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Recent trends in the synthesis of graphene and graphene oxide based nanomaterials for removal of heavy metals-A review

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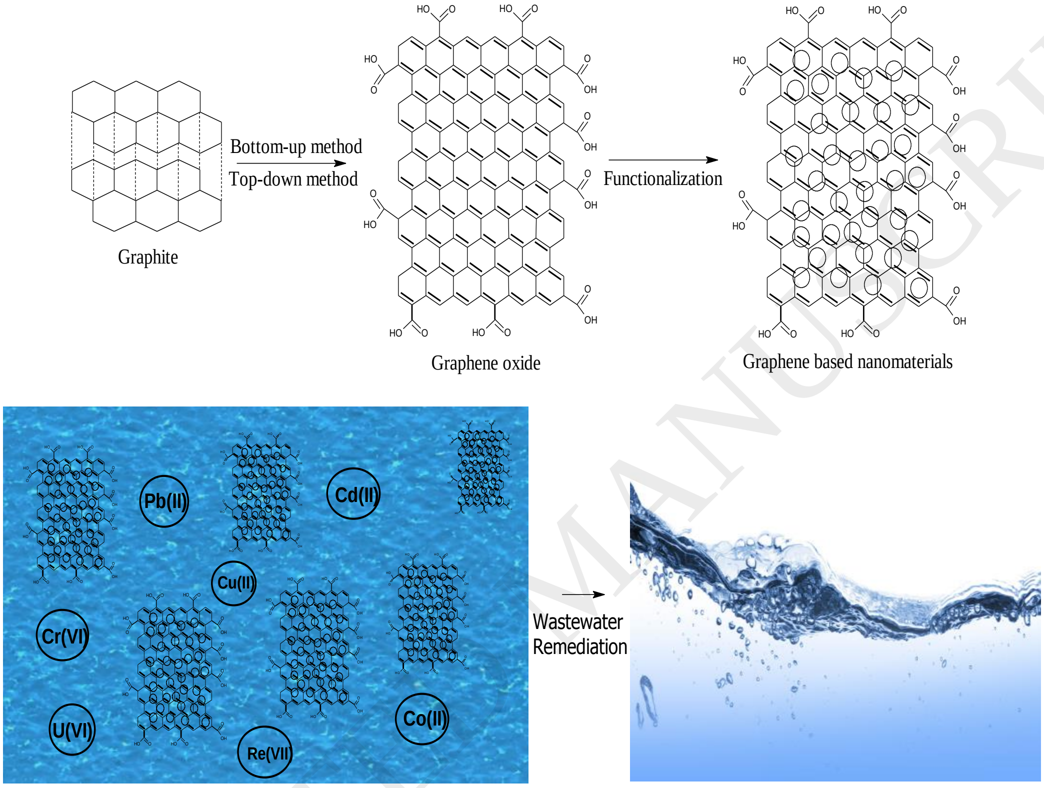
Graphical Abstract



Abstract

The advanced synthesis and development of raw graphene based on various significant functionalization has been outstanding in the wastewater treatment compared to the other alternatives such as carbon nanotubes and other carbon nanomaterials. Nano size graphene is known to possess large surface area and some promising properties in terms of mechanical, electrical, chemical and magnetism. Besides, the graphene can be generated via both Top-down and Bottom-up methods such as chemical exfoliation, chemical vapor deposition and other techniques so that it can be further functionalized to form graphene oxide-based nanomaterials. Hence, graphene oxide-based nanomaterials are discovered to be useful in the application of heavy metal removal from wastewater. In short, this paper critically reviewed on the synthesis method of graphene and application of graphene oxide-based nanomaterials in the term of heavy metal removal. The advantages, drawbacks, comparison of the data efficiencies, and research requirements are further highlighted, elaborated and discussed detailly. Lastly, the future challenges of graphene are elaborated. Therefore, it can be guaranteed that the wastewater discharged should be detected with the minimum or none of the heavy metals so that minimum effects on the ecosystem is discovered.

Key words: Graphene, Heavy metals, Nanomaterials, graphene oxide, nanoparticle

1. Introduction

Graphene can be extracted from graphite and it is merely a sheet of graphite. It is defined as a single layer of sp2 bonded carbon atoms in hexagonal lattice arrangement. At the same time, graphene possesses few promising properties such as good electronic properties caused by the bonding and anti-bonding of the pi orbitals. Furthermore, graphene is clarified to be the strongest substance in terms of mechanical strength since it possesses high tensile strength and it is light in weight. For instance, it is more than 40 times stronger than diamond and more than 300 times stronger than A36 structural steel, at 130 GPa[1]. Meanwhile, for the optical properties, high absorption of white light up to 2.3% is capable to be observed from graphene.

Besides of the impressive properties, appropriate method to produce graphene must be taken into consideration. There are two different type of methods to produce graphene which are exfoliation methods and direct growth of graphene layer which can be known as Top-down and Bottom-up methods respectively[2]. Methods to generate graphene include "Scotch Tape Method", dispersion of graphite, exfoliation of graphite oxide, epitaxial growth and lastly chemical vapor deposition (CVD)[3]. However, improved Hummers method which falls under method of dispersion of graphite is widely used since it is an improved method which excludes the usage of toxic chemical and at the same time enhances the reaction performance[4].

Lately, water pollution caused by poisonous heavy metals has led to an attentional environmental problem in world-wide[5]. In the industrial which involve manufacture of printed board, textile dyes, metal finishing and plating and semiconductor manufacturing, most likely there will be presence of heavy metals such as lead, mercury, copper, zinc, tin, cadmium and the likes in wastewater[6]. The heavy metals mentioned above are not biological degradable like organic pollutants and they are known to be harmful and toxic[7]. The presence of heavy metals in wastewater will then accumulate in living creatures or creating environmental problem if it is not treated properly. Thus, appropriate as well as effective alternatives must be applied to remove or minimise the heavy metals.

There are few popular alternatives to remove heavy metals from wastewater such as chemical coagulation, membrane separation, precipitation, electro-kinetics, electroplating and ion-exchange. However, biological remediation, activated biocarbon and micro-extraction via carbon nanotubes and ionic liquids are usually applied[8]. Yet, heavy metal removal via graphene oxide-based nanomaterials can be considered as well since it is a potential nanomaterial which possessing good properties. Graphene oxide is selected to be studied instead of graphene for heavy metal removal because functionalized of graphene oxide with other composites are easier and more effective due to the presence of other functional groups.

Generally, graphene oxide generated via improved Hummers method are prepared to be further functionalized as chemical functionalization of graphene oxide can be one of the best approach for heavy metal removal[9]. However, before functionalization takes place, the graphene oxide (GO) can be further transformed into graphene nanosheets (GNs) via acid treatment. Functionalization can be defined as the route where addition of new properties, purposes, structures, or abilities to a substance via the alteration of the material in the aspect of surface chemistry. It is acknowledged that this is an essential method utilised throughout different field such as biological engineering, chemistry, nanotechnology, materials science and the likes[10]. Functionalization can be done through the attachment of particles or nanoparticles to the surface of a substance, either via chemical bond or via adsorption. For instance, the functionalized graphene can be produced via noncovalent and covalent alteration techniques. Both techniques share a similar process which is superficial alteration of GO followed by reduction. Therefore, functionalized graphene will have a better performance on heavy metal removal compared to other nanomaterials.

In this study, the approaches to generate graphene has been critically reviewed. Besides, a summary regarding to the heavy metal removal via graphene and graphene oxide-based nanomaterials have been discussed in detail. Hence, significant contribution can be made to preserve the cleaner wastewater with minimum level of heavy metals. Lastly, future perspectives and challenges encountered of graphene are stated and elaborated based on the literature and hence recommendations are provided for the further study.

2. Synthesis of Graphene

Production of graphene can be carried out via two different strategies which are Top-Down strategy and Bottom-Up strategy[11]. The process flow chart can be illustrated as the Figure 1 below.

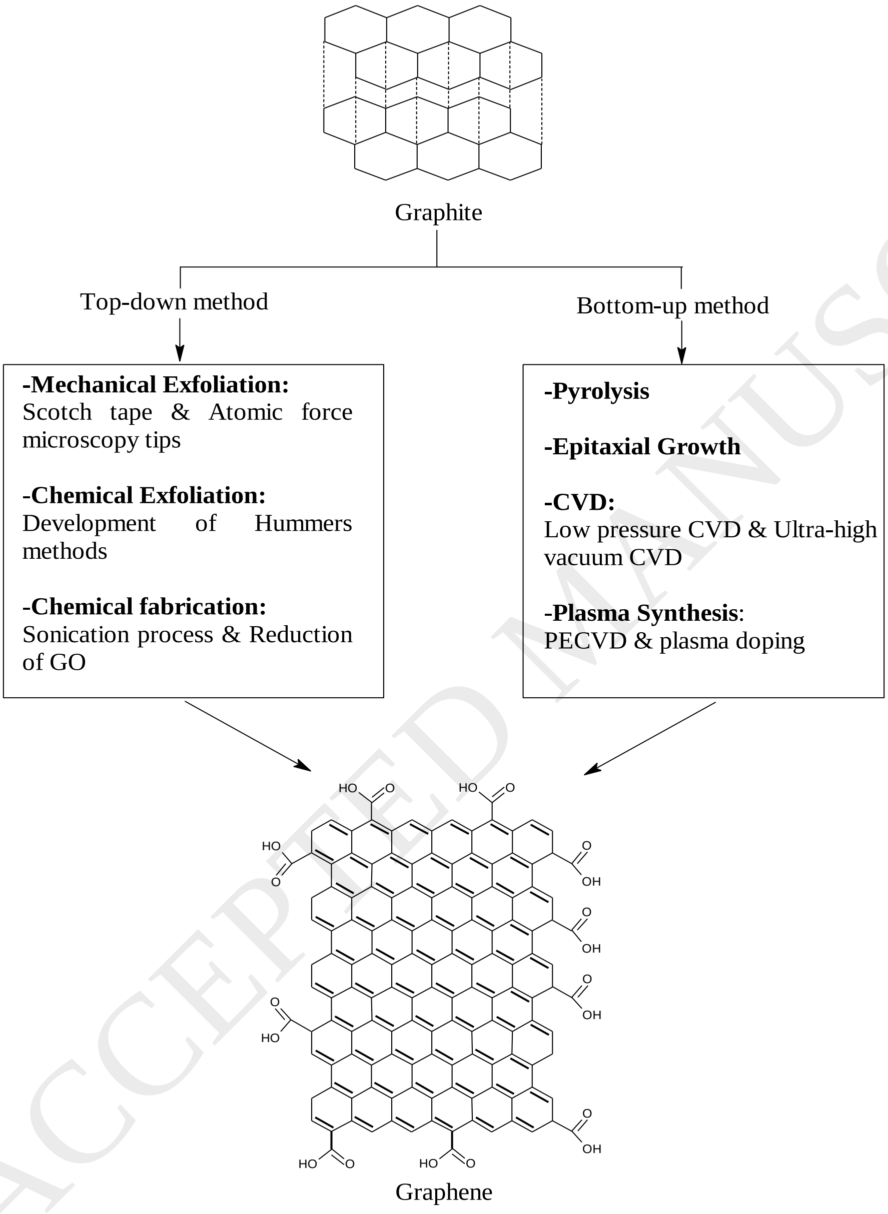


Figure 1: Process flow chart of graphene synthesis.

2.1 Top-down Technique

Top-Down strategy can be explained as the strategy which is depending on the powdered raw graphite attack. The attack will eventually separate its layer to generate graphene sheets. For instance, mechanical or chemical exfoliation and chemical synthesis are categorised in the Top-Down strategy[12].

2.1.1 Mechanical Exfoliation

Mechanical exfoliation is considered as well-known yet oddest method to extract monolayer graphene flakes on favored substrates. It is the earliest documented technique to synthesis graphene. This technique is applied in nanotechnology where the superficial of the layered materials is experiencing either transverse or longitudinal stress. Formation of graphite is done when there is stacking of single atomic graphene layers via poor van der Waals forces. For the interlayer data, the distance and bond energy value at 3.34 Å and 2 eV/nm^2 respectively[12]. However, for mechanical cleaving, requirement of external force up to 300nN/μm^2 has to be met so that separation of single atomic layer from graphite can be done[13]. Perpendicular overlapping of partially filled p orbital onto the plane of sheet which includes van der Waals forces causes sheets stacking. Exfoliation is the reverse step of stacking resulting in poor bonding and big lattice spacing in the vertical direction. Yet, in the lattice plane with hexagonal shape, it results in better bonding and tiny lattice spacing[14]. Hence, by implementing mechanical exfoliation or method such as taking off layers from graphitic substances such as natural graphite[15], mono-crystal graphite[16] and highly ordered pyrolytic graphite[17], formation of graphene sheets with various thickness can be witnessed. The exfoliation technique can be carried out via agents such as electric field[18], ultra-sonication[19], transfer printing technique[20] and scotch tape.

2.1.2 Chemical Reduction of Graphite Oxide

Besides, another Top-Down technique to generate great amount of graphene is chemical reduction of graphite oxide. Oxidation of graphite is always performed to synthesis graphite oxide. The oxidation can be done via few types of oxidants involving nitric acid, potassium permanganate and concentrated sulfuric acid. Besides, another alternative to synthesis graphene are reduction of GO and sonication. Great amount of $NaBH_4$ has been utilized as reducing agent when the alkenes is added with H_2 comes with the extrusion of N_2 gas. However, there are other reducing agents to be utilized such as hydroxylamine, ascorbic acid, glucose, phenyl hydrazine, hydroquinone, pyrrole and alkaline solutions. Furthermore, formation of graphene in large quantities can be done by electrochemical reduction. For instance, in 1962, establishment of single layer flakes of reduced GO was first done. Then, sonication of graphite oxide solution can be done to get GO nanoplatelets. Thus, the removal of oxygen groups can be done via the implementation of reducing agent such as hydrazine. Yet, the reduction process is not complete and hence there is presence of some leftover oxygen. GO is a potential material due to its hydrophilic individual layers. Next, to produce monolayer or double-layered GO, GO first should undergo suspension in water via sonication and next deposition onto surfaces via filtration or spin coating. Therefore, thermal or chemical reduction of GO can eventually generate graphene films. In addition, an easy procedure such as solvo thermal reduction alternative is favorable to form reduced GO dispersion in the organic solvent.

2.1.3 Chemical Exfoliation

However, chemical exfoliation which is the Top-Down method is best to be utilized to produce graphene. Chemical exfoliation can be done in a two-step procedure[21]. Firstly, increment of interlayer spacing is done by reducing the van der Waals forces of the interlayer. Then, fast heating process or sonication is carried out to exfoliate graphene into single to few layers thick. For instance, ultra-sonication is required to extract monolayer GO. In 1860, GO was first generated via Brodie[22], Staudenmaier[23], and Hummers[24] approaches. Then the development of Hummers method has led to the creation of modified Hummers method and Improved Hummers method[25]. Hence, the major differences, type of oxidants used, the toxicity and the significant advantages and disadvantages of each method mentioned previously are discussed in Table 1 to make comparison and show development of the methods. Hence, improved Hummers method illustrates the most suitable method to be applied due to its free toxicity and its ability to produce more organized graphene structure[26].

Table 1: Development of graphene synthesis methods.

Method	**Date discovered**	**Oxidants**	**Toxicity**	**Advantage**	**Disadvantage**	**Reference**
Brodie Method	12th May 1859	$KClO_3$, HNO_3	Yes	- Obtain small graphene sheet size and large surface area	- Poor acidity. - Soft dispersion ability in basic solutions. - Small size, limited thickness and imperfect structure provided.	[22];[27]
Staudenmaier Method	23th May 1898	$KClO_3$ ($NaClO_3$), HNO_3, H_2SO_4	Yes	- Less complexity compared to Brodie method (the complete reaction can be done in a mere vessel)	- Time-wasting and unsafe method.	[23];[25]

Hummers Method	20th March 1958	$KMnO_4$, H_2SO_4, $NaNO_3$	No (release of NO_x)	- Higher oxidation level compared to Staudenmaier or Brodie methods.	- Incomplete oxidation can be witnessed. - Purification and separation processes are tedious. - Time-wasting process.	[24]
Modified Hummers Method	22th October 2008	$KMnO_4$, H_2SO_4, $NaNO_3$	No (release of NO_x)	- Improvement in oxidation level enhances the product performance.	- Purification and separation processes are tedious. - Time-wasting process.	[28];[29]
Improved Hummers Method	22th July 2010	$KMnO_4$, H_2SO_4, H_3PO_4	No	- Less defects in the basal plane. - More oxidized graphite produced. - The reduction level results in the equal level of conductivity. - Achieved better process production compared to the	- Purification and separation processes are tedious. - Time-wasting process.	[30]

Brodie, Staudenmaier and Hummers method.

- Toxic gas free process promotes environmentally friendly process.
- More organized structure of graphite oxide achieved compared to that of Staudenmaier and Brodie methods.

2.2 Bottom-up Technique

On the other hand, Bottom-Up strategy is defined as the strategy which includes the utilization of carbonaceous gas to generate graphene. For instance, methods using Bottom-Up strategy include pyrolysis, CVD, epitaxial growth and the likes [12].

2.2.1 Pyrolysis

Throughout the pyrolysis technique, formation of graphene chemically via Bottom-Up method can be done by applying solvo thermal method. For instance, 1:1 of molar ratio of ethanol and sodium was determined in the vessel throughout the thermal reaction. Another example would be the pyrolization of sodium ethoxide via sonication. This process could easily enhance the performance of the graphene sheets detachment. Hence, the generated graphene sheets are measured up to 10μm. For instance, Raman spectroscopy, selected area (electron) diffraction and transmission electron microscopy are used to examine the graphitic nature, band structure, different layers and also crystalline structure [31].

2.2.2 Epitaxial Growth

Regarding to the methods of growth of graphene on surfaces, epitaxial growth is one of them. Preparation of graphene can be carried out by applying heat and cool down a silicon carbide (SiC) crystal. In general, on the Si face of the crystal, there will be single or bi-layer graphene however, on the C face, few-layer graphene is grown[32]. Yet, the outcomes are greatly relied on the parameters utilised, such as pressure, temperature or heating rate. Generally, it will favour the growth of nanotubes but not of graphene if it experiences too high pressure as well as temperature. Discovery of the graphitization of SiC is in 1955 but it is treated as an undesirable side effect over an approach of making graphene[33]. Lattice structure found on Nickel (III) surface is very alike to the one of graphene as the difference of the lattice constant is merely about 1.3%. Therefore, evaporation of a thin Nickel layer can be made onto the SiC crystal via the nickel diffusion approach[34]. When heat is applied, diffusion of carbon through the Nickel layer is occurred and hence formation of either graphene or graphite layer will be found on the surface but it depends on the degree of heating. Hence, the graphene formed is simpler to be separated from the exterior compared to the graphene generated by the growth on the silicon carbide crystal without Nickel. Anyhow, due to the grain boundaries and defects found, the graphene is not completely homogeneous and in addition the quality is hence is not comparable to the good quality graphene via exfoliation.

2.2.3 CVD

CVD is simply another method to make graphene. CVD can be explained as the deposition of gaseous reactants onto a substrate [35]. This method is functioned as the combination of gas molecules in a reaction chamber under optimum temperature and condition. When the substrate meets with the combined gases in the heated reaction chamber, formation of a material film is occurred on the substrate exterior. Then, the waste gases will be removed from the reaction chamber. However, temperature of the substrate is the significant condition to ensure the occurrence of reaction. Throughout the CVD process, coating is done on the substrate in a very little amount and at a very low speed like in microns of thickness per hour. This process is comparable to the physical vapour deposition (PVD) but the mere difference is that the precursors are in solid substance and hence the process is a little vary[36]. Vaporization of solid substances followed by deposition of solids onto a substrate by condensation are then carried out. For instance, there are two most famous process to carry out CVD which are low pressure chemical vapour deposition (LPCVD) and ultra-high vacuum chemical vapour deposition (UHVCVD). LPCVD is known to be operated under sub-atmospheric pressures to avoid unnecessary reactions and increase production of same coating thickness on substrate while UHCVD is operated under very low atmospheric pressures which is around 6-10 Pascal[37].

2.2.4 Plasma Synthesis

Other than LPCVD and UHVCVD, plasma synthesis of graphene is another Bottom-up method to be applied. It involves both plasma-enhanced chemical vapor deposition (PECVD) and plasma doping to generate graphene[38]. The various types of plasma such as energetic ions, highly reactive radicals, electrons, a fraction of the undissociated source gas and photons tend to vary the synthesis progressions. However, they act more actively compared to the ground-state types and hence high temperatures are required to carry out complete chemical reactions. Regarding to the PECVD technique, it can be categorized into three methods which are direct current plasma-enhanced chemical vapor deposition (DC-PECVD), inductively coupled plasma-enhanced chemical vapor deposition (ICP-PECVD) and microwave plasma-enhanced chemical vapor deposition (MW-PECVD). For the DC-PECVD, sustainability of plasma is based on the secondary electrons formed by the attack of accelerated ions among electrodes[39]. For instance, when the cathode is attacked by both of plasma ions and atoms, its atoms tend to release. Hence, the diffusion of sputtered atoms takes place through the plasma and cause impure atoms throughout the production of graphene. However, ICP-PECVD is known as a system which applies wave heating and generates plasma with the absence of electrodes and hence impurity caused by electrodes can be eliminated[40]. Application of plasma constraints including pressure, temperature and gas flow rate in the reaction cavity is done via ICP-PECVD. Therefore, accurate adjustments for both growth period and power of generated plasma can be done. Nonetheless, this method is considered as less effective yet environmental friendly and scalable. In the MW-PECVD, the plasma is produced via wave heating. Throughout the process of MW-PECVD, wet etching and transfer are not involved and hence none of the polymer pollution, remaining metallic impurities and metal catalysts are detected on the graphene films produced[41]. Other than that, for the plasma doping, graphene doped with other substances is a significant method to create various graphene with different electrical properties. For instance, one of the best efforts is introduction of heteroatoms such as nitrogen into the graphene sheets through plasma treatment to carry out the modification in its electrical properties[42]. Therefore, the nitrogen dopants have replaced the metal catalysts in producing graphene and they will affect the charge distributions of carbon atoms as well as spin density. In brief, this plasma synthesis method has some promising advantages such as lower energy requirement, improved catalyst stimulation, shorter production period, minimum environmental contaminations and lastly main properties retained throughout the process[38].

2.3 Analysis of Both Techniques

Thus, the brief history of both Top-Down and Bottom-Up methods are discussed in terms of typical dimension achieved for synthesised graphene and the advantages as well as drawbacks via Table 2. In short, the overview of different approaches to generate graphene can be summarized via Table 3 below. For instance, the Top-down methods have shown that the graphene obtained is in lower complexity. In addition, it guarantees high purity and quality but lower controllability and hence it favours the laboratory researches. However, for the Bottom-up methods, graphene produced is in high controllability, lower quality and purity and hence it merely suitable for industrial applications[2]. Thus, less defections are discovered on the graphene surfaces via Bottom-up alternatives than that of Top-down alternatives[43]. Nonetheless, generation of graphene via Bottom-up techniques is comparatively in higher complexity and costs[43]. Lastly, the Top-down and Bottom-up methods can be analogized and represented via Figure2. To summarize both main techniques mentioned above, both techniques have their advantages and drawbacks and hence new development or enhancements are required to be applied on the known approaches in order to generate Nano-sized graphene which possesses both high quality and quantity[43].

Table 2: Brief history of Bottom-Up and Top-Down methods.

Bottom-Up Method					
Method	**Typical Dimension**		**Advantage**	**Drawback**	**Reference**
	Thickness	**Lateral**			
Confined self-assembly	Single layer	100's nm	- Thickness guaranteed.	- Formation of deficiencies.	[44]
CVD	Few layer	Very large (cm)	- Bigger size. - Good quality.	- Low yield.	[45]
MW-PECVD	4-6 atomic layers	Larger than 1 μm	- Free of metallic catalyst.	- High energy consumption. - High production cost.	[46]
Arc discharge	Single, bi and few layers	Few 100 nm to a few μm	- Can generate ~10 g/h of graphene.	- Low graphene production.	[42]

				- Carbonaceous layers.	
Epitaxial growth on SiC	Few layers	Up to cm size	- Very big part of clean - Graphene.	- Very minor scale.	[47]
Unzipping of carbon nanotubes	Multiple layers	few μm long nano ribbons	- Controllable size by choice of the initial nanotubes.	- High cost preliminary material. - Oxidized graphene.	[48]
Reduction of CO	Multiple layers	Sub- μm	- Un-oxidized sheets.	- Impurity with α-Al_2O_3 and α-Al_2S.	[49]
Top-Down Method					

Micromechanical exfoliation	Few layers	μm to cm	- Big size and unchanged graphene sheets.	- Very low yield.	[50]
Direct sonication of graphite	Single and multiple layers	μm or sub-μm	- Unchanged graphene. - Low cost.	- Small production. Separation	[51]
Electrochemical exfoliation/functionalization of graphene	Single and few layers	500–700	- Sole step functionalization as well as exfoliation. - Higher conduction of electricity of the functionalized graphene.	- High cost required for ionic liquids.	[52]

Super acid dissolution of graphite	Mostly single layer	300–900 nm	- Unchanged graphene. - Measurable.	- Utilization of unsafe chlorosulfonic acid. - High cost to remove acid.	[53]

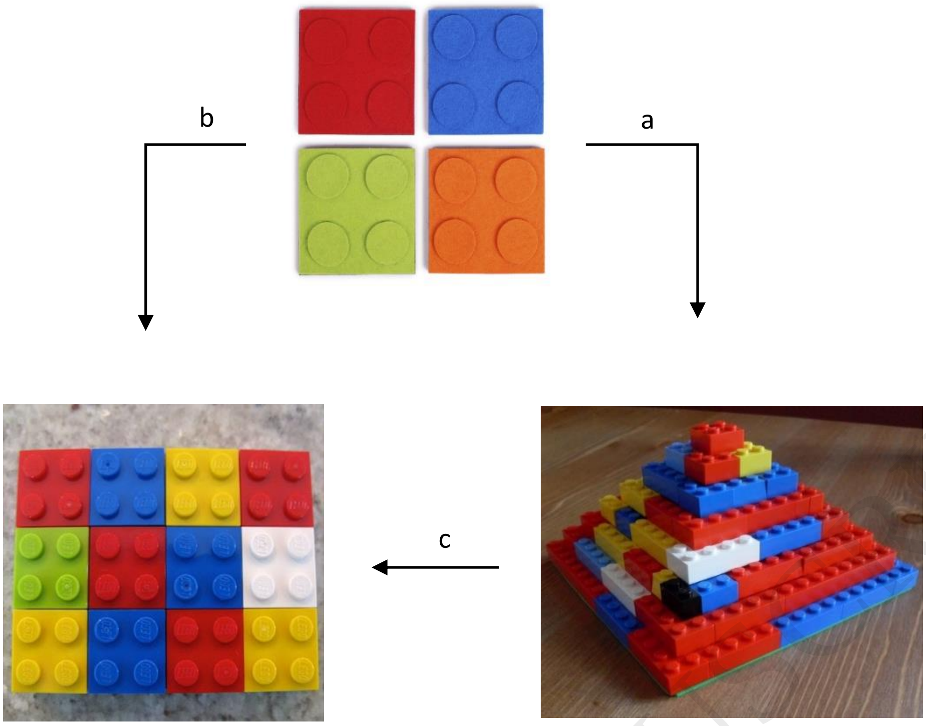


Figure 2: Comparison of Top-down and Bottom-up methods. (a) Bottom-up fabrication where a pyramid shaped Lego blocks is done through different single block of Legos. (b) Bottom-up fabrication where the different colour of Lego blocks is stacked to form a square block. (c) Top-down fabrication of a square Lego block produced from the removal of some Legos from the pyramid shaped Lego blocks.

Table 3: Overview of different synthesis methods of graphene[2].

Approaches	**CVD**	**Epitaxial growth**	**The Scotch Tape**	**Dispersion of Graphite**	**Exfoliation of Graphite Oxide**
Quantity	High	Low	Low	High	High
Quality/ Purity	Low	Low	High	High	Nil
Controllability	High	High	Low	Low	Low
Size	High	High	Low	Low	Low
Complexity	High	High	High	High	Low

3. Adsorption Mechanism of Graphene Oxide

The adsorption mechanisms of graphene oxide-based nanomaterials can be categorized into three main mechanisms which are adsorption isotherms, adsorption kinetics and adsorption thermodynamic. However, there are few specific adsorption mechanisms of graphene oxide-based nanomaterials discussed in the Table 4.

3.1 Adsorption Isotherms

Lastly, the adsorption isotherms are vital to analyse the adsorption capacity when the micro extraction of heavy metals is carried out. However, there are various kind of famous models to be used such as Temkin[54], Frenkel-Halsey-Hill[55], Henderson[56], Giles-Smith[57], DubininRadushkevich[58], MT[59], BET[60], BDST[61], Oswin[62], FerroFintan[63], GAB[64], and Peleg[65], Langmuir[66] and Freundlich[67]. However, widely used adsorption isotherms such as Langmuir and Freundlich models are focused and applied to illustrate the adsorption equilibrium between the adsorbent surface and the adsorbate[68]. For instance, single layer analysis on sorbent is assumed by Langmuir model while multilayer adsorption on sorbent is allowed via an empirical model which is Freundlich model[69].

Hence, the non-linear form of equation for Langmuir model can be expressed as below:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{1}$$

Where K_L is the constant in equilibrium (L. mg^{-1}), q_{max} is the maximum adsorption capacity (mg. g^{-1}) of sorbent, C is the concentration in equilibrium (mg. L^{-1}), q is the number of adsorbed metals at equilibrium (mg. g^{-1})[70].

However, for the linear equation, it is shown as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{b q_m} \tag{2}$$

Where q_m is the saturated single layer adsorption capacity, b is the adsorption constant in equilibrium and C_e is the concentration of sorbate in equilibrium.

For the Freundlich isotherm, the non-linear and linear form can be illustrated respectively as:

$$q_e = K_F {C_e}^{1/n}; \tag{3}$$

$$\log q_e = \log K_F + \frac{\log C_e}{n} \tag{4}$$

Where q_e is sorbate loading on sorbent at equilibrium (mg. g^{-1}); K_F is pointer of adsorption capacity (mg^{1-n}. L^n g^{-1}), n is sorption energetics and C_e is equilibrium liquid concentration of sorbate (mg. L^{-1}) [70].

3.2 Adsorption Kinetics

The kinetic predictions in the adsorption mechanism are significant and vital for the determination of adsorption equilibrium time and adsorption rate. There are few kinetic isotherms to be applied such as Bangham, pseudo-first-order, pseudo-second-order, intraparticle diffusion and Elovich equations[71]. For instance, Bangham equations is applied to define the pore diffusion during adsorption process[72]. However, pseudo-first-order is discovered to be appropriate for the first 20-30 minutes of interaction period and the rate limiting step is physisorption which explains the mechanism is not depending on the concentrations of reactants but the physical exchange such as diffusion[73]. On the other hand, pseudo-second-order fixes the rate limiting step as chemical adsorption which involves the sharing valence forces or electrons exchanges between the adsorbate and adsorbent[74]. Besides, for the intraparticle diffusion model, the identification of diffusion mechanism is taken place[75]. Yet, for the Elovich equations, it is best to explain the second order kinetic and multiple interaction mechanism by predicting the presence of energetically heterogeneous solid surfaces[76]. Yet, the pseudo-first-order and pseudo-second-order models are the frequent models to be implemented and fitted best with most of the heavy metals adsorption mechanism[68]. This is because both two kinetic models involve the processes of physisorption and chemisorption respectively.

The pseudo-first-order model can be expressed as below:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{5}$$

Where k_1 is the first order rate constant for the adsorption mechanism (min^{-1}), both q_e and q_t are the adsorbed metal ions per gram of adsorbents ($mg.\ g^{-1}$) at equilibrium and at the time of t (min)[77].

However, for pseudo-second-order model, it can be expressed as below:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \tag{6}$$

Where k$_2$ (g· mg^{-1}· min^{-1}) represents the second order rate constant for the adsorption process[77].

In addition, the rate of initial adsorption can be known as ‘h’ and the expression of ‘h’ is shown as below[77].

$$h = k_2 {q_e}^2 \tag{7}$$

3.3 Adsorption Thermodynamics

The equations below are the equations used to determine Gibbs free energy (ΔG^O, kJ/mol), enthalpy change (ΔH^O, kJ/mol), and entropy change (ΔS^O, kJ/(mol.K)) [78].

$$\Delta G^O = -RT \ln K_O$$

$$\Delta G^O = \Delta H^O - T\Delta S^O \tag{8}$$

$$\ln K_O = \frac{\Delta S^O}{R} - \frac{\Delta H^O}{RT} \tag{9}$$

(10)

where T = system temperature in unit Kelvin,

R = universal gas constant (8.314 J/(mol.K)),

K$_0$ = equilibrium constant.

The K$_0$ value can be determined via the intercepted line of the graph of ln(q$_e$/C$_e$) versus q$_e$. However, ΔG^O is determined via Equation 6. Meanwhile, ΔS^O and ΔH^O are determined via the intercept and slope of the regression of ln K$_0$ versus 1/T respectively[79].

The thermodynamic parameters are crucial to be determined to obtain more thorough data of the variations of inherent energetic. Commonly, positive ΔG^{O} and ΔH^{O} values show that the adsorption occurred is non-spontaneous and endothermic respectively while negative values show the opposing mechanism. Furthermore, the values of ΔH^{O} can determine the type of adsorption process such as physisorption or chemisorption. Most of the physisorption processes are ranged below 20 kJ/mol while physisorption-chemisorption processes are ranged dominantly at 20-80 kJ/mol and chemisorption processes are ranged dominantly at 80-400 kJ/mol[80].

Table 4: Specific adsorption mechanisms of graphene oxide-based nanomaterials for metal ions removal.

Graphene oxide-based nanomaterials	Adsorption mechanisms included for metal ions removal	Advantages	Drawbacks	References
Graphene oxide (GO)	- Electrostatic interactions - Ion exchange	- Good dispersion in water. - Great colloidal constancy. - Contains rich oxygenated functional groups.	Restricted number of sorption sites.	[81]
Reduced graphene oxide (rGO)	- Electrostatic interactions	- Restoration of sp2 domains.	- Less oxygen-containing	[82]

	- Lewis-base–acid mechanism	- Better electron-transport properties.	functional groups. - Weaker colloidal stability.	
Magnetic graphene oxide nanocomposites	- Electrostatic interactions with graphene oxide - Interactions with the particles surface - Magnetic properties of the nanoparticles	- Bigger surface area compared to the pure GO. - Increased number of binding sites compared to pure GO. - Ease the recovery process from solutions.	Co-reduction of GO during the combination of the particles weakens the colloidal stability.	[83]

Graphene oxide materials functionalized with organic molecules	- Electrostatic interactions - Complexation with organic molecules	- Bigger surface area compared to pure GO. - Great colloidal stability. - Greater number of functional groups (–NH2, –OH).	Large variations of the stability of the loaded molecules depending on the alteration approach physically or chemically.	[84]

4. Application of Graphene

Application of graphene for the wastewater remediation is predicted to be a promising as well as effective implementation. Both graphene and graphene oxide-based nanomaterials are utilized for heavy metal removal. For instance, the removal of heavy metals such as cadmium (Cd(II)), lead (Pb(II)), copper (Cu(II)), chromium (Cr(VI)) and other harmful heavy metals are necessary to preserve the free or minimum toxicity of wastewater. This is because most of the heavy metals mentioned above are not biodegradable and hence it will result in harms to living things. Therefore, to remove heavy metals mentioned above, various type of materials has been studied regarding to the fabrication of the graphene oxide-based nanomaterials.

The materials involved for cadmium removal are poly(amidoamine)/graphene oxide (PAMAMs/GO), chitosan/sulfydryl-functionalized graphene oxide (Chitosan/SH/GO), iron (III) oxide/mesoporous silica/graphene oxide (Fe_3O_4/ mesoporous silica/GO), magnetic manganese-doped iron (III) oxide nanoparticle implanted graphene (GMIO), few-layered GO nanosheets, flower-like titanium dioxide/graphene oxide (TiO_2/GO), magnetic graphene oxide (mGO), iron (III) oxide/ graphene oxide/ 1-ethyl-3-methylimidazolium tetrafluoroborate (Fe_3O_4/GO/$EMIMBF_4$), and cellulose membranes.

However, for lead removal, the materials include antimicrobial graphene polymer (PVK/GO), few-layered GO, manganese ferrite/graphene oxide ($MnFe_2O_4$/GO), poly(amidoamine)/graphene oxide (PAMAMs/GO), ethylenediaminetetraacetic acid/magnetic graphene oxide (EDTA/mGO), chitosan/graphene oxide (Chitosan/GO), ethylenediaminetetraacetic acid/graphene oxide (EDTA/GO), chitosan/sulfydryl-functionalized graphene oxide (Chitosan/SH/GO), hyperbranched polyethylenimines/graphene oxide (HPEI/GO), silver/graphene oxide (Ag/GO), 4-

aminosalicylic acid/graphene oxide (PAS/GO), L-tryptophan-functionalized graphene oxide (L-Trp/GO) and amino-functionalized graphene oxide (NH_2/GO).

Furthermore, the materials included in copper ions removal are L-tryptophan-functionalized graphene oxide (L-Trp/GO), chitosan/sulfydryl-functionalized graphene oxide (Chitosan/SH/GO), chitosan/graphene oxide (Chitosan-GO), poly (allylamine hydrochloride)/graphene oxide (PAH/GO), ethylenediaminetetraacetic acid/magnetic graphene oxide (EDTA/mGO), polyvinyl alcohol/chitosan hydrogel compounded with graphene oxide (PVA/CS/GO hydrogel beads), polyethylenimine modified magnetic graphene oxide (PEI/Fe_3O_4/GO), poly(amidoamine)/graphene oxide (PAMAMs/GO), sulfonated magnetic graphene oxide (SMGO), titanium dioxide/ graphene oxide (TiO_2/GO), graphene oxide aerogels (GO aerogels) and graphene oxide nanosheets decorated with Fe_3O_4 nanoparticles (Fe_3O_4/GO).

Moreover, the chromium (VI) ions removal requires studies of materials such as graphene oxide-alpha cyclodextrin-polypyrrole nanocomposites (PPy/α-cyclodextrin/GO), chitosan/graphene oxide (Chitosan/GO), reduced graphene oxide/ nickel oxide (RGO/NiO), magnetic ionic liquid/chitosan/graphene oxide (MCGO/IL), graphene oxide decorated with magnetic cyclodextrin (MCGN), magnetic mesoporous titanium dioxide–graphene oxide core–shell microspheres (Fe_3O_4/mTiO_2/GO), magnetic graphene oxide functionalized with 1,2-diaminocyclohexanetetraacetic acid (DCTA/E/MGO), graphene oxide functionalized with magnetic cyclodextrin-chitosan (CCGO), 2-imino-4-thiobiuret−partially reduced graphene oxide (IT/PRGO), and iron oxide decorated graphene oxide (Fe_3O_4/GO).

Lastly, other heavy metals which can be removed via graphene oxide-based nanomaterials involve cobalt (Co(II)), uranium (U(VI)) and rhenium (Re(VII)).

Therefore, the adsorbents used for the removal purpose includes ozonized GO, amino siloxane oligomer modified GO (PAS/GO), phosphate-functionalized GO (PGO), EDTA functionalized Fe_3O_4/GO (EDTA/mGO), ozonated GO (OGO), amino functionalized magnetic graphene oxide (AMGO) and graphene modified nanoscale zero-valent iron particles (NZVI/rGOs).

Therefore, throughout the Table 5-9, brief summaries have been made for the application of various types of graphene oxide-based nanomaterials to remove the heavy metals such as Cd(II), Pb(II), Cu(II) and Cr(VI) and other heavy metals respectively from wastewater. For instance, the maximum adsorption capacity, optimum conditions, adsorption isotherms, kinetic models and few crucial remarks have been discussed.

4.1 Cadmium Removal

Recently, removal of cadmium content in waste water has been raised and discussed since cadmium has been discovered in approximately 1014 of the 1669 dangerous waste sites which are included in the EPA National Priorities List (NPL)[85]. According to different sources, the average presence of cadmium in the world's oceans has been reported to have range between <5 mg/L and 110 mg/L[86]. However, at some coastal areas, it is spotted that higher levels have been found and the concentration of cadmium content is varied due to the ocean depth and most likely affected by the patterns of nutrient concentrations measured. Furthermore, a greater deviation of cadmium content is noticed in fresh waters, rainwater as well as surface waters in industrialised and urban zones.

Cadmium can be known as a minor as well as natural constituent of groundwater and surface. The existence of cadmium could be found in water as the hydrated ion either as organic complexes with humic acids or as inorganic complexes like chlorides, carbonates, sulphates, hydroxides[87]. Furthermore, cadmium might be easily penetrated water systems via few sources such as soils as well as bedrock erosion or weathering, leakage from polluted locations and landfalls, atmospheric deposition release directly from industrial processes, and the usage of fertilisers as well as sludge in the aspect of agriculture[88]. Speedy adsorption of most of the cadmium inflowing fresh waters from industrial sources by particulate substance can be witnessed and hence residue could be a major sink for cadmium discharged to the aquatic atmosphere.

According to the maximum contaminant level (MCL) standards, cadmium which is exceeding 0.01 mg/L will cause human carcinogen, kidney damage and renal disorder[6]. Hence, the environmental quality standards related to the EU priority substances has restricted the amount of cadmium released which should be less than 10 µg/L or 0.08 –0.25 µg/L[89]. In addition, regarding to the impact on plants, cadmium content in wastewater will slow down the growth rate of seed and lipid content as well. In fact, low cadmium concentration such as below 5 mg/L is hardly to receive treatment economically via chemical precipitation methods[90]. Therefore, the application of pristine graphene and functionalized graphene for removing cadmium from wastewater has been briefly summarized in the Table 5 below.

Table 5: A brief summary of cadmium removal via graphene oxide-based nanomaterials.

Adsorbent	Maximum adsorption capacity (mg/g)	Conditions	Model (adsorption isotherm; kinetics)	Remarks	Reference
GO	1792.60	303K; pH 4.0	Langmuir and Freundlich; Pseudo second-order	i. The equilibrium contact time is 120 minutes. ii. The graphene oxide is generated by using amorphous graphite.	[91]
GO	1531.70	303K; pH 4.0	Langmuir and Freundlich; Pseudo second-order	i. The contact time reached its equilibrium state at 120 minutes. ii. The graphene oxide is fabricated via flaky graphite.	[91]

PAMAMs/GO	253.81	298K; pH 5.0	Langmuir; Pseudo second-order	i. The adsorption process achieves equilibrium within 60 minutes while the contacting period is approximately 4 hours. ii. The adsorbent dosage is 0.1 g.	[92]
GNs	188.68	298K; pH 5.2	Langmuir	i. The equilibrium contact time is 40 minutes. ii. Dosage of adsorbent is 20 mg/L.	[93]
Chitosan/SH/GO	177.00	293K; pH 5.0	Freundlich; Pseudo second-order	i. The equilibrium state of the adsorption process reaches at 30 minutes. ii. The dosage of adsorbents is 0.2 mg/mL. iii. The adsorption efficiency is strongly dependent on both pH, temperature and adsorbent dosage.	[94]
Fe_3O_4/Mesoporous Silica/GO	167.00	300K; pH 7.1	Langmuir	i. The contact time is approximately 24 hours. ii. Initial concentration is fixed at 20 mg/L.	[95]

GMIO	127.00	303K; pH 5.1	Langmuir; Pseudo second-order	i. The equilibrium contact time is 58 minutes. ii. The recovery of GMIO is low but it can be enhanced by the increment of fluorescence quenching of GMIO with the larger loading amount of cadmium ions.	[96]
Few-layered GO nanosheets	106.30	303K; pH 6.0	Langmuir	i. The dosage of adsorbent is 0.1 g/L. ii. The adsorption capacity is strongly based on pH and humic acid. iii. The adsorption equilibrium period is 24 hours.	[97]
Highly ordered layered GO membranes	83.80	303K; pH 5.8	Langmuir; Pseudo second-order	i. Reuse of GO membrane can reach up to six cycles with the same adsorption capacity. ii. Dosage of adsorbent is 20 mg/L. iii. The equilibrium contact time is 15 minutes.	[98]

				iv. It is recommended to be used in industrial sites.	
TiO_2/GO	72.80	373K; pH 5.6	Langmuir	i. The increment of treatment period is done up to 12 hours to remove more cadmium ions via hydrothermal method. ii. The chemisorption of cadmium ions is taken place.	[99]
mGO	59.69	298K; pH 6.0	Langmuir; Pseudo second-order	i. Adsorption of cadmium ions on the MGO is strongly dependent on the pH value. ii. The MGO is tested on the tap water. iii. The equilibrium contact time is 165 minutes.	[100]
Fe_3O_4/GO/$EMIMBF_4$	33.7	298K; pH 6.0	Langmuir	i. Dosage of adsorbent is 20 mg/L. ii. The extraction period takes only few seconds.	[101]

				iii. Presence of superparamagnetic behaviour results in maximum saturation magnetization value which is 40.88 emu/g.	
GO/cellulose membranes	26.8	298K; pH 4.5	Langmuir; Pseudo second-order	i. Good adsorption and no precipitation of metal hydroxides can be observed in between pH 4-8 in liquid phase. ii. It can be reused up to ten cycles. iii. It is suitable to be used in analytical chemistry.	[102]

4.2 Lead Removal

Lead is described as a heavy and soft bluish grey metal with malleable properties[103]. Lead has been one of the leading and well-known heavy metal which cause water pollution because of its toxicity and its common existence in the environment[104]. However, it is widely known as industrial contaminants. Among various type of heavy metals, lead is known as the environment pollutant which can last longer[105]. It penetrates through air, soil and water to enter the ecosystem[106]. For instance, the emission of lead into atmosphere are sourced from combustion of fossil fuels and mining productions[107]. In addition, lead pollutants are found in the processing industrial sites which produce batteries, ammunition, glass and ceramic and metallurgy[108]. Besides, lead has been verified as the most unsafe heavy metal among the chemical-intensive industries. Furthermore, contamination of consumable water and erosion of domestic plumbing structures can be resulted from the industrial sewages and eventually polluted the drinking water[109].

On the other hand, great amount of lead found to be existed in the environment will eventually threaten the good condition of both ecosystems and humans in the long term[110]. Besides, lead can result in genotoxic and cancer-causing effects[111]. For instance, poisonous lead will lead to kidney failure, anaemia, damaged brain tissue and death if encounter serious poisonous condition[112]. Moreover, existence of lead will eventually disturb the central nervous system and hence constrains the generation of red blood cells. For instance, discovery of lead which is exceeding 40 lg/dL in the blood concentration will result in noticeable clinical signs in domestic animals[109]. In addition, negative effects such as insufficiencies and indirect abortions will be experienced as well with the existence of high level of lead content.

Besides, according to both World Health Organization (WHO) and Environmental Protection Agency (EPA), the maximum lead-ion allowance limit in both the consumable water and wastewater can merely be 0.05 mg/L[106]. However, the initial common concentration of lead-ion in the industrial wastewaters which is ranged from 200-500 mg/L is strictly recommended to be reduced to the concentration ranged between 0.05-0.10 mg/L before any discharge or disposal activities have been carried out so that both the sewage systems and water way can be ensured with minimum content of lead ions[113]. Lastly, EPA stated that consumption of a diet which containing the lead concentration of 2–8 mg per kilogram of bodyweight per day for sometimes will result in death[107]. Hence, proper treatment method of lead ion in wastewater via graphene and graphene oxide-based nanomaterials can be demonstrated via Table 6 below to prevent lead poisoning.

Table 6: A brief summary of lead removal via graphene oxide-based nanomaterials.

Adsorbent	**Maximum adsorption capacity (mg/g)**	**Conditions**	**Model (adsorption isotherm; kinetics)**	**Remarks**	**Reference**
PVK/GO	982.86	303K; pH 7.0	Langmuir	i. The ratio of PVK: GO is 10: 90 in terms of the weight percentage. ii. The contact time between the adsorbent and the lead ions is stated to be 90 minutes. iii. Adsorption efficiency is based on the concentration of GO.	[114]
Few-layered GO	842.00	293K; pH 6.0	Langmuir	i. pH value strongly affects the adsorption capacity. ii. The adsorption capacity is strongly independent of ionic strength.	[115]

$MnFe_2O_4$/GO	673.0	333K; pH 5.0	Langmuir; Pseudo second-order	i. The ionization of surface charge and adsorbate speciation are strongly depending on the pH value. ii. The adsorbent has high reusability and reproducibility which can sustain at least five complete cycles of adsorption process. iii. Increment of temperature increase the adsorption performance due to higher diffusion rate.	[116]
PAMAMs/GO	568.18	298K; pH 4.5	Langmuir; Pseudo second-order	i. The adsorption process achieves equilibrium within 60 minutes while the contacting period is approximately 4 hours. ii. The adsorbent dosage is 0.1 g. iii. The adsorption process is strongly based on the pH value.	[92]

EDTA/mGO	508.4	318K; pH 4.2	Freundlich; Pseudo second-order	i. 0.05g of adsorbents are considered as the maximum dosage. ii. The maximum equilibrium in removal efficiency is 40 minutes. iii. The adsorbent has good reproducibility which can recycle for at least five cycles while maintaining the good adsorption performance.	[117]
Graphene nanosheet	476.19	298K; pH 6.2	Langmuir	i. The equilibrium contact time is 35 minutes. ii. Dosage of adsorbent is 40 mg/L.	[93]
Chitosan/GO	461.30	318K; pH 6	Redlich–Peterson; Double-exponential	i. pH value is a crucial variable to determine the adsorption performance due to the protonation of functional groups. ii. The equilibrium time of the adsorption process is 30 minutes.	[118]

				iii. The adsorbent has high recyclability such as 93% of adsorption efficiency at its fifth cycle and it is suitable for industrial activities.	
EDTA/GO	454.6	298K; pH 3.0	Langmuir	i. The equilibrium time of the adsorption process is 90 minutes. ii. The adsorption efficiency is strongly based on the pH value due to the surface charge of adsorbent and protonation of functional groups. iii. The achievable contact time is approximately 5 minutes.	[119]
Chitosan/SH/GO	447.00	293K; pH 5.0	Freundlich; Pseudo second-order	i. The equilibrium state of the adsorption process reaches at 30 minutes. ii. The dosage of adsorbents is 0.2 mg/mL.	[94]

				iii. The adsorption efficiency is strongly dependent on pH, temperature and adsorbent dosage.	
HPEI/GO	438.60	298K; pH 5.0-6.0	Langmuir; Pseudo second-order	i. High recyclability up to eight cycles. ii. The adsorbent dosage used in the maximum adsorption performance is 0.1 mg/L. iii. The contacting time between the adsorbent and the lead ions is approximately 8 hours.	[120]
Ag/GO	312.57	298K; pH 5.3	Langmuir; Pseudo second-order	i. 0.05 mg of adsorbents used showed the maximum adsorption performance. ii. The equilibrium time for the lead adsorption is 50 minutes.	[121]
PAS/GO	312.50	303K; pH 4.0-7.0	Langmuir; Pseudo	i. The adsorbent dosage used in the maximum adsorption performance is 1.0 mg/L.	[122]

			second-order	ii. The contacting time between lead ion and adsorbent is approximately 7 hours.	
L-Trp/GO	222.00	293K; pH 4.0	Langmuir; Pseudo second-order	i. The contacting time between the adsorbents and the copper ions is 40 minutes. ii. The optimum adsorbent dosage is 10mg. iii. The adsorbent has high reusability since its adsorption efficiency merely reduces 5% after three cycles.	[123]
NH_2/GO	96.00	298K; pH 6.0	Langmuir; Pseudo second-order	i. Extremely low LOD is discovered which is merely 9.4 ng/ L. ii. The adsorbent is suitable to be used in the analytical chemistry.	[124]

4.3 Copper Removal

Copper is known as the major component of the effluent and wastewater detected in the manufacturing industries such as mineral processing, mining and the likes[125]. In addition, copper content can be highly detected in the wastewater produced in industrial applications due to its high concentrations and at the same time it is known as the most common heavy metals utilized in most of the industrial applications. For instance, the copper content can be discovered in industries which involve electroplating, etching, plastics and lastly metal finishing as well as processing[126]. Besides, the copper content is most likely to accumulate and hence results in high toxicity to most of the affected living things even if the quantity is very little[127]. For instance, it is found that the presence of copper concentrations in the semiconductor wastewater reached up to 100 mg/L[128]. In addition, merely 28–172 μg/L of copper concentrations discovered in the freshwater can cause severe toxicity to the aquatic ecosystems[128].

Initially, copper ions act as a vital role to develop the synthesis of enzyme, human bones and tissues[125]. Yet, excessive as well as unwarranted copper ions might lead to different injuries for liver as well as eyes and the disproportion in cellular progressions which will result in Wilson, Menkes, Parkinson's, Alzheimer's and other prion illnesses[129]. Other than that, excessive copper content found in the human body can cause kidney injuries, anaemia and intestinal pain[130]. Permissible limit of copper ions in consumable water fixed by WHO and EPA is 1.5 mg/L and 1.3mg/L respectively[131]. However, the discharge limit is varied for different countries or regions. For instance, the permissible limit of copper ions in industrial wastes has been fixed at the value of 0.5 mg/L and 1.0 mg/L for China and Korea respectively[128]. In addition, according to the EPA, the permissible limit of copper ions for the discharge purposes is fixed at 1.3 mg/L[132].

In short, it is vital to eliminate or minimize the copper content in both drinking water and wastewater so that the quality of aquatic ecosystem and superficial water can be guaranteed since copper ions are known as the trickiest water contaminants which leads to water pollution. Hence, application of graphene and graphene oxide-based nanomaterials are carried out to rectify the pollution issues caused by copper ions and it can be referred via Table 7 below.

Table 7: A brief summary of copper removal via graphene oxide-based nanomaterials.

Adsorbent	Maximum adsorption capacity (mg/g)	Conditions	Model (adsorption isotherm; kinetics)	Remarks	Reference
L-Trp/GO	588.00	293K; pH 5.0	Langmuir; Pseudo second-order	i. The contacting time between the adsorbents and the copper ions is 40 minutes. ii. The optimum adsorbent dosage is 10mg. iii. The adsorbent has high reusability and its efficiency merely reduces 5% after three cycles.	[123]
Chitosan/SH/GO	425.00	293K; pH 5.0	Freundlich; Pseudo second-order	i. The equilibrium state of the adsorption process reaches at 30 minutes. ii. The dosage of adsorbents is 0.2 mg/mL.	[94]

				iii. The adsorption efficiency is strongly dependent on pH, temperature and adsorbent dosage.	
Chitosan/GO	423.80	318K; pH 6.0	Redlich–Peterson/double-exponential	i. The equilibrium time of the adsorption process is 30 minutes. ii. The adsorbent dosage is 0.5 g/L. iii. Both internal and external diffusion take place effectively in lead adsorption process. iv. The adsorbent has high recyclability such as 91.5% of adsorption efficiency at its fifth cycle and it is suitable for industrial activities.	[118]
PAH/GO	349.03	293K; pH 6.0	Langmuir; Pseudo second-order	i. The dosage of adsorbents is 0.1 g/L. ii. The total adsorption efficiency still maintains at 87.6% after fifth cycles of usage.	[133]

				iii. The adsorption process is strongly relying on both the temperature and pH value.	
EDTA/mGO	301.20	298K; pH 5.1	Langmuir; Pseudo second-order	i. 0.10g of adsorbents are the maximum dosage. ii. pH value is crucial for the lead removal efficiencies. iii. The adsorbent has good reproducibility which can recycle for at least five cycles while maintaining the good adsorption performance.	[117]
PVA/CS/GO hydrogel beads	162.00	303K; pH 5.5	Langmuir; Pseudo second-order	i. The optimum adsorbent dosage is 0.05g. ii. The removal efficiency remains at 92% of its original adsorption capacity after the sixth cycle of adsorption process. iii. The adsorption process reaches its equilibrium state at 230 minutes.	[134]

PEI/Fe_3O_4/GO	157.48	298K; pH 5.0	Langmuir; Pseudo second-order	i. The ideal dosage of adsorbents is 1.0 g/L. ii. The contacting time between the adsorbents and the copper ions is 10 hours. iii. 84% of removal effectiveness is proven after the adsorbents are regenerated for the fifth cycle.	[135]
PAMAMs/GO	68.68	298K; pH 4.5	Langmuir; Pseudo second-order	i. The adsorption process achieves equilibrium within 60 minutes while the contacting period is approximately 4 hours. ii. The adsorbent dosage is 0.1 g. iii. It is a chemical adsorption process and the process is strongly based on the pH value.	[92]

SMGO	62.73	323K; pH 4.7	Langmuir; Pseudo second-order	i. The adsorption process reaches its equilibrium within 180 minutes. ii. The adsorption process of copper ions on the adsorbents was an endothermic and impulsive procedure.	[83]
TiO_2/GO	45.20	293K; pH 6.0	Langmuir	i. The adsorption capacity is strongly based on the pH value.	[136]
GO aerogels	19.65	298K; pH 6.2	Langmuir; Pseudo second-order	i. The dosage of adsorbents is 0.6 g/L. ii. The adsorption process reaches the equilibrium state at 15 minutes. iii. It involves ion exchange mechanism.	[137]
Fe_3O_4/GO	18.26	293K; pH 5.3	Langmuir; Pseudo second-order	i. Excellent recyclability up to five cycles. ii. Adsorption efficiency highly dependent on pH value.	[138]

4.4 Chromium (VI) Removal

The formation of chromium can be detected naturally via few phenomena such as weathering developments on the rocks which are in the rich content of chromium, releases from volcanos and lastly soil destruction[139]. Yet, most of the generated chromium in the environment is caused by the anthropogenic acts[140]. For instance, chromium is a well-known heavy metal to be used frequently in the metallurgy industries, synthetic fertilizers, crop protection goods, chemical manufacturing of pigments and paints, leather tanning processes and the likes[141]. Because of the anthropogenic acts, various types of chromium are emitted into the environment[142]. In fact, the presence of chromium species can be in various chemical oxidation states which ranges from 0 to VI[143]. However, merely Cr(III) and Cr(VI) are the species which are generated in the stable form in the environment[144]. Cr(III) is not harmful to living creatures and environment and hence merely Cr(VI) is further discussed due to its poisonous properties[145].

Cr(VI) is well-known for its high toxicity as well as its strong oxidation possibility and hence it will cause adverse mutagenic and carcinogenic effects within the cells[146]. Therefore, when the chromium concentration in consumable water surpasses 0.1mg/L, it is possible to lead to the occurrence of dizziness, abdominal pain, diarrhoea and other signs which will eventually result in diseases such as foetal deformities as well as cancers[147].

The living creatures mainly get into contact with chromium content via the inhalation of the Cr(VI) content in the contaminated air and the digestion of polluted water[148]. Thus, different nations have various rules to be obeyed regarding to the limitation and quota of Cr(VI) content in both air and water. For instance, in Europe countries, the greatest quantity of Cr(VI) in drinking water which is established by EC Directive

98/83/EC is merely 20 mg/L[139]. On the other hand, to minimise the chromium exposure to humans, WHO has fixed the maximum limit of Cr(VI) in the consumable water at 0.003mg/L[149]. However, the EPA has restricted the maximum limit of Cr(VI) concentration in both drinking water and surface water at a concentration value of 0.005mg/L and 0.1 mg/L respectively[150]. Lastly, in July 2011, the establishment of the Office for Environmental Health Hazards Assessment of California has agreed on the maximum discharge limit of 0.02mg/L of Cr(VI) onto surface water to provide a guaranteed protection[139].

In short, it is crucial to remove or minimise the Cr(VI) content from polluted water before any disposal or discharge since the chromium content is highly toxic and ease in bioaccumulation[151]. Therefore, the application of graphene oxide-based nanomaterials act as a significant role for Cr(VI) removal from wastewater and the summary can be referred via Table 8 below.

Table 8: A brief summary of chromium (VI) removal via graphene oxide-based nanomaterials.

Adsorbent	**Maximum adsorption capacity (mg/g)**	**Conditions**	**Model (adsorption isotherm; kinetics)**	**Remarks**	**Reference**
PPy/α-cyclodextrin/GO	666.67	318K; pH 2.0	Langmuir; Pseudo second-order	i. The adsorbent can be used up to three cycles. ii. The contacting time between adsorbent and Cr(VI) is 24 hours. iii. The ideal dosage of the adsorbent is 0.025g.	[152]
Chitosan/GO	310.40	318K; pH 3.0	Redlich–Peterson/double-exponential	i. The adsorbent dosage is 0.5 g/L. ii. Both internal and external diffusion take place effectively in the adsorption process.	[118]

				iii. The adsorbent has high recyclability such as 91% of adsorption efficiency at its fifth cycle and it is suitable for industrial activities.	
RGO/NiO	198.00	298K; pH 4.0	Langmuir; Pseudo second-order	i. The adsorbent has high reusability which can reach up to five cycles with 83% of the maximum adsorption efficiency. ii. Higher temperature favours the adsorption process since it is an endothermic process and possesses good thermal stability. iii. The ideal dosage of adsorbent is 10mg.	[153]
MCGO/IL	145.35	303K; pH 3.0-4.0	Langmuir; Pseudo second-order	i. The adsorbent possesses high recyclability which reached up to six cycles and maintains the adsorption capacity of 68 mg/g. ii. The adsorbent dosage is 0.10g.	[154]

				iii. Lower pH value favours the adsorption performances.	
MCGN	120.19	298K; pH 3.0	Langmuir; Pseudo second-order	i. It is investigated that pH value is a vital factor to affect the adsorption capacity. ii. The adsorbent dosage is maintained at 1.0 g/L. iii. The adsorbent can be repeatedly used for at least five cycles which maintains the adsorption efficiency at 82%.	[155]
Fe_3O_4/mTiO_2/GO	117.94	303K; pH 2.0	Freundlich; Pseudo second-order	i. The adsorbent dosage is 1.0 g/L. ii. Low pH favours the redox reaction and hence guarantees a high adsorption capacity. iii. 40 minutes of contact period is optimum.	[156]

				iv. The high regeneration of the adsorbent can have ideal adsorption efficiency up to six cycles.	
DCTA/E/MGO	80.00	303K; pH 2.0	Freundlich; Pseudo second-order	i. The contact time between the Cr(VI) ions and adsorbent is 24 hours. ii. The adsorption capacity is highly dependent on the pH values which will significantly affect the adsorbent surface charge and ionization degree. iii. The adsorption efficiency can be affected by the ionic strength via the addition of sodium chloride.	[157]

CCGO	67.66	303K; pH 1.0-3.0	Freundlich; Pseudo second-order	i. The adsorption process reached its equilibrium time at 40 minutes. ii. The adsorbent dosage is fixed at 1.0 g/L. iii. The adsorbent is proven to have high reusability that maintains the adsorption efficiency of 77% at fifth cycle.	[158]
IT/PRGO	63.00	273K; pH 5.0-5.5	Langmuir; Pseudo second-order	i. The optimum adsorbent dosage is 3.5g/L. ii. The contacting time between Cr(VI) ions and adsorbents is fixed to be within 120 minutes. iii. The adsorbent can be regeneratable easily via the addition of sodium hydroxide concentration.	[159]

Fe_3O_4/GO	32.33	293K; pH 4.5	Langmuir; Pseudo second-order	i. pH value and ionic strength are the crucial factors to affect the adsorption capacities. ii. The adsorbent dosage is 0.2 g/L. iii. The adsorption process reaches the equilibrium state within 5 hours.	[160]

4.5 Other Heavy Metals Removal

Other than Cd(II), Pb(II), Cu(II) and Cr(VI) ions, graphene oxide-based nanomaterials also manage to remove other heavy metals such as Co(II), U(VI).

Co(II) is the crucial for human because it is the major component found in vitamin B12 complex. Although the variation of the Co(II) abundance can be very wide from the range of 0.05 to 300mg/kg, the available Co(II) is ranged from 0.1 to 2.0 mg/kg which is the volume taken up by vegetation[161]. It is known to be nutritious to human but overdosed Co(II) will lead to various type of opposing effects[162]. Besides, the excessive emission of Co(II) into environment will result in cell mutations and many other human illnesses[163].

However, U(VI) is known as one of the most harmful radionuclides used by nuclear power plants due to its high fission energy, high toxicity and high radioactivity to human[164]. The escalated growth of U(VI) industries have led to serious contaminations on soils, groundwater and surface[165].

Lastly, Re(VII) is considered as precious metal to be discovered widely in chemical and petrochemical industries, aviation, metallurgy and military due to its promising properties such as high corrosive resistivity and hardness[166]. Besides, Re(VII) is always discovered in the mixture of molybdenite and sulphide copper ores and it is hardly to be traced as an individual element due to its concentration in molybdenite is extremely low and it is hard to be separated from a comparatively great amount of molybdenum (VI) in molybdenite[167].

Herein, it is necessary to remove these heavy metals via some studies on relevant adsorbents. Therefore, the graphene oxide-based nanomaterials used to remove the heavy metals mentioned above are studied and discussed via Table 9.

Table 9:A brief summary of Co(II) and U(VI) removal via graphene oxide-based nanomaterials.

Adsorbent	**Adsorbate**	**Maximum adsorption capacity (mg/g)**	**Conditions**	**Model (adsorption isotherm; kinetics)**	**Remarks**	**Reference**
Ozonized GO	Co(II)	371.90	303K; pH 6.8	Langmuir; Pseudo second-order	i. The GO is oxidized for six hours. ii. Increased degree of oxidation improves the adsorption capacity.	[161]
PAS/GO	U(VI)	310.63	298K; pH 5.5	Langmuir; Pseudo second-order	i. High recyclability up to five cycles. ii. Adsorption capacity is strongly dependent on pH level.	[168]
OGO	U(VI)	291.80	303K; pH 5.5	Langmuir	i. The adsorption is not based on ionic strength. ii. It is endothermic procedure.	[169]

EDTA/mGO	U(VI)	277.43	298K; pH 5.5	Langmuir; Pseudo second-order	i. High recyclability up to five cycles. ii. Adsorption capacity is 2-3 times better than that of mGO.	[170]
PGO	U(VI)	251.70	303K; pH 4.0	Langmuir; Pseudo second-order	i. Acidic conditions favour the adsorption efficiency. ii. 24 hours of contact time is required	[171]
AMGO	U(VI)	141.20	298K; pH 5.9	Langmuir; Pseudo second-order	i. The adsorption is highly dependent on pH value. ii. It is regenerable up to four complete cycles.	[172]
NZVI/rGOs	Re(VII)	85.77	293K; pH 3.0	Langmuir; Pseudo first-order	i. Surface adsorption takes place. ii. Removal equilibrium reaches at 90 minutes.	[173]

4.6 Advantages and drawbacks of the application of graphene oxide-based nanomaterials in the environmental pollution management

In the actual environment remediation via graphene oxide-based nanomaterials, there are few significant advantages and drawbacks to be highlighted so that future developments can be done effectively to preserve better environment.

The advantages of utilising graphene oxide-based nanomaterials include the fast contact and adsorption period with various types of heavy metal ions. The fast adsorption processes improve the heavy metal removals in the industrial sites. Besides, graphene oxide-based nanomaterials are promising to be applied in analytical applications due to its high mechanical strength, high thermal conductivity and free of metallic impurities[174]. For instance, interlinkage of graphene oxide with carbon nanotubes can be done to generate a highly performed, transparent and flexible electrodes which is comparable to the commercialized indium-tin oxide[175]. Furthermore, most of the graphene oxide-based nanomaterials tend to have high regeneration ability which is up to three cycles[176]. Therefore, high recyclability has saved the production costs of the industries while the adsorption capacity is still maintained. Other than that, graphene-based sensor devices are discovered to be easily adjusted to precise microfabrication methods compared to carbon nanotubes[177]. In addition, due to the flat morphology of graphene, it eases the process to assemble the graphene layers for the separation functions. Lastly, its production cost is relatively low due to the various generation methods and the ease of the production[178].

On the other hand, for the drawbacks of the graphene oxide-based nanomaterials, one of them is the aggregation and restack of the graphene found especially on the applications which depend on the large surface area of graphene[179]. The attribution of the aggregation is mainly caused by the imperfect synthesis of graphene oxide-based nanomaterials. Therefore, adsorption performances will be affected and could not achieve the targeted effects. Besides, graphene sheets have high probability to stick together to produce multi-layer graphene sheets during the process of fabricating single graphene sheet[180]. Therefore, thorough and detailed characterization are required to evaluate the produced graphene sheet[177]. Another significant drawback will be the difficult separation of graphene oxide-based nanomaterials from wastewater because of their nanosized particle and high surface energy[68]. However, regarding to the toxicity of graphene oxide-based nanomaterials, it is still under evaluation due to various results are shown via different studies. Nonetheless, for the low concentration of graphene content in the environment, the toxicity can be neglected and hence graphene oxide-based nanomaterials are very significant to be applied in the environment remediations[181].

5. Future Challenge

The synthesis of graphene has been widely done by the latest and greatest method which is improved Hummers method. However, the experimental procedures to complete the fabrication of the graphene is time consuming although the experimental complexity is considerably low. Therefore, replacement or removal of certain chemicals are required to be further discovered and studied to shorten the fabrication period and result in a better fabrication method. In addition, reduction of chemical or replacing the chemical with a cheaper alternative in the fabrication process will ensure the entire process to be more cost effective and applicable in the actual industries sites.

It is crucial to obtain the sources of clean water since the demands for clean water has been considerably escalating in recent decades. Yet, it is a challenging task to carry out enforcement of alternatives to produce clean water. For instance, the challenging parts of the enforced alternatives are most likely the heavy metal removal efficiency and the cost required for the entire process. Therefore, various types of graphene oxide-based nanomaterials are considerably one of the most potential materials to eliminate most of the heavy metals contaminants from wastewater. This is because the raw material can be obtained easily. In addition, higher removal effectiveness can be guaranteed due to larger surface area for adsorption process and at the same time the production cost is lower. Nonetheless, these nanomaterials have been tested for their efficiency for heavy metal removal from wastewater in lab scale and positive results have been discovered. Thus, the major challenge would be realizing the lab scale experiments into the actual industrial sites since the graphene oxide-based nanomaterials have been readily available to be commercialized due to their high regeneration and reusability. For instance, the nanomaterials should be implemented in the actual wastewaters and natural water from the industrial sites so that the actual conditions involving best and worst conditions could be detected to evaluate on its effectiveness and usability to remove the heavy metal pollutants.

Moreover, during the experimental process of fabricating these graphene oxide-based nanomaterials, the dosage of nanomaterials should be higher and at the same time the research or experimental period should be carried out for a longer period. As a result, the long-term effectiveness of nanomaterials can be tested and guaranteed for the wastewater treatment. Therefore, it is recommended to compare the implementation of these nanomaterials for treating wastewater in both long term and short term. Besides, these graphene nanomaterials can be further functionalized either through surface modification or alkaline as well as acid treatments to improve the adsorption capacity for the heavy metal removal from wastewater. Hence, researchers are encouraged to focus more on the utilization of rich resources including biomass waste for the formation of graphene oxide-based nanomaterials to save cost effectively for the entire wastewater treatment. Furthermore, the regeneration or reusability of the nanomaterials is vital to be studied and researched as well to make it more sustainable and durable in the industrial usage especially for those nanomaterials which have low reusability. Once most of the graphene oxide-based nanomaterials could be realized and applicable in the actual industrial areas, the promising properties of the nanomaterials will be very useful especially in the metallurgy industries. Hence, development of more wastewater treatment plant could be achieved efficiently to ensure minimum heavy metal to be discovered in the wastewater and preserve the health of the living creatures.

6. Conclusion

In short, for the synthesis of graphene, Top-down method such as chemical exfoliation is more recommended to be used since Top-down methods can produce the least layers and smaller size of graphene compared to Bottom-up methods. For instance, production of graphene by using chemical exfoliation method such as improved Hummers method could result in Nano-sized graphene which fulfil the requirement of producing graphene oxide-based nanomaterials for heavy metal removal from wastewater.

Furthermore, by referring to the Tables 5-8, some nanomaterials are capable to remove few types of heavy metals. For instance, PAMAMs/GO can remove Cd(II), Pb(II) and Cu(II) ions while L-Trp/GO and EDTA/mGO can eliminate both Pb(II) and Cu(II)ions. Besides, chitosan/SH/GO are used to remove Cd(II) and Cu(II) ions but graphene nanosheets can be used to adsorb both Cd(II) and Pb(II) ions. Lastly, chitosan/GO can be act as the adsorbent to remove Pb(II), Cu(II) and Cr(VI) ions. In short, Pb(II) ions are the most favourable heavy metal to be adsorbed among the nanomaterials mentioned previously.

On the other hand, the optimum pH value of the adsorbents for Cr(VI) ions removal is studied to be slightly low which ranges from pH 1.0-5.5. However, the adsorbents for Cu(II) ions removal ranges from pH 5.0-6.2. Yet, the pH value for the adsorbents for both Pb(II) and Cd(II) ions are in the range of 3.0-7.0 and 4.0-7.1 respectively. The widest range covered of pH values are detected in nanomaterials which remove Pb(II) ions compared to other ions because it is assumed that Pb(II) ions are more electronegative and have larger ionic radius. Hence, stronger interaction with the GO and graphene oxide-based nanomaterials could take place.

Besides that, it is discovered that pure graphene oxide has higher adsorption capacity compared to graphene oxide-based nanomaterials. For instance, for the adsorbent of GO generated via both amorphous and flaky graphite to remove Cd(II) ions from wastewater, the maximum adsorption capacities are the highest among all the graphene oxide-based nanomaterials which are 1792.60 and 1531.70mg/g respectively. The adsorbents in this study are found to be have high reusability for at least three cycles with high adsorption efficiency. Lastly, most of the GO and graphene oxide-based nanomaterials are best fitted with Langmuir isotherm and pseudo second-order kinetic model. Hence, it is proven that the GO and graphene oxide-based nanomaterials undergo adsorption process via single layer interactions and it is chemisorption. In short, graphene itself and graphene oxide-based nanomaterials are known to be promising adsorbents associated with the latest technologies and fabrication methods for the heavy metal removal from wastewater to protect the water quality.

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