss the adsorption of dyes to other than graphene oxide-based adsorbents. The schema of the data collection and sorting process is shown in Figure 1. 1,104 papers collected from the database are selected for titles and abstracts according to inclusion and exclusion criteria so that 28 articles are obtained. The selection results were examined in depth by reading all the documents to discuss the remaining 21 papers in this literature review.

3. Result and Discussion

3.1. Dye adsorption Applications in Textile Wastewater Treatment Systems

The dye removal process in the textile industry has involved further processing, which is determined based on the disposal limit considerations. One of the advanced processing processes for dye removal is adsorption, an advanced physicochemical process (Dutta et al., 2021; Helmy et al., 2022). Through various adsorbent separation, attraction, free radical reactions, catalytic oxidation, and electrochemical reactions, dye molecules in the liquid phase are moved onto the solid surface during the adsorption process (Manera et al., 2018; Rachna et al., 2019). Various adsorbents have been investigated for their performance in removing textile waste dyes. Despite operational drawbacks such as saturation, the adsorbent can be regenerated to be reused in the treatment operation (Widajatno et al., 2022). Fazal et al. (2015) provide an example of a textile industry wastewater treatment system, which uses conventional wastewater treatment units with the addition of advanced ozonation and adsorption with granular activated carbon (GAC). An example of this explanation is presented in Figure 2.

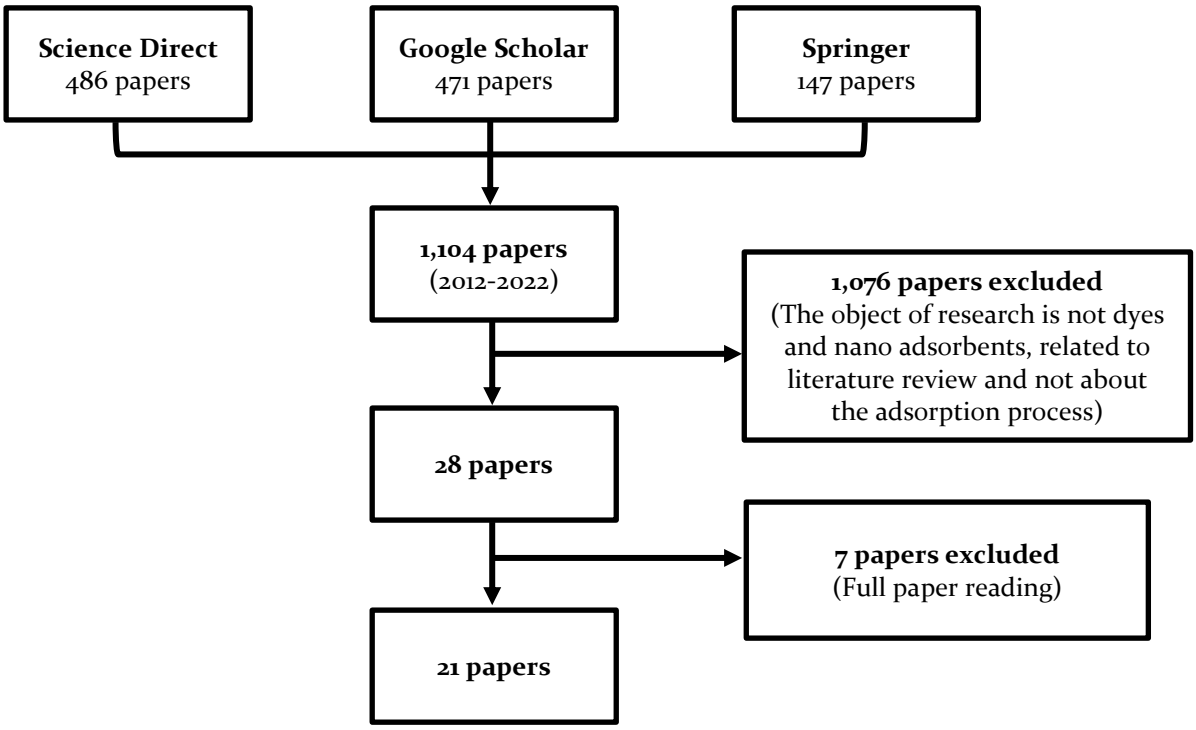

Figure 1. Schematic of the data source screening process

3.2. Removal of Dye with GO-Based Nano Adsorbent

GO an advanced graphite product, is a highly oxidative form of graphene with multiple oxygen functions. It has attracted considerable research interest due to its role as a precursor for the mass production and cost-effectiveness of graphene-based materials. However, there has been much discussion over the precise chemical makeup of GO, and there are still questions about the variety and distribution of functional groups that contain oxygen. That is primarily due to the material's complexity and its amorphous, berthollide origin, nonstoichiometric atomic composition. Various models have been proposed to understand GO structure, the most notable of which is the Leaf-Klinowski model, which was developed using NMR spectroscopic data. This model states that the hydroxyl and epoxy functional groups are added to the carbon planes of GO. Additionally, there are carbonyl groups, most likely in the form of carboxylic acids at the sheet's

borders and organic carbonyl defects inside the sheet (Chowdhury and Balasubramanian, 2014; Kim et al., 2018).

Manufacture of GO can be done by various methods such as the Brodie method, Staudenmaier method, and the most commonly used method, the Hummers method and its variations (Chowdhury and Balasubramanian, 2014; Ciğeroğlu et al., 2021). Furthermore, recent studies have shown that modified GO by chemical approach can make GO materials more stable and prevent aggregation. Additionally, it can increase its processability and interact with various organic and inorganic contaminants (Lertcumfu et al., 2020; Sherlala et al., 2018; Zhang et al., 2016). The attached functional groups may be organic polymers or nano-sized metal oxides (NMOs) (Huang et al., 2012; Zare-Dorabei et al., 2016). With so many GO modification paths, the methods used vary according to the functional groups used.

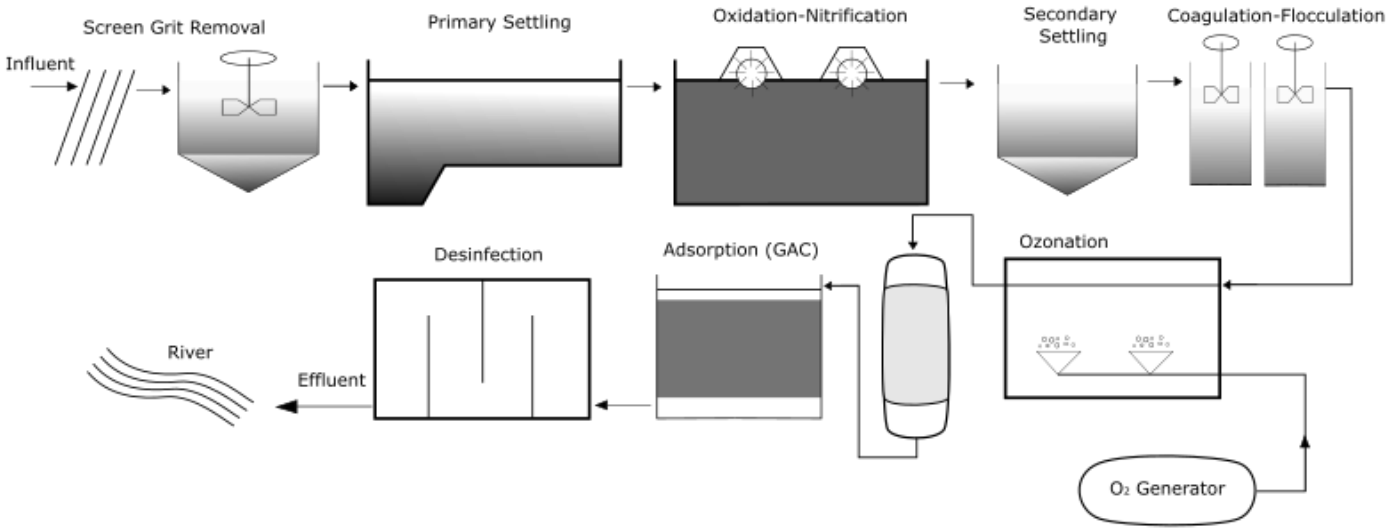

Figure 2. Schematic of the textile wastewater treatment process with adsorption

Co-precipitation is commonly used to produce GO nano adsorbent products with metal oxide composites or magnetic GO (Faghihi et al., 2016; Neolaka et al., 2020; Singh et al., 2019; Wu et al., 2016). GO modified with other composites that are magnetic using suitable methods such as the Massart method (Hejazi Khah et al., 2021), solvothermal (Chen et al., 2021), polymerized complex (Tran et al., 2020) or other modifications. Organic composites have also been widely studied with various functional groups. Several paths to obtaining organic-GO composites are dispersion approaches (Noreen et al., 2021; Wang et al., 2022), free radical polymerization (Pashaei-Fakhri et al., 2021)and ultrasonic technique (Calimli et al., 2020). Meanwhile, GO nano adsorbents without composite were adjusted for particle size to nano size. Data regarding the sources of articles using GO-based nano adsorbents to remove dyes are shown in Table 1.

Table 1. Recent studies on the removal of dye using GO-based nanoadsorbents

Adsorbent	Adsorbate	Adsorbent Dosage (g/L)	Dye Concentration (mg/L)	pH	Contact Time (h)	Adsorption Capacity (mg/g)	Reference
Magnetic cyclodextrin–chitosan/graphene oxide (MCCG)	Methylene blue	0.1	100	11.0	1.33	84.32	(Fan et al., 2013)
β-cyclodextrin multi-conjugate magnetic	Methylene blue	0.7	40	13.0	2.5	196.2	(Cao et al., 2016)

Adsorbent	Adsorbate	Adsorbent Dosage (g/L)	Dye Concentration (mg/L)	pH	Contact Time (h)	Adsorption Capacity (mg/g)	Reference
nanoparticles and graphene oxide (MNPs/GO-βCD)							
Fe_3O_4/GO-freeze dried (MGO-FD)	Rhodamine B	0.14	30-80	2.7	24	126.58	(Faghihi et al., 2016)
Magnetic polypyrrole nanocomposite (MGO/PPy)	Methylene blue	0.25	100	8.0	2.33	323.2	(Nezhad et al., 2018)
GO-Fe3O4@P4VP	Methylene blue	0.1-2	10-100	2.5	10	152.51	(Li et al., 2019)
Magnetic IO-Incorporated CSGO Hydrogel (CSGOIO)	Methylene blue	0.2	1.6-16	7.4	5	74.93	(Singh et al., 2019)
Magnetic/graphene/ chitosan nanocomposite (MGCH)	2-naphthol	0.005	10-40	2.0	1	169.49	(Rebekah et al., 2020)
Graphene	Congo red	0.9	81	5.5	2	109.18	(Tran et al.,
oxide@CoFe2O4	Methyl red	1.5	92	5.0	2	78.81	2020)
($GO@CoFe_2O_4$)	Crystal violet	1.2	81	7.0	2	137.95	
Fe_3O_4-graphene@mesoporous SiO_2 (MG@m-SiO_2)	Methylene blue	0.2	10-50	11.0	24	102.22	(Wu et al., 2016)
Ni@reduced-graphene oxide (Ni@rGO)	Methylene blue	0.02	32	8.3	2.5	946.12	(Calimli et al., 2020)
Fe_3O_4@C/GO	Methylene blue	1	30-120	12.0	48	116.5	(Chen et al., 2021)
Graphene oxide (GO)	Basic blue 41	0.01-0.04	50-200	-	1	1429	(Hosseinabadi-Farahani et al., 2015)
	Basic red 18	0.02-0.08	50-200	-	1	1250	
	Basic red 46	0.06-0.12	50-200	-	1	476	
N-doped GO (NGO)	Congo red	0.2	10-100	2	12	19.49	(Yokwana et al., 2018)
Graphene oxide (GO)	Ethyl violet	-	10-50	-	-	4.585	(Odiongenyi, 2019)
Graphene oxide (GO)	Methylene blue	0.5	6.25-100	10.0	4	311.74	(Ciğeroğlu et al., 2021)
Graphene oxide (GO)	Basic red 46	0.4	150	11.0	3	360	(Shoushtarian et al., 2020)
Cellulose nanocrystals and graphene oxide (CNC:GO)	Basic blue 7	0.1	400	6	5	1948.02	(da Silva et al., 2021)
	Reactive orange 122	0.1	100	6	5	516.04	
	Methyl	0.1	100	6	5	681.82	

Adsorbent	Adsorbate	Adsorbent Dosage (g/L)	Dye Concentration (mg/L)	pH	Contact Time (h)	Adsorption Capacity (mg/g)	Reference
	orange						
MATCHA-co-AA@GO	Malachite green	1	20	6.5	1.5	67.5	(Niknezhad and
	Methylene blue	1	20	6.5	2	70.3	Mansour Lakouraj, 2021)
GO/PAN	Actacid	0.2	150	2.0	2	67.11	(Noreen et
GO/PPy	orange RL	0.2	150	6.0	2	72.44	al., 2021)
GO/PSty		0.2	150	3.0	2	54.99	
Acrylamide/graphene oxide bonded sodium alginate (AM-GO-SA)	Crystal violet	0.25-5	10-300	10	5	100.3	(Pashaei-Fakhri et al., 2021)
Barium alginate-bentonite-graphene oxide composite (3D-BA/GO) hydrogel	Methylene blue	0.2	200	6	60	710.8	(Wang et al., 2022)

Methylene blue (MB) is a contaminant widely found in industrial production, so it has been widely studied as an essential parameter for evaluating removal capacity (Chen et al., 2015). Several studies have been reported on the MB dye adsorption process (Table 1). The use of different types of nano adsorbents has the consequence of varying adsorption capacities and mechanisms. Ciğeroğlu et al. (2021) reported MB removal by GO nano-adsorbent without composite. The dye adsorption capacity slightly declined from 311.74 mg/g to 295.46 mg/g when the temperature was raised from 298 oK to 318 oK, while the maximum MB removal was 94% at pH 10.0. The adsorption kinetics follows a pseudo-second-order (PSO), and intraparticle diffusion is not the only one influencing the adsorption process. Freundlich isotherm equation fits the adsorption equilibrium data more closely than Langmuir and Tempkin equations. The thermodynamic parameters' estimation showed that MB's adsorption to GO nano adsorbent was a spontaneous, exothermic, and physisorption process. Calimli has reported better results for MB removal (2020) using Ni@reduced-graphene oxide (Ni@rGO). At 318 oK, the highest dye adsorption capacity was 946.12 mg/g. Similar to the study conducted by Ciğeroğlu et al. (2021), the MB adsorption process occurs in physisorption. Still, the reaction that occurs is not spontaneous and endothermic.

Pashaei-Fakhri (2021) investigated the use of acrylamide/graphene oxide bonded sodium alginate (AM-GO-SA) for crystal violet removal. AM-GO-SA showed a dye adsorption capacity of 100.3 mg/g and reached equilibrium after 200 minutes. In addition, it is reported that there are impulsive and exothermic reactions in the adsorption mechanism based on thermodynamic studies. The possibility of regeneration and reuse of adsorbents was conducted. It was observed that there was no significant change during ten cycles of the adsorption-desorption process with an efficiency of >80%. Tran et al. (2020) reported maximum CV adsorption capacity using adsorbent Graphene oxide@$CoFe_2O_4$ is 137.95 mg/g at pH 7.0. The results of the adsorption kinetics are best demonstrated with a PSO model, while the isotherm follows the Langmuir model.

Congo red (CR) is one of the dyes of most dyes that can be a source of mutagenic and carcinogenic (Habiba et al., 2017). Yokwana et al. (2018) have investigated the potential of nano-adsorbent N-doped GO (NGO) in removing CR dyes. This study obtained the highest CR adsorption capacity at the Langmuir isotherm at 19.49 mg/g with NGOp adsorbent at pH 2. The adsorption mechanism that occurs is chemisorption and follows a pseudo-second-order kinetic. At acidic pH, the

synergistic effect of adsorption between NGO and CR occurs because of the strong electrostatic attraction of the two positively charged imidazolium rings and the protonated amine group on the CR with the negatively charged oxygen function of the NGO surface. CR adsorption studies were also carried out by Tran et al. (2020) with GO@ ($CoFe_2O_4$) adsorbent, which has maximum CR adsorption capacity following the Langmuir isotherm model of 109.18 mg/g at pH 5.5. Like Yokwana et al. (2018), the best results of adsorption kinetics were obtained in pseudo-second-order.

Faghihi et al. (2016) have conducted adsorption studies of rhodamine B (RhB) dye using an MGO-FD adsorbent. The Langmuir isotherm equation provides the highest adsorption capacity of 126.58 mg/g at pH 2.7. Adsorption capacity decreases more when pH rises due to the H+ ions' competitive effect and the electrostatic attraction among dye molecules, and the active site of the positively charged adsorbent. The adsorption mechanism followed a pseudo-second-order model, according to the findings of the adsorption kinetics investigation. RhB adsorption on MGO-FD appeared to be a spontaneous, endothermic, and physisorption process, according to thermodynamic analyses. Tests of regeneration and reuse of adsorbents showed no significant change in adsorption capacity in five cycles.

GO adsorbents are effective in removing dyes in wastewater. Hosseinabadi-Farahani et al. (2015) reported that GO nano adsorbents could effectively remove BB41, BR18 and BR46, with each highest adsorption capacity of 1429, 1250 and 467 mg/g. The kinetics and isotherm analysis results show that the adsorption processes of BB41, BR18 and BR46 follow pseudo-second-order kinetic and Langmuir isotherm models. GO also indicated good adsorption capacity for single and binary systems. Shoushtarian et al. (2020) also evaluated the adsorption process of BR46 onto GO nano adsorbents. They discovered that the highest adsorption capacity of BR46 corresponds to the Langmuir isotherm equation 360 mg/g at pH 11.0. The kinetics study found that the adsorption mechanism matched pseudo-second-order kinetic, which explains why chemical adsorption occurred. In the adsorbent reuse test, the adsorption capacity was reduced to 41.9% in 4 experimental cycles.

Da Silva et al. (2021) studied BB7, RO and MO adsorption processes. The adsorbents used were cellulose nanocrystals (CNC) and graphene oxide (GO) with a CNC: GO composition of 70:30. The adsorption process of CNC: GO showed the adsorption capacities of BB7, RO and MO each were 1943.02, 681.82 and 516.04 mg/g. The kinetics and isotherm analysis of the adsorption experiment was best suited to the pseudo-second-order kinetic and Redlich-Peterson (RP) isotherm, indicating that adsorption increased with increasing contaminant charge. The exciting thing about this report is that the nano adsorbent reaches saturation after 19.5 hours, longer than the previous study report (Akar et al., 2018).

Noreen et al. (2021) investigated the adsorption of AO-RL using three types of GO composite nano adsorbents, i.e. GO/PAN, GO/PPy and GO/PSty. The maximum adsorption capacities for GO/PAN, GO/PPy and GO/PSty adsorbents were 67.11, 72.44 and 54.99 mg/g, respectively. Kinetic and isotherm analyzes show that pseudo-second-order kinetic models and Langmuir isotherms are most suitable for adsorption. The thermodynamic analysis explained that the adsorption mechanism of AO-RL dye to three types of adsorbents was spontaneous and exothermic. The best results were obtained applying 0.05 N NaOH as eluent based on the desorption study. In addition to the reports already mentioned, several other studies use GO-based nano-adsorbents to remove dyes. Odiongenyi's (2019) report said that GO nano adsorbent could be used to remove ethyl violet with the highest adsorption capacity of 4.585 mg/g. Niknezhad and Mansour Lakoraj (2021) reported that MATCHA-co-AA@GO removed malachite green (MG) with the highest adsorption capacity following the Langmuir model of 67.5 mg/g at pH 6.5. Thermodynamic analysis shows that the adsorption process occurs spontaneously, chemisorption and endothermic. Rebekah et al. (2020) mentioned that MGCH adsorbent has an adsorption capacity of 169.49 mg/g at pH 2.0 and was effective at removing 2-naphthol. Meanwhile, Tran et al. (2020) research investigated the methyl red (MR) adsorption to GO@$CoFe_2O_4$. According to the findings, the maximal MR adsorption capacity at pH 5.0 was 78.81 mg/g.

3.3. Isotherm Models and Adsorption Kinetics

Many different models are frequently used to investigate the kinetics and process of adsorption. The connection between the quantity of contaminant adsorbed per unit weight of adsorbent and the concentration of a pollutant at a specific temperature, under equilibrium circumstances, is the basis of the adsorption isotherm. Although Temkin, Dubinin-Radushkevich (DR), and Redlich-Peterson (RP) models have also been employed, Freundlich and Langmuir's isotherms are the most common ones utilized for heavy metal adsorption. Langmuir and Freundlich's isotherm model has extensively studied the dye sorption process. The articles that have been summarized use the Langmuir and Freundlich model in addition to other models shown in Table 2.

According to the Langmuir isotherm model, the adsorption process occurs at specific active sites localized on the surface of the adsorbent, and all of these sites are homogeneous energy. All the binding sites have the same affinity for the adsorbate, forming a single layer of adsorbate (Neolaka et al., 2020). Therefore, this model describes adsorption as a chemisorption process. The Freundlich isotherm model is suitable for inhomogeneous adsorbent surfaces containing more than one type of active site and has been widely used for dye adsorption studies. Assuming multilayer adsorption, this model highlights the adsorbent's surface heterogeneity (Chowdhury and Balasubramanian, 2014). Langmuir and Freundlich's equations have been applied for adsorption data in various research on GO-based nano-adsorbents for dye adsorption. However, the Langmuir model is more suitable for most study reports (Table 2). That clarifies that dye adsorption utilizing GO-based nano adsorbents often occurs as a single layer process and is a surface occurrence.

Meanwhile, several studies report that the Redlich-Peterson (RP) model is the best model that best fits the experimental adsorption data. The Freundlich and Langmuir isotherm equations are combined in the RP model so that both models may be used to describe the adsorption process. It is said that the adsorbent/adsorbate interaction begins in the single layer and afterwards, by occupying the active sites of the composite during the adsorption process, begins to occur in the double layer (Bonilla-Petriciolet et al., 2017).

Table 2. Kinetic models and adsorption isotherms for dyes by GO-based nano adsorbents

Adsorbent	Dye	Adsorption isotherm	Adsorption kinetics	Reference
Magnetic cyclodextrin–chitosan/graphene oxide (MCCG)	Methylene blue	Langmuir	PSO	(Fan et al., 2013)
Fe_3O_4/GO-freeze dried (MGO-FD)	Rhodamine B	Langmuir	PSO	(Faghihi et al., 2016)
Magnetic polypyrrole nanocomposite (MGO/PPy)	Methylene blue	Langmuir	PSO	(Nezhad et al., 2018)
GO-Fe3O4@P4VP	Methylene blue	Freundlich	PSO	(Li et al., 2019)
Magnetic IO-Incorporated CSGO Hydrogel (CSGOIO)	Methylene blue	Freundlich	PSO	(Singh et al., 2019)
Magnetic/graphene/chitosan nanocomposite (MGCH)	2-naphthol	Freundlich	PSO	(Rebekah et al., 2020)
Graphene oxide@CoFe2O4 ($GO@CoFe_2O_4$)	Congo red	Langmuir	PSO	(Tran et al., 2020)
	Methyl red	Langmuir	PSO	
	Crystal violet	Langmuir	PSO	
Fe_3O_4-graphene@mesoporous SiO_2 (MG@m-SiO_2)	Methylene blue	Langmuir	PSO	(Wu et al., 2016)

Adsorbent	Dye	Adsorption isotherm	Adsorption kinetics	Reference
Ni@reduced-graphene oxide (Ni@rGO)	Methylene blue	-	PSO	(Calimli et al., 2020)
Fe_3O_4@C/GO	Methylene blue	Langmuir	PSO	(Chen et al., 2021)
Graphene oxide (GO)	Basic blue 41	Langmuir	PSO	(Hosseinabadi-Farahani et al., 2015)
	Basic red 18	Langmuir	PSO	
	Basic red 46	Langmuir	PSO	
N-doped GO (NGO)	Congo red	Langmuir	PSO	(Yokwana et al., 2018)
Graphene oxide (GO)	Ethyl violet	Langmuir	PSO	(Odiongenyi, 2019)
Graphene oxide (GO)	Methylene blue	Freundlich	PSO	(Ciğeroğlu et al., 2021)
Graphene oxide (GO)	Basic red 46	Langmuir	PSO	(Shoushtarian et al., 2020)
Cellulose nanocrystals and graphene oxide (CNC:GO)	Basic blue 7	Redlich-Peterson	PSO	(da Silva et al., 2021)
	Reactive orange 122	Redlich-Peterson	PSO	
	Methyl orange	Redlich-Peterson	PSO	
MATCHA-co-AA@GO	Malachite green	Freundlich	PSO	(Niknezhad and Mansour Lakouraj, 2021)
	Methylene blue	Freundlich	PSO	
GO/PAN	Actacid orange - RL	Langmuir	PSO	(Noreen et al., 2021)
GO/PPy		Langmuir	PSO	
GO/PSty		Langmuir	PSO	
Acrylamide/graphene oxide bonded sodium alginate (AM-GO-SA)	Crystal violet	Redlich-Peterson	PSO	(Pashaei-Fakhri et al., 2021)
Barium alginate-bentonite-graphene oxide composite (3D-BA/GO) hydrogel	Methylene blue	Freundlich	PSO and Elovich	(Wang et al., 2022)

The study of the adsorption kinetics of dye onto GO-based nano-adsorbent indicated that adsorption takes place in two steps. When there are many active sites on the adsorbent's surface, the dye ion absorbs quickly, then slowly as the active sites fill up (Chen et al., 2016). That shows that the overall adsorption rate is controlled by the speed of sorbate adsorption in the operational areas (Wang and Guo, 2020). The initial rapid stage happens quickly after the process begins, whereas the second phase controls the remainder and is frequently the rate-limiting step. The kinetic data were fitted to several models, such as pseudo-first-order (PFO), pseudo-second-order (PFO), and so on, to investigate the adsorption kinetics thoroughly. Among the various models, the PSO kinetic model is the best match for adjusting the experimental data for dye adsorption by GO-based nano adsorbents (Table 2).

Almost all studies reported that PSO is a kinetic model ideal for the adsorption mechanism because its R2 value is the best compared to other kinetic models. According to the PSO model, the adsorption process involves chemisorption, which explains an excellent electronic change with the formation of covalent bonds between molecules and one or more atoms on the surface. That is different

from physisorption, where there is almost no change in atomic or molecular structure (Oprea et al., 2019). Chemisorption implies adsorption occurring on a single molecular layer or surface layer involving electron transfer between sorbate and nano-adsorbent adsorption sites. However, there is still no in-depth explanation of the molecular or atomic changes in the adsorption process.

3.4. Durability and Reusability

Durability and reusability are crucial factors to consider when developing adsorption materials for wastewater treatment. A suitable adsorbent must be durable and capable of being reused several times while retaining specific capacity. Whereas durability prevents adsorbents from being released into the environment, which can cause secondary contamination, reuse increases cost-effectiveness. Many researchers have researched about reusability of various GO-based adsorbents for dye adsorption, with reported excellent recyclability rates. Regeneration of used adsorbents involves desorbing the dye using a solid base or acid (Chen et al., 2021; Wang et al., 2022).

Faghihi et al. (2016) used adsorbent MGO-Freeze Dried to adsorb rhodamine B and discovered that the adsorbent could be used up to 8 repetitions without damaging adsorbent material. Despite this, adsorption capacity went down from 114 mg/g to 104 mg/g during the eighth cycle, a loss of just 8.77 per cent. In another study, Singh et al. (2019) used CSGOIO adsorbent for methylene blue adsorption and obtained a decrease in adsorption capacity of about 4% after four repetitions. Chen et al. (2021) have done a similar study on the adsorption of methylene blue, which showed a 6% decrease in the adsorption capacity of Fe_3O_4@C/GO after five cycles. However, while most of these investigations have demonstrated that GO-based nano-adsorbents are reusable, their stability has not been thoroughly investigated. As a result, additional research in this area will be required.

4. Conclusions

These decade-long studies clearly show that GO-based nano-adsorbents have brought up new avenues in discovering efficient adsorbents to remove environmental contaminants. Continuous efforts in developing GO-based adsorbents are modifications to increase their adsorption capacity against pollutants such as dyes. Using GO composites, both magnetic and organic, has opened up opportunities to develop GO-based adsorbents. The good performances of GO-based adsorbents have stimulated much interest in developing GO-based nano-adsorbents, thanks to many reports on the topic. Furthermore, aspects such as the suitable synthesis method, interplay between surface functional groups and dye ions, and stability of the synthesis product need to be studied further.

References

Akar, T., Uzun, C., Çelik, S., Akar, S.T., 2018. Biosorption of basic blue 7 by fungal cells immobilized on the green-type biomatrix of phragmites australis spongy tissue. Internationa Journal Phytoremediation 20, 145–152.

Bonilla-Petriciolet, A., Mendoza-Castillo, D.I., Reynel-Ávila, H.E., 2017. Adsorption processes for water treatment and purification, 1st ed, Adsorption Processes for Water Treatment and Purification. Springer International Publishing.

Calimli, M.H., Nas, M.S., Burhan, H., Mustafov, S.D., Demirbas, Ö., Sen, F., 2020. Preparation, characterization and adsorption kinetics of methylene blue dye in reduced-graphene oxide supported nanoadsorbents. Journal of Molecular Liquids 309.

Calza, P., Zacchigna, D., Laurenti, E., 2016. Degradation of orange dyes and carbamazepine by soybean peroxidase immobilized on silica monoliths and titanium dioxide. Environmental Science and Pollution Research 23, 23742–23749.

Cao, X.T., Showkat, A.M., Kang, I., Gal, Y.S., Lim, K.T., 2016. β-Cyclodextrin multi-conjugated magnetic graphene oxide as a nano-adsorbent for methylene blue removal. Journal of Nanoscience and Nanotechnology 16, 1521–1525.

Chen, D., Zhang, H., Yang, K., Wang, H., 2016. Functionalization of 4-aminothiophenol and 3-aminopropyltriethoxysilane with graphene oxide for potential dye and copper removal. Journal of Hazardous Materials 310, 179–187.

Chen, F., Liang, W., Qin, X., Jiang, L., Zhang, Y., Fang, S., Luo, D., 2021. Preparation and recycled simultaneous adsorption of methylene blue and Cu2+ co-pollutants over carbon layer encapsulated Fe3O4 /graphene oxide nanocomposites rich in amino and thiol groups. Colloids Surfaces A Physicochem. Eng. Asp. 625.

Chen, J.H., Xing, H.T., Sun, X., Su, Z.B., Huang, Y.H., Weng, W., Hu, S.R., Guo, H.X., Wu, W.B., He, Y.S., 2015. Highly effective removal of Cu(II) by triethylenetetramine-magnetic reduced graphene oxide composite. Applied Surface Science 356, 355–363.

Chowdhury, S., Balasubramanian, R., 2014. Recent advances in the use of graphene-family nanoadsorbents for removal of toxic pollutants from wastewater. Advances in Colloid and Interface Science.

Ciğeroğlu, Z., Haşimoğlu, A., Özdemir, O.K., 2021. Synthesis, characterization and an application of graphene oxide nanopowder: methylene blue adsorption and comparison between experimental data and literature data. Journal of Dispersion Science and Technology 42, 771–783.

da Silva, P.M.M., Camparotto, N.G., Figueiredo Neves, T., Mastelaro, V.R., Nunes, B., Siqueira Franco Picone, C., Prediger, P., 2021. Instantaneous adsorption and synergic effect in simultaneous removal of complex dyes through nanocellulose/graphene oxide nanocomposites: Batch, fixed-bed experiments and mechanism. Environ. Environmental Nanotechnology, Monitoring & Management 16.

Dehghani, M.H., Karri, R.R., Alimohammadi, M., Nazmara, S., Zarei, A., Saeedi, Z., 2020. Insights into endocrine-disrupting Bisphenol-A adsorption from pharmaceutical effluent by chitosan immobilized nanoscale zero-valent iron nanoparticles. Journal of Molecular Liquids 311, 113317.

Dutta, S., Gupta, B., Srivastava, S.K., Gupta, A.K., 2021. Recent advances on the removal of dyes from wastewater using various adsorbents: A critical review. Materials Advances 2, 4497–4531.

Faghihi, A., Vakili, M.H., Hosseinzadeh, G., Farhadian, M., Jafari, Z., 2016. Synthesis and application of recyclable magnetic freeze-dried graphene oxide nanocomposite as a high capacity adsorbent for cationic dye adsorption. Desalin. Water Treat 57, 22655–22670.

Fan, L., Luo, C., Sun, M., Qiu, H., Li, X., 2013. Synthesis of magnetic β-cyclodextrin-chitosan/graphene oxide as nanoadsorbent and its application in dye adsorption and removal. Colloids Surfaces B Biointerfaces 103, 601–607.

Fazal, S., Zhang, B., Zhong, Z., Gao, L., Chen, X., 2015. Industrial wastewater treatment by using MBR (membrane bioreactor) review studyJournal of Environmental Protection 06, 584–598.

Guo, H., Jiao, T., Zhang, Q., Guo, W., Peng, Q., Yan, X., 2015. Preparation of graphene oxide-based hydrogels as efficient dye adsorbents for wastewater treatment. Nanoscale Research Letters 10, 1–10.

Habiba, U., Siddique, T.A., Joo, T.C., Salleh, A., Ang, B.C., Afifi, A.M., 2017. Synthesis of chitosan/polyvinyl alcohol/zeolite composite for removal of methyl orange, Congo red and chromium(VI) by flocculation/adsorption. Carbohydr. Polym 157, 1568–1576.

Hejazi Khah, M., Jamshidi, P., Shemirani, F., 2021. Applicability of an eco-friendly deep eutectic solvent loaded onto magnetic graphene oxide to preconcentrate trace amount of indigotin blue dye. Journal of Molecular Liquids 342.

Helmy, Q., Suryawan, I.W.K., Notodarmojo, S., 2022. Ozone-based processes in dye removal 91–128.

Hosseinabadi-Farahani, Z., Hosseini-Monfared, H., Mahmoodi, N.M., 2015. Graphene oxide nanosheet: preparation and dye removal from binary system colored wastewater. Desalin. Water Treat. 56, 2382–2394.

Huang, X., Qi, X., Boey, F., Zhang, H., 2012. Graphene-based composites. Chemical Society Reviews 41, 666–686.

Jiao, T., Zhao, H., Zhou, J., Zhang, Q., Luo, X., Hu, J., Peng, Q., Yan, X., 2015. Self-assembly reduced graphene oxide nanosheet hydrogel fabrication by anchorage of chitosan/silver and its potential efficient application toward dye degradation for wastewater treatments. ACS Sustain. Chemical Engineering 3, 3130–3139.

Khurana, I., Saxena, A., Bharti, Khurana, J.M., Rai, P.K., 2017. Removal of dyes using graphene-based composites: a review. Water, Air, & Soil Pollution 228.

Kim, S., Park, C.M., Jang, M., Son, A., Her, N., Yu, M., Snyder, S., Kim, D.H., Yoon, Y., 2018. Aqueous removal of inorganic and organic contaminants by graphene-based nanoadsorbents: A review. Chemosphere.

Lertcumfu, N., Jaita, P., Thammarong, S., Lamkhao, S., Tandorn, S., Randorn, C., Tunkasiri, T., Rujijanagul, G., 2020. Influence of graphene oxide additive on physical, microstructure, adsorption, and photocatalytic properties of calcined kaolinite-based geopolymer ceramic composites. Colloids and Surfaces A: Physicochemical and Engineering Aspects 602, 125080.

Li, Y., Lu, H., Wang, Y., Zhao, Y., Li, X., 2019. Efficient removal of methyl blue from aqueous solution by using poly(4-vinylpyridine)–graphene oxide–Fe 3 O 4 magnetic nanocomposites. Journal of Materials Science 54, 7603–7616.

Majhi, D., Patra, B.N., 2020. Polyaniline and sodium alginate nanocomposite: a pH-responsive adsorbent for the removal of organic dyes from water. RSC Advances 10, 43904–43914.

Manera, C., Tonello, A.P., Perondi, D., Godinho, M., 2018. Adsorption of leather dyes on activated carbon from leather shaving wastes: kinetics, equilibrium and thermodynamics studies. Environmental Technology 40, 2756–2768.

Neolaka, Y.A.B., Lawa, Y., Naat, J.N., Riwu, A.A.P., Iqbal, M., Darmokoesoemo, H., Kusuma, H.S., 2020. The adsorption of Cr(VI) from water samples using graphene oxide-magnetic (GO-Fe3O4) synthesized from natural cellulose-based graphite (kusambi wood or Schleichera oleosa): Study of kinetics, isotherms and thermodynamics. Journal of Materials Research and Technology 9, 6544–6556.

Nezhad, A.A., Alimoradi, M., Ramezani, M., 2018. One-step Preparation of graphene oxide/polypyrrole magnetic nanocomposite and its application in the removal of methylene blue dye from aqueous solution. Materials Research Express 5.

Niknezhad, M., Mansour Lakouraj, M., 2021. Development of pH-sensitive hydrogel nanocomposite based on acrylic acid/ graphene oxide/acryloyl tetra ammonium thiacalix[4]arene for separation of cationic dyes. Journal of Polymer Research 28.

Noreen, S., Tahira, M., Ghamkhar, M., Hafiz, I., Bhatti, H.N., Nadeem, R., Murtaza, M.A., Yaseen, M., Sheikh, A.A., Naseem, Z., Younas, F., 2021. Treatment of textile wastewater containing acid dye using novel polymeric graphene oxide nanocomposites (GO/PAN,GO/PPy, GO/PSty). Journal of Materials Research and Technology 14, 25–35.

Odiongenyi, A.O., 2019. Removal of Ethyl Violet Dye from Aqueous Solution by Graphite Dust and Nano Graphene Oxide Synthesized from Graphite Dust. Communications Physics 103–109.

Oprea, A., Degler, D., Barsan, N., Hemeryck, A., Rebholz, J., 2019. Basics of semiconducting metal oxide–based gas sensors. Gas Sensors Based Conduct. Met. Oxides Basic Understanding, Technology Application, 61–165.

Pashaei-Fakhri, S., Peighambardoust, S.J., Foroutan, R., Arsalani, N., Ramavandi, B., 2021. Crystal violet dye sorption over acrylamide/graphene oxide bonded sodium alginate nanocomposite hydrogel. Chemosphere 270.

Rachna, K., Agarwal, A., Singh, N.., 2019. Rice husk and Sodium hydroxide activated Rice husk for removal of Reactive yellow dye from water. Materials Today: Proceedings 12, 573–580.

Rahim Pouran, S., Abdul Raman, A.A., Wan Daud, W.M.A., 2014. Review on the application of modified iron oxides as heterogeneous catalysts in Fenton reactions. Journal of Cleaner Production 64, 24–35.

Rebekah, A., Bharath, G., Naushad, M., Viswanathan, C., Ponpandian, N., 2020. Magnetic graphene/chitosan nanocomposite: A promising nano-adsorbent for the removal of 2-naphthol from aqueous solution and their kinetic studies. International Journal of Biological Macromolecules 159, 530–538.

Sharma, S., Hasan, A., Kumar, N., Pandey, L.M., 2018. Removal of methylene blue dye from aqueous solution using immobilized Agrobacterium fabrum biomass along with iron oxide nanoparticles as biosorbent. Environmental Science and Pollution Research 25, 21605–21615.

Sherlala, A.I.A., Raman, A.A.A., Bello, M.M., Asghar, A., 2018. A review of the applications of organo-functionalized magnetic graphene oxide nanocomposites for heavy metal adsorption. Chemosphere.

Shoushtarian, F., Moghaddam, M.R.A., Kowsari, E., 2020. Efficient regeneration/reuse of graphene oxide as a nanoadsorbent for removing basic Red 46 from aqueous solutionsJournal of Molecular Liquids 312.

Singh, N., Riyajuddin, S., Ghosh, K., Mehta, S.K., Dan, A., 2019. Chitosan-Graphene Oxide Hydrogels with Embedded Magnetic Iron Oxide Nanoparticles for Dye Removal. ACS Applied Nano Materials 2, 7379–7392.

Tran, T. Van, Nguyen, H.T.T., Dang, H.H., Nguyen, D.T.C., Nguyen, D.H., Pham, T. Van, Tan, L. Van, 2020. Central composite design for optimizing the organic dyes remediation utilizing novel graphene oxide@CoFe2O4 nanocomposite. Surfaces and Interfaces 21.

Wang, J., Guo, X., 2020. Adsorption kinetic models: Physical meanings, applications, and solving methods. Journal Hazard Mater 390, 122156.

Wang, L.C., Ni, X. jiong, Cao, Y.H., Cao, G. qun, 2018. Adsorption behavior of bisphenol A on CTAB-modified graphite. Applied Surface Science 428, 165–170.

Wang, M., Li, Y., Cui, M., Li, M., Xu, W., Li, L., Sun, Y., Chen, B., Chen, K., Zhang, Y., 2022. Barium alginate as a skeleton coating graphene oxide and bentonite-derived composites: Excellent adsorbent based on predictive design for the enhanced adsorption of methylene blue. Journal of Colloid and Interface Science 611, 629–643.

Widajatno, R.L., Kardena, E., Arifianingsih, N.N., Helmy, Q., 2022. Activated Sludge: Conventional Dye Treatment Technique 119–153.

Wu, J., Andrews, M.P., 2020. Carboxylated Cellulose Nanocrystal Microbeads for Removal of Organic Dyes from Wastewater: Effects of Kinetics and Diffusion on Binding and Release. ACS Applied Nano Mater 3, 11217–11228.

Wu, X.L., Shi, Y., Zhong, S., Lin, H., Chen, J.R., 2016. Facile synthesis of Fe3O4 -graphene@mesoporous SiO 2 nanocomposites for efficient removal of Methylene Blue. Applied Surface Science 378, 80–86.

Xing, R., Wang, W., Jiao, T., Ma, K., Zhang, Q., Hong, W., Qiu, H., Zhou, J., Zhang, L., Peng, Q., 2017. Bioinspired Polydopamine Sheathed Nanofibers Containing Carboxylate Graphene Oxide Nanosheet for High-Efficient Dyes Scavenger. ACS Sustainable Chemistry & Engineering 5, 4948–4956.

Yokwana, K., Kuvarega, A.T., Mhlanga, S.D., Nxumalo, E.N., 2018. Mechanistic aspects for the removal of Congo red dye from aqueous media through adsorption over N-doped graphene oxide nanoadsorbents prepared from graphite flakes and powders. Physics and Chemistry of the Earth 107, 58–70.

Zare-Dorabei, R., Ferdowsi, S.M., Barzin, A., Tadjarodi, A., 2016. Highly efficient simultaneous ultrasonic-assisted adsorption of Pb(II), Cd(II), Ni(II) and Cu(II) ions from aqueous solutions by graphene oxide modified with 2,2′-dipyridylamine: Central composite design optimization. Ultrason. Sonochem. 32, 265–276.

Zhang, Y., Zhang, S., Gao, J., Chung, T.S., 2016. Layer-by-layer construction of graphene oxide (GO) framework composite membranes for highly efficient heavy metal removal. Journal of Membrane Science 515, 230–237.

Zhao, H., Jiao, T., Zhang, L., Zhou, J., Zhang, Q., Peng, Q., Yan, X., 2015. Preparation and adsorption capacity evaluation of graphene oxide-chitosan composite hydrogels. Science China Materials 58, 811–818.