

A Review on Heavy Metal Ions and Containing Dyes Removal Through Graphene Oxide-Based Adsorption Strategies for Textile Wastewater Treatment

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Abstract: Textile wastewater heavy metal pollution has become a severe environmental problem worldwide. Metal ion inclusion in a dye molecule exhibits a bathochromic shift producing deeper but duller shades, which provides excellent colouration. The ejection of a massive volume of wastewater containing heavy metal ions such as Cr (VI), Pb (II), Cd (II) and Zn (II) and metal-containing dyes are an unavoidable consequence because the textile industry consumes large quantities of water and all these chemicals cannot be combined entirely with fibres during the dyeing process. These high concentrations of chemicals in effluents interfere with the natural water resources, cause severe toxicological implications on the environment with a dramatic impact on human health. This article reviewed the various metal-containing dye types and their heavy metal ions pollution from entryway to the wastewater, which then briefly explored the effects on human health and the environment. Graphene-based absorbers, specially graphene oxide (GO) benefits from an ordered structured, high specific surface area, and flexible surface functionalization options, which are indispensable to realize a high performance of heavy metal ion removal. These exceptional adsorption properties of graphene-based materials support a position of ubiquity in our everyday lives. The collective representation of the textile wastewater's effective remediation methods is discussed and focused on the GO-based adsorption methods. Understanding the critical impact regarding the GO-based materials established adsorption portfolio for heavy metal ions removal are also discussed. Various heavy-metal ions and their pollutant effect, ways to remove such heavy metal ions and role of graphene-based adsorbent including their demand, perspective, limitation, and relative scopes are discussed elaborately in the review.

Keywords: Adsorption, Graphene Oxide, Heavy metal removal, Textile effluent treatment, Wastewater treatment methods

1. Introduction

The rapid industrialisation, urbanisation and population have created huge stress on water usage and polluted drastically, which increase the demand for clean water. Water pollution

has been attributed due to the ability of water to dissolve more substances than any other liquid on the earth. This characteristic makes water pollution easily, and water resources such as rivers, reservoirs, lakes and our ocean are drowning in chemicals, waste, plastics and other toxic pollutants. The number of individuals living in water scare areas will increase to around 3.9 billion by 2030, as assessed by the World Water Council.^[1] The current and forthcoming water scarcity has increased the need for wastewater treatment and fit for household activities, industries or agricultural activities. Textiles manufacturing is a large industry globally that generates significant quantities of wastewater. Wastewater management and potable water purification are crucial to sustain human society's rapid development and mitigate

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environmental pollution and health hazards. Leaching harmful substances and accordingly, their contamination has come to be seen as a societal problem and has caused health problems for millions of people. Figure 1 shows the schematic representation of water pollution originates from industries effluent. Textile industrial wastewater pollution is a particular threat to water resources and a growing economy. An estimated 38354 million litres per day (MLD) sewage is generated in India's major cities, but the sewage treatment capacity is only of 11786 MLD. Similarly, only 60% of industrial wastewater, mostly large-scale industries, is treated. India's environmental technology sector is expanding rapidly, with evident business opportunities for pollution abatement technology innovations. The United Nations (2015: 6.3) has specifically targeted improvements to "water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, having the proportion of untreated

wastewater and substantially increasing recycling and safe reuse globally" by 2030.^[2,3] The research addresses other sustainable development goals (SDGs), including among other things: SDG3 (good health); SDG11 (sustainable communities); and SDG12 (responsible consumption).^[4]

In this scenario, wastewater treatment becomes of topmost importance. The discharge from different range of industries such as textile industries, paper and pulp industries, dye and dye intermediates industries, pharmaceutical industries, tannery industries, paint industries and kraft bleaching industries are considered a wide variety of organic pollutants introduced into the natural water resources from which textile industries (54%) generates half of the existing dye effluents seen in the world-wide environment followed by the dyeing industries (21%), paper and pulp industries (10%), tannery and paint industries (8%) and the dye manufacturing industries (7%) shown in Figure 2.^[5] These industries' effluents cause severe



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Figure 1. Schematic representation of water pollution originates from industries effluent.

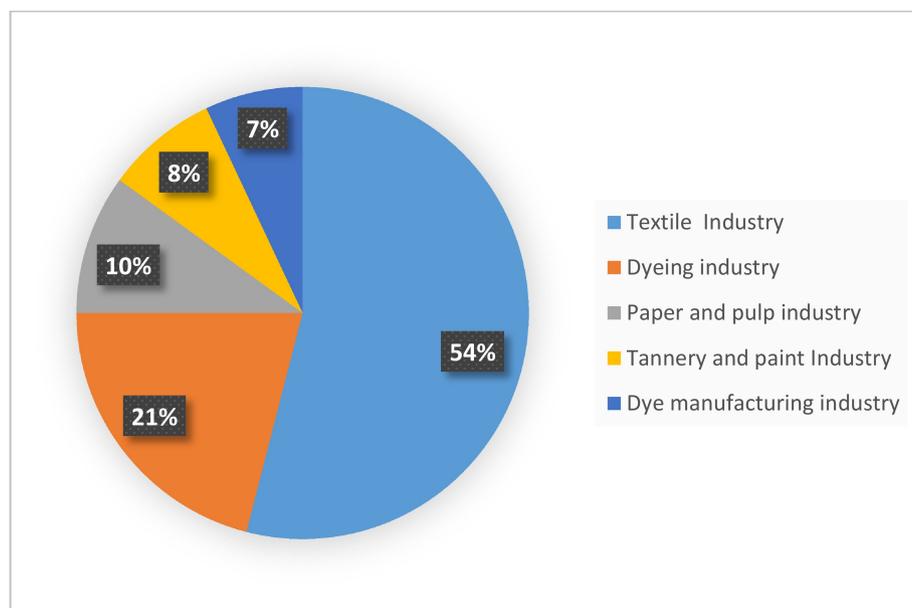


Figure 2. Comparison of dye effluent discharge from various industries.^[5]

environmental impact, especially from the textile industry. It generates a massive impact on our ecosystem because around 10,000 different textile dyes are produced based on a colour index, resulting in the production of ~700,000 tons of dye production worldwide.^[6] Among the effluent mentioned above, the textile industry's discharging industries play a major role in any other countries worldwide' economic development. Including India, globally few other countries play a predominant role in the textile industry: China, United States, Pakistan, Brazil, Indonesia, Taiwan, Turkey, Bangladesh, and

South Korea. India is one of the largest textile producers, contributing 5% of GDP (Gross domestic product), 14% of the industrial production contribution and 13% of export contribution earnings. Moreover, nearly 45 million peoples are directly employed by this industrial sector. The textile industry uses distinct types of raw materials such as cellulose fibre, protein fibre, and synthetic fibres. Cellulose cotton fibre plays a significant role in textile industry production, which is the backbone of this industry a 60% share of earning. A study indicates that the textile industry consumes roughly 1.6

million litres of water per day for producing 8000 kg/day of fabric, out of which 8% of water utilised for printing and 16% of the water used in dyeing process which clearly shown in Figure 3.^[7]

In the textile industry, the fabric manufacturing procedure undergoes two main processes: mechanical and chemical processes. Mechanical operation includes spinning, weaving and garmenting which requires less water, whereas chemical processing operations namely de-sizing, scouring, bleaching, mercerizing, dyeing, printing and finishing stages are required a considerable quantity of water. During the chemical process, bleaching and dyeing generate a massive amount of effluent which contains an immense volume of significant pollutants such like a higher concentration of chemical oxygen demand (COD), biological oxygen demand (BOD), suspended solids (SS), organic nitrogen, traces of heavy metals, dispersants, levelling agents, salts, carriers, acids, alkali and various dyes. Hence, above stated pollutants discharge degrades the water quality, spreading toxicity and seriously affects the photosynthesis activity in plants. Furthermore, it creates a massive impact on the aquatic environment because of low light penetration and insufficient oxygen consumption. Therefore, before discharging effluents must be adequately treated, increasing the significant focus on water reusability alternatives.

The textile industries can be classified into two categories, such as dry fabric related and wet fabric-related industries. The dry fabric industry generates solid wastes, whereas the wet fabric industry generates liquid wastes. The textile industry uses a different type of raw materials namely cellulose fibres (cotton, viscose, linen, jute, hemp, lyocell and ramie), protein fibres (wool, silk, mohair, angora, cashmere and alpaca) and synthetic fibres (rayon, nylon, polyester, acetate, acrylic, ingeo, polypropylene acrylic, spandex polyester, polyamide, polyacrylonitrile, polyurethane, and polypropylene). Amongst these fibres, cellulose cotton and wool require more water than synthetic fibres due to the hydrophilic nature. In contrast, synthetic fibres are hydrophobic, which means it does not absorb the water. Natural fibres absorb water along with dyes and other chemicals. Each type of fibre is dyed using different types of dyes, namely reactive dyes, vat dyes, indigo dyes, direct dyes, naphthol dyes, acid dyes, basic dyes, sulphur dyes, disperse dyes and natural dyes, which are an unsaturated organic compound that absorbs light and give colour to the visible region.^[8]

The wet fabric industrial wastewater is the primary focus of this review. The amount of water utilised and an equivalent amount of wastewater generated as effluent from this wet dyeing process. The large quantities of dyes impart during the dyeing to the fabrics. A significant number of dyes are remaining unfixed in textile effluents that are toxic, carcino-

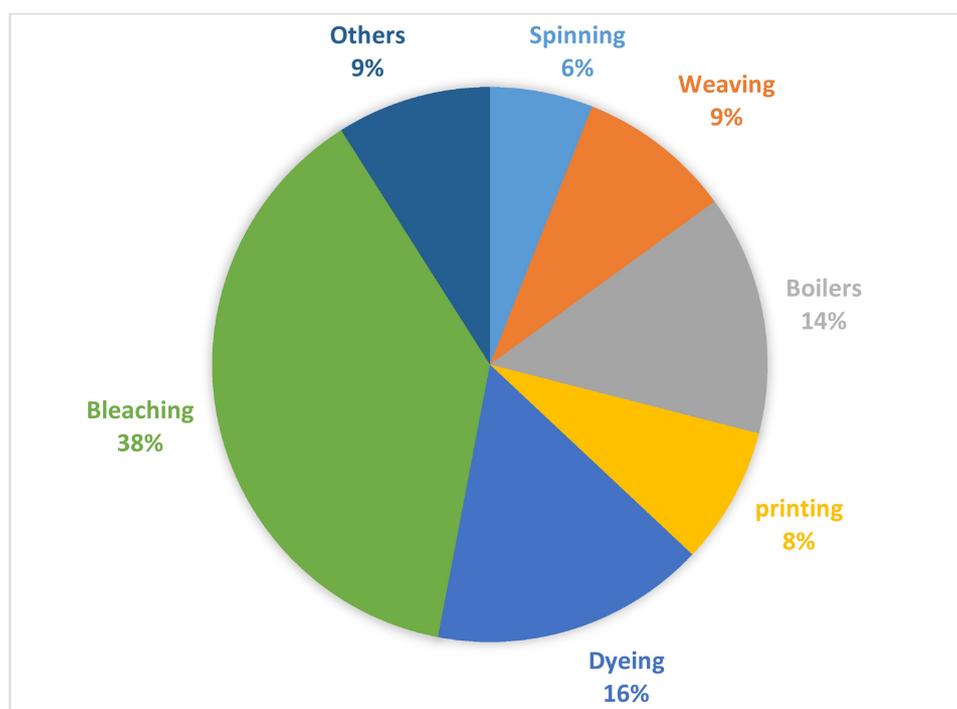


Figure 3. Water consumption in wet textile processing.^[7]

genic and mutagenic to all living things. These toxic dyes can remain in the environment for an extended period when released without appropriate treatment. Therefore, several primary, secondary and tertiary treatment methods are available to treat the textile effluent mentioned above. The textile effluent treatments are categorised into three main types such as physical (oxidation, ozonation & electrolysis), chemical (filtration, reverse osmosis, adsorption & coagulation/flocculation) and biological methods (Enzymes & microorganisms). These methods are used separately to treat the effluents, which highly depends on the type and quantum of pollutants load. Dyes give high dense colour to water and cause diseases like haemorrhage, ulceration of skin, nausea, severe irritation of skin and dermatitis. Generally, dye-containing wastewater is unacceptable because of their colour and carcinogenic, toxic and nonbiodegradability, thus causing huge environmental problems.^[9,10,11] In general, polluted water components come under six categories: main ions, dissolved gases, biogenous substances, organic substances, microelements and pollutants.^[12] Accordingly, textile effluent contains dyes, heavy metals and microorganism from which heavy metal examples such as Lead(Pb), Arsenic(As), Chromium(Cr), Nickel(Ni), Copper(Cu), Cadmium(Cd), Mercury(Hg), Zinc(Zn) etc., are known for their toxicity and worse effect in human health and environmental impact. Heavy metals are emerging from pre-treatment, dyeing, printing and finishing steps due to the use of metal-containing chemicals and metal-containing complex dyes. For example, during textile processing chemicals from the catalyst, oxidising agents, fixing agent cross-linking agent etc., and for getting bright dark colours chrome or mordant dyes and metal complex dyes are utilised. Heavy metals considered high density exceeds 5 mg per cubic centimetre, which are non-biodegradable and harder to cleanse because of its complex chemical form. In general, textile industries are discharging a large amount of heavy metal such like Cr (VI), Cd (II), Pb (II) and Zn (II) are the most common metal ions found in textile effluents. Except for textile industry other heavy metals producing industries are paper industries, pharmaceuticals, electroplating, rubber and plastics, metal finishing, organic chemicals, timber and wood items, pesticides, tanneries, metal plating industries, mining industries etc., emit these noxious heavy metals to the environment which causes serious environmental issue across the world; hence it is essential to treat the textile effluent before discharge to protect the contamination through the food chain. As a result of an increase in pollution, it demands useful materials in significantly efficient, economic, and easy application and applicable for different pollutants. In this perspective, this review articles' main focus is to address the efficient and economical material and appropriate methods to remove the heavy metals from textile effluents. Even if several studies have been reported so far on removing a heavy metal, the efforts are

still equally needed to efficiently detect heavy metals. For that graphene and its derivatives can be a potentially excellent selection. Graphene oxide-based nanocomposites received much attention and play an essential role in separation and purification technology because of their unique properties namely high surface area, minimal in size, surface modification ability, excellent conductivity, cost-effective synthesis and mainly biologically compatible.

1.1. Textile Processing Operations

In textile processing, fibres are transformed into yarn and reshaped into the fabric and then undergo several textile processing stages. Generally, the textile processing operations divided into two categories, such as dry process and wet process. The dry process needs minimum water which includes the following steps (i) opening, blending, and mixing, (ii) carding, (iii) combing, (iv) spinning, (v) weaving and (vi) knitting. The wet process requires more water which includes the steps such as (i) sizing, (ii) desizing, (iii) scouring, (iv) bleaching, (v) mercerizing, (vi) Dyeing and (vii) printing and finishing as shown in Figure 4. Below is the explanation of the various steps.

- i Sizing is the first preparation step where sizing agents are included to strengthen the fibres and protect the breakage.
- ii Desizing is used to remove sizing materials before weaving.
- iii Scouring helps to remove the impurities from the fibres by using alkali solution usually sodium hydroxide, which helps to break down the natural oils, waxes, and surfactants and helps to emulsify and suspend impurities in the scouring bath.
- iv Bleaching is the step used to remove the fibre's unwanted colour by using chemicals like sodium hypochlorite and hydrogen peroxide.
- v Mercerizing is the continuous chemical process used to increase dye's ability, enhance brightness, and intensify the fibre appearance, during this process concentrated alkaline solution applied. An acid solution is used to wash the fibre before the dyeing.
- vi Dyeing is the process to impart colour on to the fibre. During this process, many chemicals like metals, salts, surfactants, organic processing aids, sulphide and formaldehyde are added to improve dye adsorption onto the fibres where a large volume of water utilised in the dye bath, not only in the dye bath but also a large quantity of water used in rinsing step.
- vii Printing and Finishing is the last step in this process.

From the above steps of processing, a diverse range of pollutants are generated from different stages of the above stated textile wet process, briefly discussed in Table 1.

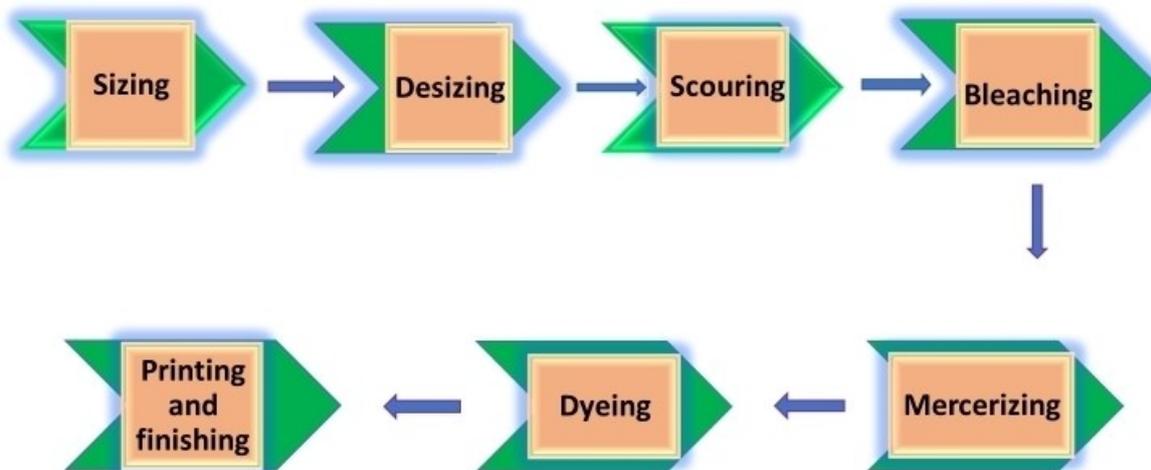


Figure 4. Various steps of wet textile processing.

Table 1. Pollutants generated during textile wet processing steps and their health effects.

Textile process	Chemical used	Pollutant nature	Health effects
Sizing	Starch, waxes, carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA) and wetting agents.	High in Biological oxygen demand (BOD) and chemical oxygen demand (COD).	Affects central nervous systems, carcinogenic and mutagenic.
Desizing	Starch, CMC, PVA, fats, waxes and pectin.	High in BOD, COD, high suspended solids (SS) and high dissolved solids (DS).	Bloating and diarrhoea, irritation to eyes and skin.
Scouring	NaOH, surfactants, soaps, fats, pectin, oils, sizes and waxes.	Disinfectants, insecticide residues, NaOH, detergents oils, knitting lubricants, spin finishes and spent solvents.	Non-ionic detergents may cause bloating and diarrhoea, irritation to eyes and skin.
Bleaching	Sodium hypochlorite, H ₂ O ₂ , acids, surfactants, sodium silicate (Na-SiO ₃), sodium phosphate, short cotton fibres, organic stabilizers and alkaline pH.	High alkalinity and high suspended solids, H ₂ O ₂ , stabilizers and high pH.	Causing severe irritation to respiratory tract, prolonged exposure will affect the liver and kidney, leading to death.
Mercerizing	Sodium hydroxide and cotton wax.	High pH, low BOD and high dissolved solids.	–
Dyeing	Dyestuffs, urea, reducing agents, surfactants, metals, salts, oxidising agents, acetic acid, detergents and wetting agents.	Intense colour, high in BOD and dissolved solids, low in suspended solids, heavy metals, salt, surfactants, organic assistants, cationic materials, colour, COD, sulphide, acidity/alkalinity and spent solvents.	Eye and respiratory problem.
Printing	Metals, colour, formaldehyde, pastes, urea, starches, gums, oils, binders, acids, thickeners, crosslinkers, reducing agents and alkali.	Strong colour, high in BOD, oily appearance, suspended solids, slightly alkaline, urea, solvents, colour, metals, heat and foam.	Harmful health hazards.
Finishing	Softeners, solvents, resins and waxes.	COD, suspended solids, toxic materials and solvents.	Suppression of the haematological system.

2. Heavy Metal Pollution

Textile effluents contain high concentration dyes and chemicals and contain traces of heavy metal capable of causing several health-related issues and contain microorganism. Occasionally, heavy metals can occur naturally in the fibre structure.

Alternatively, it can be reintroduced into the textile fabric during manufacturing processes those comes from dyeing and finishing processes due to the use of high fastness and dye resistance properties. The heavy metal also occurs from four primary dyes: metal complex acid dyes, chrome acid dyes, reactive metal-containing dyes and direct metal-containing

dyes. Heavy metals can also come from fibres' chemical treatment to improve resistance to light and wet factors and fabric bleaching processes where metals are used as catalysts for oxidants.^[13] Heavy metal pollution through industrial waste is a serious environmental issue throughout the world. Heavy metals are a group of metals and metalloids with an atomic density of more than 4000 kg.m⁻³, atomic weights between 63.5 and 200.6 and gravity > 5.0^[14] Lead, cadmium, copper, arsenic, nickel, chromium, zinc and mercury have been recognized as hazardous heavy metals, because of their high solubility in the aquatic environments. Besides, heavy metals can be absorbed by living organisms, which are toxic even at low concentration. These metals are harder to clean due to its complex chemical form and non-biodegradability. Moreover, the above-mentioned heavy metals are stable, toxic and carcinogenic, accumulation in living organisms cause a severe health problem. Our natural soil and natural water resources are noxiously polluted by these heavy metal discharge which then adsorbed by plants through contaminated soil and then entering other living organisms through the food chain, affecting the environmental activities. Apart from the textile industry, other heavy metal toxicities releasing industries are mining, electroplating, metal processing, battery manufacturing, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic

industries.^[15,16] World health organisation (WHO) and Environmental protection agency (EPA) set permissible discharge standard limit for heavy metal to control the environmental pollution, which is shown in Table 2.^[17,18,19] When people continuously exposed to these toxic heavy metal causes various severe health-related deceases such as cancers and cardiovascular, pulmonary, immunological, neurological and endocrine disorders.^[20,21,22] Heavy metal removal from inorganic effluent can be achieved by conventional treatment processes which include chemical precipitation,^[23] electrochemical treatment,^[24,25] adsorption,^[26,27] coagulation-flocculation,^[28] membrane separation,^[29] ion exchange,^[30,31] reverse osmosis and biological treatment^[32] and so on. These methods are efficient in heavy metal removal even though they have some limitations such as high energy consumption, incomplete removal, secondary pollutants, high cost, high-energy requirements, and toxic sludge production.^[33] According to the previous literature review, the adsorption process is one of the low expenses among these remediation methods, a highly efficient advantageous method for removing heavy metals. From that point of view, this review focuses on the adsorption of heavy metals from textile wastewater; specifically, metal ions such as chromium (Cr), cadmium (Cd), lead (Pb) and zinc (Zn).

Table 2. Maximum contaminant level (MCL) standards in drinking water for the heavy metals and their effects on human health set by the US Environmental Protection Agency (US EPA) and WHO for these contaminants.

Heavy metal	Maximum contaminant level (MCL) mg.L ⁻¹	Possible sources	Health effects
Cd	0.01	Steel and plastics industries, nickel-cadmium batteries, cooling tower blowdown, electroplating, metal plating, coating operations, welding, metal alloys and electronic components additive, paint pigments, textile, anti-corrosive metal coatings and stabilizers.	Human carcinogenic, respiratory disease, gastrointestinal diseases, renal failure, damage to kidney and kidney stone formation, ^[34,35] stomach and urinary bladder cancers, bronchiolitis, COPD, emphysema, fibrosis, skeletal damage, weaken the bone, congenital disabilities, anaemia and inhibits the calcium control in biological systems.
Cr	0.05	Metal plating, coating operation, photography, tannery, ceramic, cooling tower blowdown, electroplating, glass industries, catalysts, pigments, paints, fungicides, chrome alloy and metallurgic industries. ^[36]	Asthma attacks, rhinitis, laryngitis, pulmonary fibrosis, acute gastrointestinal pain, liver and kidney damage, necrosis diarrhoea, nausea, carcinogenic and genotoxic, lung cancer, cancer of prostate, stomach, kidney, urinary system and bones. ^[37,38]
Pb	6.0 × 10 ⁻³	Paint, pesticides, smoking, automobile emissions, textile, burning coal and mining, storage batteries, building materials, fuel and pigment additive.	Circulatory and nervous disorders, anaemia, neurotoxic, damages the developing infant brain, kidney failure, cerebral disorders, renal, affects the sense organs, loss of voluntary muscle function, damage reproductive, cardiovascular and gastrointestinal systems, impaired intellectual ability and behavioural problems in children.
Zn	0.80	Alloy production, anticorrosion coatings, electrical devices, brass plating, wood pulp production, ground and newsprint paper production, steelworks with galvanizing lines, paints, pesticides, zinc and brass metal works, refineries, plumbing rubber and tyre industries.	Depression, stomach nausea, skin irritations, cramps, vomiting, anaemia, neurological signs, lethargy, increased thirst and dizziness.

2.1. Sources of Metal Contamination from Textile Processing

During textile processing, a diverse range of chemicals and auxiliary chemicals are consumed for achieving the appropriate quality of the textile fabric. The textile wastewater effluent contains various chemicals including chlorinated solvents, hydrocarbon solvents, oxygenated solvent, soils, waste fabrics soaked in grease and oil, together with dyestuffs and pigments which are utilised at various stages of textile manufacturing. As mentioned above, the chemicals are discharged mainly as wastewater effluent, which is highly toxic and hazardous to the environment. From this above table, hazardous substances have been identified for risk assessment studies of textile chemicals. Wastewater in textile mainly developed from four sectors which are pre-treatment, dyeing, printing and finishing. Wide range of heavy metals and salts is utilised in textile production and finishing, which is briefly listed in Table 3 and Table 4.

2.2. Types of Heavy Metals from Textile Wastewater

The role of heavy metal ions is constrained with mostly the light fastness and the wash fastness of the directly dyed fabrics, mainly cotton, which can be improved after treatment with various metal ion-induced salts. The metal atom is to form a complex with the dyestuff already present on the fabric. The major heavy metal ions generating from textile industries are discussed in the following section.

2.2.1. Chromium (Cr)

Heavy metal pollution from textile has become a serious environmental issue that affects human health and ecological balance. Apart from the textile, chromium has been widely used in the metallurgy, electroplating, metal deep processing, steel manufacturing, atomic power plants, fungicides, tanning,

printing, pigments, polishing, dye industries.^[40,41,42,43] Chromium (Cr) is a harmful heavy metal and oxidation states ranging from +2 to +6. Among these ranges, the trivalent and hexavalent states are considered more toxic, non-biodegradable, carcinogenic, teratogenic and mutagenic because of its oxidizing properties.^[44,45,46] Cr (III) is one of the essential elements for living being's health at a low level with a nontoxic concentration of 0.20 mg/day whereas Cr (VI) is a strong carcinogenic and pestilential to humans and animals. Furthermore, chromium is categorized as group 1 carcinogenic by the International Agency for Research on Cancer (IARC) for animals and humans. The toxicity of hexavalent chromium Cr (VI) is normally 1000 times higher than that of Cr (III) trivalent chromium.^[47] Accordingly, the World Health Organization (WHO) recommends that the chromium content in drinking water must be < 50 ppb or 0.05 mgL⁻¹^[48] and European Union require that the discharge of Cr (VI) to surface water should be below 50 µgL⁻¹.^[49] Chromium (VI) is dangerous to health when the limit (0.05 mgL⁻¹) exceeds in potable water.^[50] Various methods available to treat this metal ion, including ion exchange,^[40] photo-catalysis,^[51,52] electrochemical flocculation,^[53] membrane separation,^[54,55] chemical precipitation,^[56,57] ion exchange^[58] and adsorption^[59,60,61] have been used to decontaminate chromium ions from aqueous solution and reach the WHO permissible limit. Among these methods, adsorption is a highly efficient method due to its simple operation, high efficiency, and economic feasibility.^[62,63] Adsorbents, such as activated carbon,^[64] ion-exchange resins,^[65] inorganic nanomaterials,^[66] and natural waste material^[67] were reported to remove chromium ions in wastewater. Because of the limitations of these materials such as high cost, slow and less amount of adsorption efficiency enhanced the demand for low-cost adsorbent with high removal efficiency.

Table 3. Shows metal contamination from different dyeing method.^[39]

Dyeing method with metal contamination	Dyeing method with metal contamination
Vat dyes	Vat dyes contain these heavy (Cu, Fe, Mn, Ba &Pb) metals due to their production process.
Reactive dyes	Heavy metals can be present both as impurities and from the production process and as an integral part of the chromophore.
Chrome dyes	Phthalocyanine reactive dyes used for mostly blue and turquoise colours. Chromium present in the final colourant is not contained in the molecule. Instead, it is added as dichromate of chromate salt during the dyeing process to allow dye fixation during printing with printing paste chromium (III)salts such as chromium fluoride and chromium acetate rarely used.
Metal complex dyes	Cr (III) is an integral part of the chromophores; metals can be found in the effluent due to unfixed dye. For example, dyes 1:2 cobalt complex dye, 1:2 chromium complex dyes, 1:1 chromium complex dye and 1:2 chrome azo dye.

Table 4. Represents the metal-containing chemicals from different stages of textile processing^[39].

Textile Processing Stage	Used Chemicals	Origin of the Pollutant	Heavy metal derivative	
Fibre production	Lead and Lead Acetate	Dyeing auxiliary/ Mordant	Pb (II)	
	Cadmium	Pigment stage	Cd (II)	
	Zinc Salt	Catalyst	Zn (II)	
	Mercury	Metal impurities	Hg (II)	
	Tin	Metal impurities	Sn (II)	
Colouring, dyeing and Printing	Chromium Compound	Oxidising agent	Cr (VI)	
	Lead Acetate	Oxidising /reducing agent	Pb (II)	
	Copper acetate	Oxidising /reducing agent	Cu (II)	
	Copper nitrate	Oxidising /reducing agent	Cu (II)	
	Sodium/Potassium dichromate	Oxidising /reducing agent	Cr (VI)	
	Sodium dichromate	Fixing agent	Cr (VI)	
	Potassium dichromate	Fixing agent	Cr (VI)	
	Chromium compound	Fixation(dye)	Cr (VI)	
	Zinc compound	Fixation	Zn (II)	
	Zinc	Fixation and biocide	Zn (II)	
	Zinc sulphoxylate formaldehyde	Fixation	Zn (II)	
	Tin (II)chloride	Reducing agent/discharging agent, The oxidising agent, printing auxiliary	Sn (II)	
	Tin (IV) chloride	Oxidising/reducing agent Dyeing auxiliary, mordant	Sn (II)	
	Catalyst, cross-linking auxiliary, flame retardant and finishing-Softening treatment	Cobalt compound	Dye	Co (II)
		Copper compound	Dye	Cu (II)
Chromium compound		Dye (Fixation)	Cr (VI)	
Nickel compound		Cross-linking agent and dying	Ni (II)	
Zinc chloride		Catalyst and wrinkle-resistant treatment	Zn (II)	
Finishing-water repellent treatment		Waxes modified with Aluminium salt	Impregnating agent (plasticizer, spinning and spooling)	Al(III)
	Protein compounds as complexed with aluminium salts and dichromate	Impregnating agent	Al(III)	
	Aluminium triacetate	Impregnating agent	Al(III)	
	Aluminium triformate	Impregnating agent	Al(III)	
	Chromium/ fatty acid complex	Impregnating agent	Cr (VI)	
	Zinc salts	Impregnating agent	Zn (II)	
Finishing-easy care treatments	Zinc nitrate	Catalyst and wrinkle-resistant treatment	Zn(II)	
	Zinc fluoroborate	Wrinkle-resistant treatment	Zn (II)	
Finishing	Magnesium chloride	Catalyst, wrinkle-resistant treatment	Mg (II)	
	Copper naphthenate	Antimicrobial finishing (preventing deterioration)	Cu (II)	
	Antimony oxide	Flame retardant auxiliary	Sb(V)	
	Antimony pentoxide	Flame retardant additive	Sb(V)	
	Antimony trichloride	Flame retardant	Sb(V)	
	Antimony trioxide	Flame retardant additive	Sb(V)	
	Chrome (III) oxide	Cross-linking agent	Cr (III)	
	Cobalt (II) oxide	Cross-linking agent	Co (II)	
	Silver nitrate	Antimicrobial. biocide agent	Ag (I)	
	Silver oxide	Antimicrobial. biocide agent	Ag(I)	
	Silver(I) Iodide	Antimicrobial. biocide agent	Ag(I)	
	Copper oxychinolate/ copper quinolinolate	Antimicrobial finishing (preventing deterioration)	Cu (II)	
	Cadmium selenide	Antimicrobial finishing (preventing deterioration)	Cd (II)	
	Aluminium hydroxide	Finishing agent	Al (III)	
	Aluminium powder	Finishing agent	Al (III)	
Vanadium oxide	Cross-linking agent	V(V)		

Table 4. continued

Textile Processing Stage	Used Chemicals	Origin of the Pollutant	Heavy metal derivative
Softening, water repellent, easy-care treatment	Aluminium oxide	Cross-linking agent, filler and flame retardant	Al (III)
	Aluminium silicate dihydrate	Surface modifying agent	Al (III)
	Manganese (II) (III) oxide	Cross-linking agent	Mn (II), Mn (III)
	Silver	Antimicrobial agent	Ag (II)
	Aluminium chloride	Catalyst	Al (III)
	Aluminium potassium sulphate	Finishing agent	Al (III)
	Nickelous oxide	Cross-linking agent	Ni (II)
	Palladium (II) oxide	Cross-linking agent	Pd (II)
	Zinc Salt (dimethyl di thiocarbamate)	Antimicrobial finishing (preventing deterioration)	Zn (II)
	Zinc fluoroborate	wrinkle resistant treatment	Zn (II)
	Magnesium chloride	Catalyst, wrinkle-resistant treatment	Mg
	Zinc nitrate	Catalyst and wrinkle-resistant treatment	Zn (II)
	Zinc chloride	Surface modification (catalyst, wrinkle resistant treatment)	Zn (II)
	Waxes modified with Aluminium salt	Impregnating agent (plasticizer, spinning and spooling)	Al(III)
	Protein compounds as complexed with -aluminium salts -dichromate	Impregnating agent	Al & Cr (VI)
	Aluminium triacetate	Impregnating agent	Al(III)
	Aluminium tri formate	Impregnating agent	Al(III)
Chromium/ fatty acid complex	Impregnating agent	Cr(VI)	
Zinc salts	Impregnating agent	Zn(II)	
Dyeing printing and finishing	Aluminium acetate	Functional repellent with finishing	Al(III)
	Aluminium sulfate	Textile auxiliary, dyeing auxiliary, flame retardant	Al(III)
	Chromium compounds	Fixation(dye) dye (Fixation	Cr (VI)
	Chromium (III)	Acid dye	Cr (III)
	Chromium (VI)	Acid dye	Cr (VI)
	Cobalt	Cross-linking agent, anti microbiotic and dye	Co (II)
	Copper sulfate	Dyeing auxiliary/mordant	Cu (II)
	Copper (II) oxide	Dyeing auxiliary/mordant	Cu (II)
	Copper (II) chloride	Cross linking agent/ finishing agent/ antimicrobial agent/ trace element delivering agent	Cu (II)
	Copper (I) iodide	Cross linking agent/ finishing agent/ antimicrobial agent/ trace element delivering agent	Cu (II)
	Copper (I) oxide	Cross linking agent/ finishing agent/ antimicrobial agent/ trace element delivering agent	Cu (II)
	Ferrous sulphate	Dyeing auxiliary/mordant	Fe (II)
	Copper	Cross-linking agent, dye and biocide	Cu (II)
	Copper acetate	Oxidising /reducing agent	Cu (II)
	Copper nitrate	Oxidising /reducing agent	Cu (II)
	Aluminium potassium sulfate dodecahydrate	Dyeing auxiliary/Mordant	Al (II)
	Printing/Discharge printing Pigment	Chromic acid	Oxidising agent
Iron oxide (Fe ₂ O ₄)		Colouring with pigment	Fe (II)
Iron oxide (Fe ₃ O ₄)		Colouring, dyeing and printing with pigment	Fe (III)

Table 4. continued

Textile Processing Stage	Used Chemicals	Origin of the Pollutant	Heavy metal derivative
Finishing and printing with pigments	Titanium dioxide	Cross linking agent, titanium white and printing with pigment	Ti (IV)
Antimicrobial treatment	Mercury compounds	Biocide	Hg (II)
	Copper compounds	Biocide	Cu (II)
	Cadmium selenide	Biocide	Cd (II)
	Tin compounds	Biocide	Sn (II)
	Zinc compounds	Biocide	Zn (II)
	Copper naphthenate	Biocide	Cu (II)
	Copper quinoline	Biocide	Cu (II)

2.2.2. Lead (Pb)

Groundwater contamination is one of the most serious environmental issues which results through anthropogenic activities and atmospheric input,^[68,69] therefore World Health Organization (WHO) and Environmental Protection Agency (EPA) set the maximum permissible discharge limit in both the consumable water and wastewater can only be $6.0 \times 10^{-3} \text{ mgL}^{-1}$.^[70] Heavy metal pollution is associated with primarily industrial wastewater, wastewater producing industries such as dyeing textile, hydrometallurgical, tanning, smelting of ores, metal plating, battery industries, fertilizers and herbicides production, motor, electrochemical, house paint, gasoline additives and plumbing pipes,^[71] carry heavy metals such as Cr (III,VI), As(III,V), Cd(II), Pb(II), Cu(II), Zn(II) and Hg(II) which are dangerous to the environment and living organisms, among these lead (Pb) one of the toxic heavy metal due to its non-biodegradable harmful effect. Exposure to lead can cause digestive problems, neurological disorders, high blood pressure, reproductive health problems, kidney dysfunction, muscle and joint pain, fertility problems in adults, and the most lead exposure, leading to damage to the developing brains of infants and young children. Several conventional treatment techniques have been applied for the removal of Pb (II) which are flocculation, ion exchange, reduction, membrane filtration, solvent extraction, biosorption, chemical precipitation, reverse osmosis, adsorption, etc.^[72,73] Most of these methods have numerous limitations such as high operational cost, huge capital investment and secondary pollutants disposal complications. Accordingly, many researchers reported that the adsorption method is considered to be highly effective and economical at present.^[14,74] Adsorption of heavy metal ions on to different solid support such as ion exchange resins, activated charcoals, zeolites and ion chelating agents that are highly effective and economical as easy regeneration process besides these agents usually inactive on inorganic supports for decontamination of industrial wastewater effluents. Many researchers are currently

focusing on the latest treatment technology method to remove lead, therefore aspiration towards achieving and exploring efficient adsorbents to improve the adsorption effectiveness. Specifically, the carbonaceous materials have been proved to be effective adsorbents for removing metal ions because of well-developed internal pore structure, large surface area, and mainly containing a wide range of functional groups. Multiple reports indicated that a carbon surface's oxidation treatment increases the functional groups' mainly oxygen-containing group with high adsorption^[75] potential of metal ions and its hydrophilicity.^[76,77] From that perspective, recently large numbers of adsorbents were investigated, for example, carbon nanotubes, activated carbon, clay minerals, microorganisms, and plant and agricultural wastes, among which graphene oxide (GO) has been in the centre of attention^[78,79,80] due to its unique two-dimensional structure and large specific surface area ($\sim 2600 \text{ m}^2 \cdot \text{g}^{-1}$), researchers stated that the graphene becomes an incomparable perfect material for the adsorption of heavy metal ions.^[79] Therefore oxidation of graphite to GO with increased functional groups enhance the removal efficiency of heavy metal ion and their complexes from water; additionally, GO can be recycled, and reusable capabilities, from this point of view the adsorption of lead Pb(II) over GO, functional groups exist on the surface of GO plays a crucial role, and adsorption ability of GO was found to be higher than graphite; therefore the author concluded that GO could be a promising material for the removal of lead that present in wastewater.^[81]

2.2.3. Cadmium (Cd)

Cadmium (Cd) is a group IIB member of the periodic table with mass number 112.48 and atomic number 48, and the common oxidation state of cadmium is +2. Some of them are +1 oxidation state present in the ecosystem. Cd, is one of the most toxic heavy metal found in industrial effluent which has been utilized broadly in textiles, batteries, ceramics, electronic

and metal-finishing industries, electroplating industries, pigments, petroleum products, insecticides, solders, television sets, metallurgical industries, steel, photography plastics and synthetic chemicals.^[82] Because of the anthropogenic activities, water is contaminated by Cd(II) which predominantly occurs by the following actions: mining, smelting, smoking, industrial wastewater discharge, and airborne particulate matter.^[83] Due to the discharge effluent from different sources to accessible drinking water bodies, the higher cadmium concentrations are found in a few types of fish, mussels, and clams in the contaminated seaside regions. This metal toxic brings out the health effects such as lung cancer, respiratory problem, kidney, liver and reproductive organs.^[84,85] Therefore, the discharges from the industrial wastewater are the potential sources of cadmium contamination in drinking water. The acceptable limit of cadmium in drinking water prescribed by the BIS is 0.003 mgL^{-1} .^[86] According to the maximum contaminant level (MCL) standards, allowable cadmium limit is 0.01 mgL^{-1} when the limit exceeds then human carcinogen will develop.^[87] Following the EU environmental quality standards, cadmium containing effluent released should be less than $10 \mu\text{gL}^{-1}$. Further, USA International Agency for Research on Cancer and the National Toxicology Program recognized cadmium as group 1 carcinogenic metal ion yet considered lethal with vomiting and nausea at 15.0 mgL^{-1} concentration. The impact on plants and Cd content in wastewater will slow down seed and lipid content growth. Therefore, it is crucial to prevent Cd-containing products' use to reduce its harmful impacts on humans, living organisms, and our environment. Recently graphene materials gained more attention in removing toxic heavy metal removal due to their unique properties.

2.2.4. Zinc (Zn)

Zinc (Zn) is one of the most significant heavy metals found in various effluents sources, which then travels through the food chain via bioaccumulation.^[88] Zn plays a vital role in regulating many biochemical processes and living tissue physiological functions. The industrial sources of zinc include brass plating, wood pulp production, textile waste, ground and newsprint paper production, steelworks with galvanizing lines, zinc, and brass metal works. Waste concentrations of zinc range from less than 1 to more than $48,000 \text{ mgL}^{-1}$. However, the presence or exposure of zinc in excess causes eminent health problems, such as stomach cramps, nausea, skin irritations, cramps, vomiting, and anaemia.^[14,89] These effects on human health and environment and needed for effective treatment for removing zinc from the wastewater effluent. Although zinc is considered an essential micronutrient for life, it can be toxic beyond permissible limits. The World Health Organization (WHO) recommends that the maximum acceptable concen-

tration of zinc in drinking water is 5 mgL^{-1} .^[90] Various zinc removal techniques include chemical precipitation, electrochemical treatment, ion exchange, membrane separation, and adsorption.^[91] Generally, adsorption has been the most often used and studied method because it is a cheap, effective and easy application.^[92,93] Materials such as biomass,^[94] carbon nanomaterials,^[95,96] active carbon,^[97] bentonite^[93] and resin^[98] are well-known for efficient removal of Zn (II) from aqueous solution. Among them, graphene oxide-based materials are the most effective with high adsorption capacity with excellent performance.^[99]

3. Textile Dye Classifications

The dyes are natural and synthetic compounds that make the world beautiful through colours. Colourants can be classified as dyes and pigments. The dyes are soluble compounds capable of absorbing the light radiation in the spectrum's visible range and reflecting or scattering additional radiation and dyeing a substance in a sustainable approach.^[100] Chemical structures of dyes specify their colour properties. The pigments are coloured, colourless, or fluorescent colouring insoluble compounds which can be available as solids and powders used in paints, printing inks, ceramics and plastics. Their solubility differentiates dyes and pigments. Dye structure contains chromophore groups and auxochromes, which are essential components and combined with aromatic structure. All those have specific properties that enhance the colour and the bond between the fibre during dyeing and printing process.^[101] Table 5 and Table 6 show the chemical structures of chromophores and auxochromes. Chromophores are involving in the function of imparting colour to the dye. In contrast, auxochromes have intensified the colour of that dye with fibres in the arrangement of strong chemical bonds. Classification of dyes comes under two different types based on chemical structure and dye application method. Chemical category based on the structure of the dyes, specifically the chromophore groups, includes azo, azine, acridine, anthraquinone, indigoid, methine, nitro nitroso xanthene dyes, phthalocyanine dyes, diphenylmethane and triphenylmethane dyes. Application method classification of dyes is acid dyes, basic dyes, azoic dyes, direct dyes, mordant or chrome dyes, vat dyes, reactive dyes, indigo dyes and sulphur dye which are briefly explained below.

3.1. Classification of Textile Dyes by Application Method

Classification of dyes depends on a few parameters, namely solubility, affinity with various fibres and the fixation rate. Generally, cationic, anionic and non-ionic dyes are used in the textile industry depending on their particle charge dissolution

Table 5. Main chromophore groups in dyes and their chemical structures.

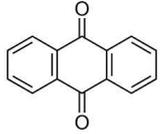
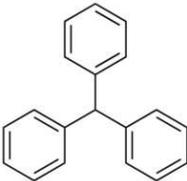
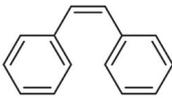
Chromophores	Structure	Chromophores	Structure
Azo	(-N=N-)	Anthraquinone	
Nitroso	(-NO or -N-OH)	Triphenylmethane	
Carbonyl	(=C=O)	Stilbene	
Carbon	(=C=C=)	Carbon-sulphur	(=C=S; ≡C-S-S-C≡)
Carbon nitrogen	(=C=NH or -CH=N-)	Ketone-imine	(=C=NH)
Nitro	(-NO ₂ or =NO-OH)	Polymethine	(=HC-HC=CH-CH=)

Table 6. Main auxo chromic groups in dyes and their structures.

Auxo chromes	Structure
Amino	-NH ₂
Methylamino	-NHCH ₃
Dimethylamino	(-N(CH ₃) ₂)
Sulfonic radicals	-SO ₃ H
Carboxyl	-COOH
Hydroxyl	-OH
Alkoxy	(-OR)
Electron donor groups	(-NO ₂) (-CO ₂ H) (-SO ₃ H) (-OCH ₃) Cl, Br, I, At

in aqueous solutions.^[102] Based on the solubility, two subdivisions are water-soluble dyes and water-insoluble dyes. Water-soluble anionic dyes are direct, acid, and reactive dyes; a water-soluble cationic dye is basic whereas disperse, sulphur, and azoic indigo and vat dyes are some other examples of the insoluble dyes which are shown in Figure 5. These dyes and their characteristics, along with possible pollutants, including toxicities, are briefly explained below in Table 7.

3.1.1. Water-Soluble Anionic Dyes

3.1.1.1. Reactive Dyes

Reactive dyes are water-soluble anionic dyes, introduced in 1956, used for dyeing and printing for cellulose fibres. Reactive dyes are available as pourable granules, finished powders, highly concentrated aqueous solutions, and commercially few fibre-reactive dyes available for proteins and

polyamide fibres. Most of the reactive dyes come under the azo and anthraquinone-based reactive dyes. Reactive dyes form a covalent bond with the fibre: it produces high wash-fastness properties. It has good resistance to degrading sunlight due to the firm, stable electronic arrangement dye structure. Generally, textile materials with reactive dyes have excellent lightfastness. Still, azo chromophore reactive dyes give low lightfastness while metal complex azo reactive dyes give brighter lightfastness properties. Removal of metals from complex dye form has gained much attention in recent years in consequences of environmental effect, metal-based reactive dyes are bound with copper, chromium and nickel, discharging the metal-containing effluent spreading heavy metal toxicity to the environment that can end up in the food chain at the end.^[103]

3.1.1.2. Direct Dyes

Direct dyes are water-soluble anionic dyes, have a strong affinity with cellulosic fibres, for example, cotton, viscose, linen, jute, hemp and ramie. Almost all direct dyes are azo dyes, containing one or more sulphonic acid groups to impact water solubility. The chromophores in natural dyes include the following: (i) Azo dyes such like disazo, trisazo and polyazo dyes, (ii) Stilbene, (iii) Oxazine (iv) Phthalocyanine, (v) Thiazole and (vi) Copper complex azo dyes. The forces of attraction between the direct dye and cellulosic fibre include hydrogen bonding, dipolar forces and non-specific hydrophobic interactions which are highly dependent upon the nature of the dye structure and the polarity of the dye

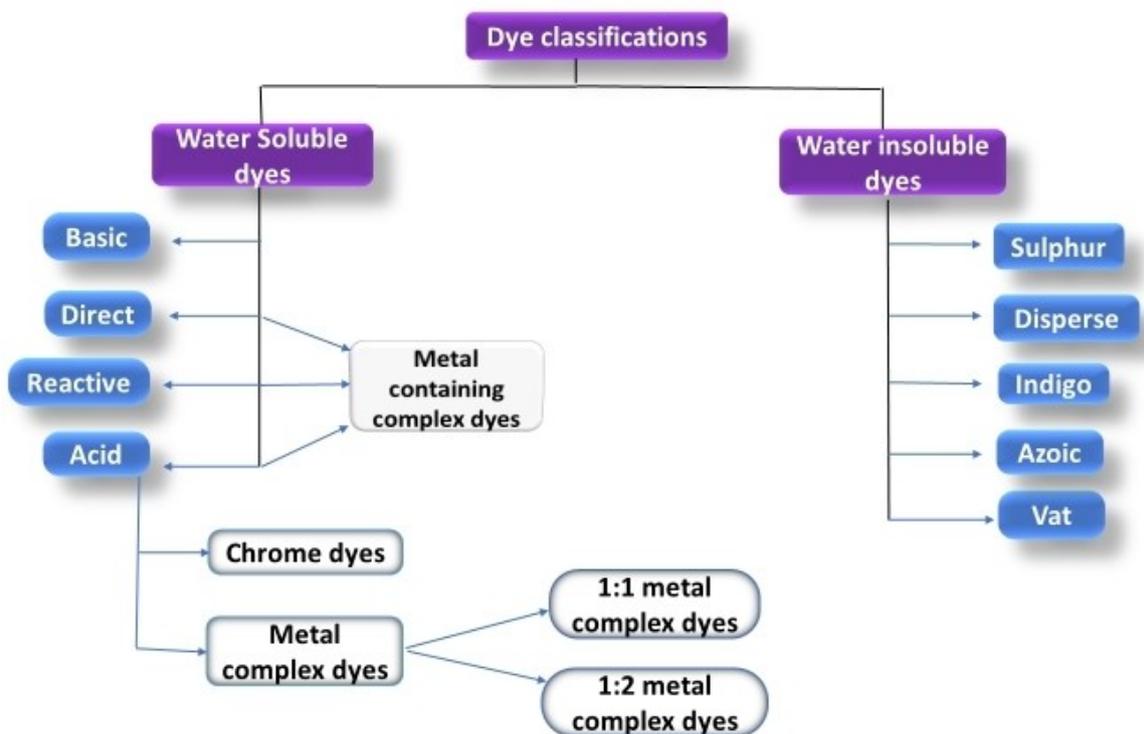


Figure 5. Classification of dyes used in the textile industry.

molecule. Direct dyes are the best substitute for the carcinogenic benzidine dyes; for example, Congo Red is carcinogenic, usually synthesised from benzidine.

3.1.1.3. Acid Dyes

Acid dyes are water-soluble anionic dyes, mostly applied on natural fibres such as wool, silk, mohair, angora, alpaca and synthetic polyamide like nylon, slightly to acrylic and blended of these materials. Generally, affinity in cellulosic fibre is very poor; most acid dyes are sodium salts of aromatic sulphonic acids and some carboxyl groups acid dye. Commonly acid dyes contain 1–4 sulphonic acid groups in the dye structure and the molecular weights range from 300 to 800. Animal protein fibres and synthetic nylon fibres contain many cationic sites on the fibre which have effective attraction affinity with anionic acid dye molecule. According to the chemical structure, acid dyes are divided into three divisions: azo, anthraquinone, and triphenylmethane. Chromophores in acid dyes are, namely nitro, indigoid, quinoline, azine, phthalocyanine, xanthane, carbolan dyes, etc., The proportion of acid dyes in each group is azo (65%), anthraquinone (15%), triphenylmethane (12%) and others (8%). Main advantages of using these dyes are easy to apply, inexpensive, excellent fastness properties, and moderate fastness in dry cleaning. Most parts of acid dyes are

non-toxic, according to the Ecological and Toxicological Association (ETAD), two shades are toxic, namely C.I. Acid Orange 150 and C.I. Acid Orange 165. However, another acid dye C.I. Acid Violet 17 has an allergic effect. Metal complex acid dyes or pre-metallised dyes are complexed with acid dyes formed combined transition metal called metal complex acid dyes which are economical and produce excessive light fastness and wet fastness. Metal complex acid dyes are brighter than chrome dyes but duller than acid dyes. Chrome mordant dyes are widely used in high-quality fibres because of their easy application and colour fastness properties. Metal complex acid dye has two different groups which are acidic dyeing 1:1 metal complex and neutral dyeing 1:2 metal complex acid dyes which mean one dye molecule is combined with one metal atom in acidic condition and two dye molecules is combined with one metal ion in neutral dyeing which briefly discussed in the metal complex dye category.

3.1.1.4. (i) Metal Containing Dyes

3.1.1.4.1. (a) Metal Complex Dyes

Metal complex dyes are mordant and pre-metallised dyes which show most excellent affinity towards protein fibres, in metal complex dye one or two molecules of dyes, are coordinated with a metal ion through the covalent bond

Table 7. Dyes characteristics and possible pollution with toxicity.

Dye type	Characteristics	Fibre type	Fixation rate (%)	Possible pollutants	Toxicity
Direct dyes	Water-soluble, anionic compounds, low wash fastness.	Cellulose fibres	70–95	Colour, salt, unfixed dyes, copper salt and dye-fixing agents.	Carcinogenic
Acid dyes	Water-soluble, anionic compounds.	Natural fibres and synthetic polyamide.	80–93	Colour, organic acids and dyeing auxiliaries.	Carcinogenic
Basic dyes	Water-soluble, applied from weakly acid bath and very bright shades.	Wool, silk, cotton and modified acrylic fibres.	97–98	Colour, organic acids and dyeing auxiliaries.	Carcinogenic
Reactive dyes	Water soluble, covalent bond with fibre and most favourable dye class.	Cellulose fibres	60–90	Colour, salt, alkali, unfixed dye and soaping agents.	Dermatitis, allergic conjunctivitis, rhinitis, occupational asthma or other allergic reactions.
Azoic dyes or naphthol dyes	<i>In-situ</i> colour formation by coupling reaction.	Cellulose fibres	–	Alkali, unfixed colour, naphthol, diazotised base, soaping agent	Carcinogenic
Sulphur dyes	Water-insoluble, sulphur-containing organic compounds, solubilised on a weak alkaline reduction	Cellulose fibres, especially with polyester, nylon and acrylic	60–70	Colour, sodium sulphide, alkali, oxidising agent	–
Vat dyes	Water-insoluble, chemically complex, solubilised on a substantial alkaline reduction	Cellulose fibres, wool, nylon, polyester and acrylics	80–95	Colour, alkali, sodium hydrosulphite, alkali, soaping agent	–
Disperse dyes	Water-insoluble, low molecular weight	cellulose acetate and triacetate, polyamide and acrylic fibres	80–92	Colour, organic acids, dispersing agents, carriers	Carcinogenic and allergic reactions

formation. Metal-complex dyes generally cannot be said as belonging to a particular application dye. Metal-complex dyes belong to numerous application classes of dyes. For example, they are found among direct, acid, and reactive dyes. When applied in the dyeing processes, metal-complex dyes are used in pH conditions regulated by user class and fibre type (wool, polyamide, etc.). class. These dyes are generally used to dye wool, silk and nylon to produce fast shades. In metal complex dyes, dye molecule and atom are combined with the specific composition either 1:1 or 1:2, which means one atom combined with one dye molecule or one atom combined with two dye molecules. For example, the dye molecule could be a mono azo group containing hydroxyl, carboxyl or amino, capable of forming a potent coordination complex with transition metal ions such as chromium cobalt, nickel and copper. There are two reasons for metals present in dyes, and firstly metals are used as catalysts during the manufacturing of dyes so that metals can be present as impurities. Secondly, in

some dyes, the metals are chelated with the dye molecule to form an integral structural element. Metal content in different dye types mentioned in Table 8.^[104] Besides copper, chromium, cobalt and nickel complexed reactive dyes are used to produce turquoise blue and brilliant green; alternatively, ecological issues have forced dye manufacturers to introduce phthalocyanine groups with comparable results.^[105] Due to their ease of application and fastness properties, they are used for dyeing high-class dress materials. Chemically speaking, metal complex dyes can be broadly classified into two classes. 1:1 metal-complexes, where, one organic molecule gets co-ordinated with a single metal atom (Figure 6a). Besides, in 1:2 metal complexes, one metal atom is co-ordinated with double organic molecules. Both ionic and coordinates bonds are formed with metal complex dyes and fibre (Figure 6b). Figure 6c represents the Cu's chemical structure containing metal complex dyes, which generates different colours by

Table 8. The table of the heavy metal content of dyes.

Heavy metals	Typical concentration (ppm)	Dye type with the highest metal content
Arsenic	< 1–1.4	Reactive dyes
Cadmium	< 1	All types of dyes
Chromium	3–83	Vat dyes
Cobalt	< 1–3.2	Acid dyes
Copper	33–110	Vat dyes
Lead	6–52	Reactive dyes
Mercury	0.5–1	Vat dyes
Zinc	3–32	Basic dyes

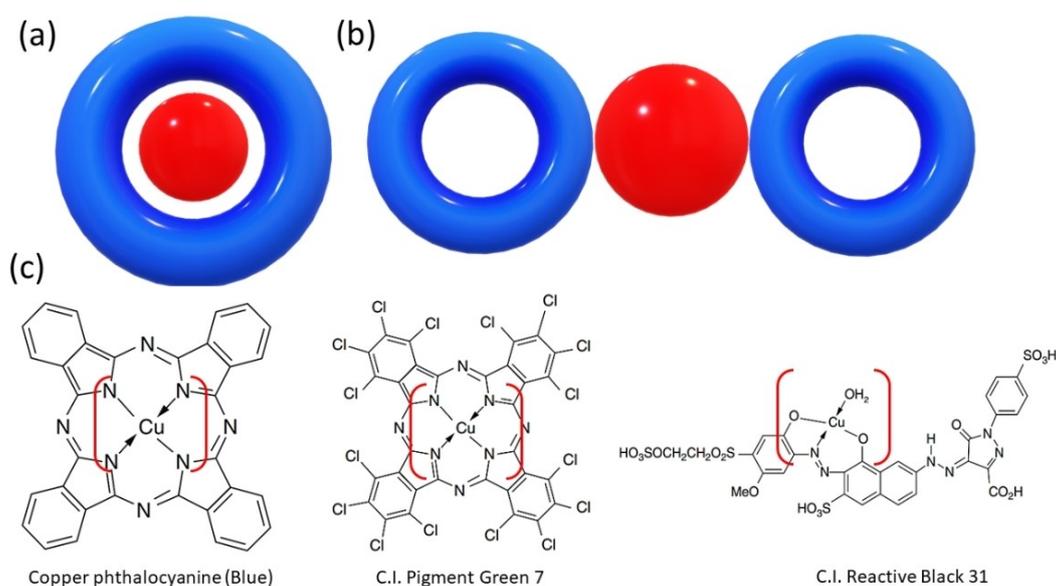


Figure 6. Schematic representation of (a) 1:1, (b) 1:2, metal-organic dye coordination, respectively, (c) chemical structure of a Cu-contained metal complex dyes, an indication by variation of organic surroundings and coordination approaches, leading to generate different colours.

forming metal-organic coordination and zwitterion complex with the organic molecules.

The above mentioned four metals are soluble in perspiration at varying extents, showing a negative impact on human health and our ecosystem. A research stated that 1:1 metal-complex dyes of copper, nickel, cobalt or zinc metal ions with 5-cyano-6-methyl-2,2'-bipyridine were highly effective on protein fibres.^[106] These metal complex dyes are currently available in the market, mainly containing Chromium and Cobalt metals in the chemical structure; these types of metal dyes are developed in 1915. Chromium metal is widely used in two different oxidation states: trivalent Chromium Cr (III) and hexavalent chromium Cr (VI).^[105] 1:2 metal complex dyes are mainly used in wool dyeing which provide extreme colour fastness to wet treatments, thus increased the utilisation of 1:2 metal complex dyes compared to 1:1 metal complex dye; further their advantages and limitations are shown in Table 9. Chromium complexed dyes are predominantly used on substrates due to the high light and wash fastness qualities which not found in other dyes.^[107] In the colour index, metal complex dyes are incorporated in the acid dye group, closely related to chrome mordant dyes. Chrome mordant dyes have some limitations; therefore, acid dyes are preferred by the dyer's point of view. Metal complex dyes are brighter than chrome dyes but duller than acid dyes. Chrome mordant dyes are used in high-quality fibres because of their easy application and colour fastness properties. In the decade 1940–50, 1:1 metal complex dye had been established in wool dyeing and 1951 Geigy developed a new series of 1:2 metal complex dyes under the trade name 'Irgalan'. Metal complex dyes are found among 65% of acid dyes, 12% reactive dyes and 10% of direct dyes, during dyeing process metal complex dyes used under certain pH conditions which are regulated by the user

class of dyes and the fibre category such as wool and polyamide etc., The pH level for the wool fibre typically from 1.8 to 4 which is strongly acidic for 1:1 metal complex dye category and for 1:2 metal complex category pH range from 4 to 7 which is moderately acidic neutral. Examples of dyes containing bound metals are copper and nickel in phthalocyanine groups, copper in blue copper-azo-complex reactive dyes and chromium in metal-complex dyes used for wool silk polyamide. The standard discharge limits for heavy metals are strict due to animals' toxicity and aquatic life. Metal-complex dyes contain chelated chromium, cobalt, copper, lead and nickel-metal ions. Some cationic dyes contain zinc and trace concentrations of mercury, cadmium, and arsenic as impurities from intermediates. The metal is an integral part of the dye molecule, non-biodegradable and potential for bioaccumulation. Further, the treatment methods such as filtration and adsorption on activated sludge, which remove the dye from the wastewater, also reduce the amount of bound metal in the final effluent. Few examples for metals containing metal complex dye chemical structures with molecular formulas and molecular weights are given in Table 10.

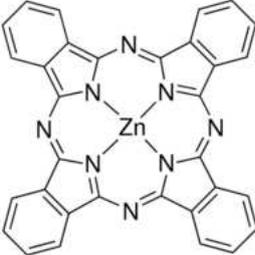
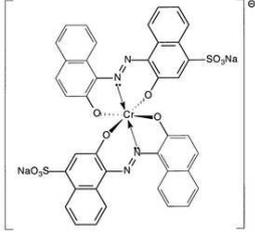
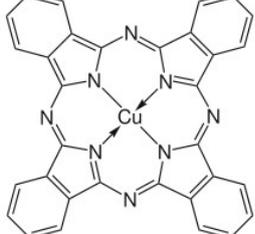
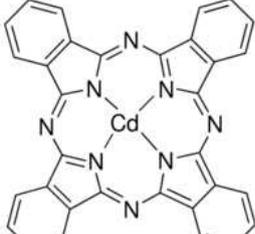
3.1.1.4.2. (b) Chrome Dyes or Mordant Dyes

Chrome dyes or acid mordant dyes are acid dyes, water-soluble, mainly used for dyeing fibres like wool, silk and polyamides the mordant dyes have no affinity for textile fibres; therefore, they attached to the fibre with the help of mordants which have affinity both for the dye and the fibre. During mordant dyeing, fibre is first treated with a metal which then becomes metal attached fibre called mordanted fibre and then dyed by a complexed agent like a chelating agent is known as an acidic dye. Approximately 30% of chrome dyes used to

Table 9. Metal complex dyes advantages and disadvantages.

Complex metal ions	Advantages	Limitations
1:1 metal complex acid dye	Dyeing method is simple Uniform and level dyeing. Suitable for wool fibre, tops, hanks and fabric Shading and brightening is possible Excellent fastness properties such as washing, seawater, light, dry cleaning, crocking, etc., Excellent reproducibility Excellent dyeing behaviour in the combination process Good migration property	Poor fastness compared to chrome dyes Addition of sulphuric acid must be done in 2–3 time-bound to avoid fibre degradation.
1:2 metal complex acid dye	Excellent fastness properties Better level dyeing Better reproducibility Less damage on wool Shorter dyeing cycle More exhaustion of dyes	–

Table 10. Examples of metal-containing dyes with the chemical structure.

Metal containing dyes	Chemical structure	Chemical Structure and Molecular Weight
Zinc phthalocyanine		$C_{32}H_{16}N_8Zn$ 577.91
C.I Acid blue 193		$C_{40}H_{22}CrN_4Na_2O_{10}S_2$ 880.7
Copper (II) phthalocyanine		$C_{32}H_{16}CuN_8$ 576.07
Lead (II) phthalocyanine		$C_{32}H_{16}N_8Pb$ 719.72
Cadmium phthalocyanine		$C_{32}H_{16}CdN_8$ 624.93

dyes the wool for getting black and navy shades on wool. Mordant dyes are best for dark shades similar to 1:2 metal complex dyes. Chromium salts are mainly used as a mordant because of the cost-effectiveness and less variation in shades. Chromium compound is nothing but sodium or potassium

dichromate substance (heavy metal salt). Chromium acts as a link between dye and fibre, strengthening the bond between them and providing excellent fasten properties. Chrome dyes have various chemical classes, namely azo, anthraquinone, triphenylmethane and Xanthene. Advantages are one-step

process, high production and easier shade matching. Limitations are shade range is limited, impossible to correct the unlevel dyeing, longer time dyeing cycles and the potential release of chromium in wastewater, such as dyes C.I. Mordant Red 7 (maroon).

3.1.2. Water-Soluble Cationic Dye

3.1.2.1. Basic Dyes

Basic dyes are water-soluble cationic dye, perfect for synthetic dyes and mainly applied to wool, silk, cotton and modified acrylic fibres for brightness and tinctorial strength. The chromophores in basic dyes contain positively charged ions with functional groups like $-NR_{3+}$ or $=NR_{2+}$. It consists of amino groups, or alkylamino groups, as their auxochromes which perform poorly on natural fibres but work very well on acrylics. The first synthetic dye mauve of Perkin (1856) belongs to this dye group which contains the following chromophores, such as (a). Diphenylmethane (b). Triphenylmethane (c). Azine (d). Thiazine (e). Oxazine, and (f). Xanthene. Various cationic basic dyes are highly toxic to an aquatic environment, for example, C.I. Basic Blue 3, C.I. Basic Blue 7, C.I. Basic Blue 81, Basic Red 12, Basic Violet 16 and Basic Yellow 2. Fixation rate for this dye is nearly 100% when appropriately applied; the problem occurred when handled improper procedures and spillage. Moreover, basic dyes are water-soluble and produce coloured cations in solution; they are attracted electrostatically to substrates with a negative charge. Advantages of using these dyes are high tinctorial strength, moderate substantivity, relatively economical, wide shade range and show good brightness properties; limitations are poor shade stability, high acid content and poor lightfastness.

3.1.3. Water-Insoluble Dyes

3.1.3.1. Indigo Dyes

Indigo dyes are insoluble in water, alcohol and ether but capable of soluble in chloroform, nitrobenzene, or concentrated sulfuric acid. Indigo is one of the oldest dyes used in textile dyeing and printing; Asian countries like India, China and Japan had used this dye for centuries. In olden days, this dye was considered precious because the dye's leading source from the natural plant leaves woad (*Isatis tinctorial*), which had a very minimum amount of dye about 2–4% which is significant for blue colour. Indigo dye was first found in India, in the 19th century British procured a large amount of indigo from India. The demand for natural indigo dropped when the synthetic indigo was innovated. In 2002, 17,000 tons of synthetic indigo were produced worldwide, which then primarily used for cotton yarn, indigo is mainly for the production of denim cloth for blue jeans. On average, a pair of

blue jean trousers requires 3–12 g of indigo, and a small amount is used for dyeing wool and silk. Due to synthetic indigo's health and environmental pollution effects, the demand for natural indigo increased again in many countries. Chemical structures of synthetic and natural are same; the chemical in Indigo is also called Indigotin (2,2'-bisindoleindigo, or 2,2'-biindoline-3,3'-dione) which is responsible for the blue colour. Indigo dye divided into two groups, namely, (i). A natural form is insoluble in water and cannot dye the fibre, (ii). Leuco form is soluble in water and can dye the fibre. Indigotin dye needs to be activated to Leuco form, which means indigo should be converted into soluble in water for better affinity to the fibre during dyeing. The best dyeing achieved between the pH 11.5–12.5 due to the enhanced dye molecule penetration with increased pH. Indigotin is insoluble in water, and which must be first reduced to the water-soluble leuco form and then reoxidized to become a blue dye united within the fibre. Natural indigo is used on handmade textiles and on natural fibres to impart blue colour, natural indigo is a bit expensive than synthetic indigo, during the dyeing process around 3800 L of water consumed in making just a pair of jeans along with 312.4 kg of carbon dioxide produced, which severely generate an impact on climate change. Various research identified that the textile effluents are mainly responsible for the mutagenic effect and cause potential health risk by being a non-genotoxic carcinogen. However, if the effluents contain a higher concentration of indigo indigoid which leads to genotoxic.

3.1.3.2. Azoic Dyes or Naphthalene Dyes

Azoic are also called naphthalene dyes which are water-insoluble, mainly used for cellulose fibres, particularly cotton, rayon, and other cellulosic fibres including silk. The application process is called naphtholation; naphthol dyes are classified as fast dyes cheaper than vat dyeing, containing insoluble azo group ($-N=N-$) known as azoic dyes. The naphthols are phenols, soluble in alkaline solution and good affinity to cotton, particularly salt. Azoic dyes were introduced in 1881 by Reed Holiday which is generally called as ice colours or azoic colours, the first dye obtained from -naphthol and diazotized 4-nitroaniline, known as Para Red. It gives a wide range of colours such as yellows, orange, scarlet, red, blues, black and few greens. Naphthol dyes are recommended for bright and fast shades in maximum depth similar to vat dyeing. For the past few decades, these dyes' usage reduced due to the ecotoxicology and carcinogenic of some azoic diazo components derived from amines. Advantages are low dyeing cost, excellent fastness properties, which produce full bright depths that are not achievable from other dyes. Limitations are application procedure, which is a time-consuming process and complicated and have poor lightfastness in light shades.

3.1.3.3. Sulphur Dyes

Sulphur dyes are insoluble in water, widely used on cellulosic fibres and their blends, especially polyester, nylon and acrylic. Sulphur dyes are highly used for raincoat because of the rubber coating and laminated with polyurethane foam. It can produce a wide range of shades on cotton and rayon fabrics, dyed mainly on cheap cotton goods. Moreover, sulphur dyes are fairly cheap among all other synthetic dyes. Sulphur dyes are available in the form of powder, pre-reduced powders, grains, disperse powders, disperse pastes, liquids and water-soluble brands. The liquid sulphur black dye has more excellent adsorption than sulphur dye in powder. Besides, brightly painted, excellent equalizing, operator simplicity, eco-friendly, convenient to use beside no harmful and carcinogenic substance inside. Another significant feature of utilising this liquid sulphur is a low cost, less dyeing time, convenient process and importantly lesser pollution loads when compared with vat dye and reactive dye.^[108]

3.1.3.4. Vat Dyes

Vat dyes are insoluble in water, used for dyeing of cotton and other cellulose fibres which can also be applied to wool, nylon, polyesters, acrylics and modacrylics with the use of a mordant. Vat dyes can be soluble in water when the alkaline conditions reduced, reducing agents such as sodium dithionite (sodium hydrosulphite). Again, it can be converted into insoluble form by oxidation. Vat dyes contain heavy metal impurities such as Cu, Fe, Pb, Ba, and Mn used during production. After oxidation vat dyes are water-insoluble makes largely it can be eliminated by adsorption remediation method using activated sludge in wastewater treatment.^[109]

3.1.3.5. Disperse Dyes

Dispersed dyes are insoluble in water and suitable for dyeing hydrophobic fibres such as cellulose acetate and triacetate, polyamide and acrylic fibres. During disperse, dyeing temperature and pH played a significant role where above 100 °C is required for high-temperature dyeing method, besides the pH should be in an acidic condition, which means pH between 4.5 and 5.5. Majority of the disperse dyes are azo structure. Generally disperse dyes are derivatives of azo, anthraquinone,^[110] nitro and quinine groups from which monoazo is the largest class nearly 50%, anthraquinone based 25%, 10% of diazo compound based, 3% of methylene dyes, 3% of styryl dyes, 3% of acetylene benzimidazole, 3% of quinonaphthalon dyes, 1% of Amino naphthyl amide, 1% of naphthoquinone imine and 1% of nitro disperse dyes in the market, therefore 85% of disperse dyes constituted by monoazo, diazo and anthraquinone based disperse dyes.

Monoazo dyes are cheap and easy to manufacture however have poor sublimation fastness, but for diazo based compounds have excellent fastness properties suitable for application by the thermo fixation process. Anthraquinone dyes are expensive and brighter whereas the monoazo had a low affinity, but the diazo has a good lightfastness. Azo-based dispersed dyes are widely used in the printing process. Due to dischargeable flexibility, anthraquinone-based dispersed dyes are non-dischargeable, primarily used in the simple dyeing process. These dyes are among the stubborn class of dyes due to uncontrollable nature and non-biodegradable reactions.^[111]

4. Environmental Impact and Toxicity of Textile Wastewater

4.1. Dye Toxicity to Human Health and Environment

- Dyes are toxic even at small concentrations (1 mgL^{-1}) present in the environment, which are stable complex chemical structure against breakdown. Most of the dyes are non-biodegradable, leading to a severe environmental problem.
- Dye polluted water causes substantial health issues such as skin rashes, headaches, lack of concentration, nausea, diarrhoea, fatigue, muscle and joint pain, dizziness, difficulty breathing, irregular heartbeat, seizures and remarkably leads to cancer.
- Toxicity from textile dyes is considered under two subdivisions: acute toxicity and chronic or genotoxicity. Oral ingestion and inhalation issues come under acute toxicity; genotoxicity is the significant long-term potential health hazard of few textile dyes. Genotoxic chemicals damage deoxyribonucleic acid (DNA) usually by chemical reaction.
- Phthalocyanine dyes are considered non-genotoxic due to the large size to pass through the cell membranes. Among textile dyes, reactive dyes are generally causing skin irritation and skin sensitisation, dermatitis, allergic conjunctivitis, rhinitis, occupational asthma or other allergic reactions.

Chrome mordant is another type of toxicity spreading dye for both human carcinogen and environment. A mordant is a heavy metal salt of aluminium, iron, copper, chromium or tin in which alum and ferrous sulphate are relatively safe mordants rather than copper and chromium.

4.2. Heavy Metal Toxicity to Human Health and Environment

- The exposure of heavy metals into human beings is mainly discovered through the three notable routes: oral ingestion, inhalation and dermal exposure.

- Heavy metal pollution in agricultural soil is another serious environmental problem due to the wide distribution of the heavy metals in the environment and its effects (acute and chronic) on plants' growth.
- The heavy metals in high concentration can produce serious health issues. The heavy metal toxicity may harm or decrease the mental and central nervous activities, damage the lungs, liver, kidneys, blood compositions and other fundamental organs. The long exposure of toxic heavy metals may cause muscular dystrophy, Alzheimer's disease, different types of cancers and multiple sclerosis.
- The food intake is considered one of the essential routes of these heavy metal exposures while it was compared with inhalation and dermal exposures. Inhalation is regarded as a necessary way of occupational exposure.
- The exposure of heavy metals on human beings provides health impacts, including cancer, developmental retardation, kidney damage, immunological impact, endocrine disruption, and neurological impacts.

The removal of toxic heavy metals from textile wastewater is a significant issue because these metals can provide severe health dangers to people and other living organisms. From this perspective, it is consequential to develop treatment strategies to remove harmful metal ions from textile waste to decrease the pollution load to nature.

5. Remediation Techniques for Heavy Metal Removal from Textile Wastewater

Environmental Pollutions such as dyes, organic pollutants, heavy metals are widely contaminating the aquatic ecosystem. However, these methods are not used widely due to their high cost and economic disadvantage. An adsorption technique is the most versatile and widely used techniques for water purification. The most common adsorbent materials are alumina-silica, metal hydroxides and activated carbon. Many researchers proved that removing dyes by activated carbon is economically favourable and technically easier. Activated carbon is widely used as an adsorbent due to its high adsorption capacity, high surface area, microporous structure, and a high degree of surface, respectively. Another technique for removing dye molecules is photocatalytic degradation by semiconducting nanomaterials. These nanoscale particles are promising in this area due to their unique properties such as small particle sizes, large surface to volume ratio and UV-visible absorption properties. Thus the removal of poisonous hazardous substances from water is a significant environmental challenge, hence during the last decades' researcher have developed many tools and techniques to identify, monitor, assess and to treat the aqueous environment, which are coagulation, flocculation, adsorption, bioremediation, mem-

brane separation, oxidation, ion exchange, ozonation, chlorination, electrochemical and chemical precipitation have been developed and widely used to eliminate the toxic and hazardous substances. Many industries generate a considerable amount of coloured wastewater in which many of these dyes are carcinogenic and cause serious threats to human beings and other living organisms, accordingly, it is must treat the above-mentioned polluted wastewater before they discharge into the water bodies All these methods have their advantages and disadvantages which mentioned in Table 11.

5.1. Coagulation

In coagulation, Coagulant is used to increase the density of colloidal form. The coagulant's effectiveness depends on the coagulant types, the dosage of coagulant, pH, temperature, alkalinity, and depends upon the mixing conditions. In this process, chemical reagents or inorganic flocculants like $\text{Al}_2(\text{SO}_4)_3$, $\text{Fe}_2(\text{SO}_4)_3$ and FeCl_3 ^[112] and derivatives of these materials such as poly aluminium chloride and poly ferric chloride were used as flocculants in the wastewater effluent treatment process. Even though coagulation is efficient for removing heavy metals from wastewater, the main disadvantage is that it generates secondary pollutants that will be harmful to both the human and environmental ecosystem; therefore, it has to undergo further secondary treatment for the complete removal. Additionally, it produces enormous sludge formation due to the extensive utilisation of chemicals, limiting its wide usage range. After the coagulation process, the sludge formation contained heavy metals like cadmium, chromium, nickel, lead and zinc.

5.2. Ion Exchange

Ion exchange is a separation process which substitutes the ions with one another for the high removal efficiency. Comparatively the sludge production is low in this method, which is the greatest advantage. Ion exchange resins are cross-linked, long-chain organic polymer, microporous and carrying exchangeable ions. These resins are classified into two types such as synthetic and natural resins; among these, synthetic resins are widely favoured than the natural resins to separate the metals infinitely.^[113] The only disadvantage in this process is fouling of matrix happens in high concentrated metal solution.^[114] Further, the main drawback is secondary pollutants caused by ion exchange resin's regeneration. In addition to that, operational cost is high. Furthermore, it cannot be utilised in large scale industries for wastewater treatment.^[115] In conclusion, Ion-exchange process is expensive because it requires a large amount of resin to treat the large volume of the wastewater, which consists of lower metal ions concentration.

Table 11. Comparison of advantages and disadvantages of various treatment techniques accessible for the removal of heavy metals from wastewater.

Techniques	Advantages	Disadvantages
Coagulation	Simple method cost effectiveness. Significant reduction in COD and BOD. Remarkably efficient for suspended solids and colloidal particles. Dewatering qualities and produced sludge with good settling. Rapid and efficient for insoluble contaminants removal.	Generating a large volume of sludge. Requires addition of non-reusable chemicals. Utilization of chemical is high and required additional treatment.
Membrane filtration	High removal of heavy metals, lower space requirement, simple and easy to fabricate. Rapid and efficient, even at high concentrations. Produces a high-quality treated effluent No chemicals required Low solid waste generation. Eliminates all types of dyes, salts and mineral derivatives.	Very expensive and energy requirement is high. Membrane fouling, complicated process, low permeate flux and consume high operation pressure. High maintenance and operation costs.
Adsorption	Easy operation, less sludge production, utilization of low-cost adsorbents. High adsorption capacity, regenerable, wide pH range, and low operation cost. Excellent ability to separate a wide range of pollutants. Highly effective process with fast kinetics. Excellent quality of the treated effluent.	Desorption, nanosized adsorbents require moderate materials, and regeneration could result in secondary pollution. Relatively high investment and regeneration are expensive.
Electrochemical treatment	Efficient method for the removal of metal ions and low chemical usage. Adaptation to different pollutant loads and different flow rates. More effective and rapid organic matter separation than in traditional coagulation.	The initial investment is high and also need a high electrical supply. Requires addition of chemicals such as coagulants, flocculants, salts.
Ion exchange	Speedy reaction, a high transformation of components and high treatment efficiency. Straightforward method and well-established process. Easy to use with other techniques, for example, precipitation and filtration in an integrated wastewater process. Rapid and efficient process and produce a high-quality treated effluent. Relatively inexpensive and efficient for metal removal cleans up to ppb levels. Resins can be selective for certain metals. Attractive and efficient technology for the recovery of valuable metals.	Removes only limited metal ions, expensive due to synthetic resin/beads, low selectivity regeneration could result in secondary pollution. Large volume requires large columns. Performance sensitive to pH of effluent, conventional resins not demanding. Selective resins have limited commercial use which is not adequate for certain target pollutants such as disperse dyes, drugs, etc.
Biological treatment	This technology is beneficial in removing heavy metals. The application of microorganisms for the biodegradable of organic contaminants is simple. Economically attractive method but time consuming.	Requires maintenance of microorganisms and pre-treatment like physicochemical treatment is inefficient on non-biodegradable compounds or toxic compounds. Generation of biological sludge and uncontrollable degradation products. Need to be developed.
Chemical precipitation	A simple method, efficient and economically advantageous. Adaptable to high pollutants load. Extremely useful for metals and fluoride removal.	High chemical consumption (lime, oxidants and H ₂ S). Ineffective in the removal of metal ions at low concentration. Sludge production is high and disposal problems.

5.3. Membrane Filtration

Membrane technology is the growing technology in water purification; the membrane can be classified as dense and porous according to the driving force and ionic and molecular movement mode through the membrane. Membrane filtration method showed excellent results for removing heavy metals from the wastewater.^[116] This method's main advantage is higher removal efficiency; lesser space requirement and operation is easier. The different types of membranes, including reverse osmosis, ultrafiltration, microfiltration, nanofiltration, and electrodialysis, have been successfully employed to remove toxic metal ions from the wastewater. This method's main disadvantages are handling the rejection, membrane fouling, and high-power cost and advantages are high efficiencies, relatively lower energy requirements, reliability, and easy operation.^[117] Generally, this treatment method was successfully employed to treat industrial wastewater effluent, generation of drinking and desalination process of seawater, recovery of useful materials from industrial effluents, and salts' manufacture of salts.^[118]

5.4. Chemical Precipitation

Chemical precipitation method is used to treat the wastewater effluent because it is affordable and handy to operate.^[119,120] It includes sulphide precipitation and hydroxide precipitation. Hydroxide precipitation is the most widely used chemical precipitation method for removing heavy metals because of its low cost, easy to use and comfortable to control the pH.^[121] Hydroxide precipitation agents such as calcium hydroxide (Ca(OH)₂) and sodium hydroxide NaOH are utilised to remove the heavy metal, such as copper and Chromium from the industrial wastewater.^[122] To improve the efficiency coagulants like alum salt of iron and organic polymer will be supplemented to achieve the high-efficiency removal of industrial wastewater. Besides hydroxide precipitation, sulphide precipitation effectively removed the heavy metal from the industrial wastewater and reached a successfully high level of metal removal over a wide range of pH conditions.^[14] Both hydroxide and sulphide precipitation have their limitation, such as sulphide method has its separation issues in either filtration or sedimentation processes. In contrast, the hydroxide method requires many chemicals to decrease the metals to an adequate level for release into the environment.^[123]

5.5. Electrochemical Methods

The electrochemical methods are extremely effective wastewater treatment methods, particularly for removing heavy metal ions from industrial wastewater effluent. This method

involves recovering the heavy metals in the elemental metallic state using the anodic and cathodic reactions in the electrochemical cell. Moreover, it requires a large amount of capital investment and more power supply, limiting its vast industrial applications. Some of the electrochemical methods include electrocoagulation, electrodeposition, and electro flotation techniques have been analysed in the removal of heavy metal ions from wastewater. The significant advantage of using this method is recovering metal in the purest form; operating cost is less and no complication in the disposal of sludges.^[124,125] Electrochemical methods are quick and well-controlled treatment methods for removing heavy metals from industrial wastewater, which needs less amount of chemicals, generates less quantity of sludge formation and provides the maximum metal ions removal. The heavy metal removal is also applicable in dye molecule removal, fluoride removal, nitrates, sulphides, pharmaceuticals, and phenolic compounds from wastewater.^[126,127] Another widely used method for heavy metal removal is electro flotation technique which is solid-liquid separation process where toxic metals are floating on the water surface by small bubbles of oxygen and hydrogen gases produced from the water electrolysis.^[128] Electrochemical methods are quick and well-controlled treatment methods for removing heavy metals from industrial wastewater, which needs fewer chemicals, generates less sludge formation and provides the maximum metal ions removal. It also has few limitations: higher capital investment and high power supply utilisation, limiting its utilisation. In conclusion, the electrochemical method plays an outstanding role in removing heavy metals from industrial effluent.

5.6. Bioremediation

Bioremediation involves microorganism for the removal of industrial wastewater effluents. This microbe-assisted method is also widely used in removing toxic heavy metal pollutants, but the traditional wastewater treatment method is not financially effective. Also, it causes unfavourable secondary contaminants on the aquatic environment. In conclusion, biological processes can remove industrial wastewater, but efficiency is insufficient compared to other physicochemical techniques.

5.7. Adsorption

Among the above-stated methods, the adsorption process is a convenient method for treating industrial wastewater effluent with low operating cost, low fouling problems, and the most economical way for heavy metal removal from the industrial effluent. Adsorption happens when a liquid solute(adsorbate) gets adsorbed on some solid(adsorbent) surface. In this adsorption process, adsorbents can be recreated by the

desorption of its reversible technique, and the regenerated adsorbent can be reused for many purposes. For the regeneration of adsorbent, there are different techniques available and widely used methods are electrochemical regeneration, thermal generation pressure swing method, which confirmed that the adsorption process is considered an environmentally friendly method. Adsorption technique is easy to use, flexible to handle, compact design, moreover this process has become one of the leading techniques in the industrial wastewater effluent treatment methods. Heavy metal removal efficiency increased by using high or large surface area, pore volume or pore size distribution, proper functionalities or functional groups, and the adsorbent's polarity determines the efficiency of the adsorption process.^[129] Elimination of effluent pollutants depends upon the variable such as adsorbent dose, initial concentration, temperature, pH, ionic strength, mixing speed and contact time are being optimised.^[81,130] Extensively, adsorption treatment method was successfully utilised to treat industrial wastewater effluent by many researchers, concurrently adsorption capacity has tremendously originated by various adsorption materials.

Among these treatment methods, adsorption is one of the most beneficial strategies for treating wastewater due to its cost-effective and efficient pollutant removal results. Over the past few decades, the researchers have deputed that the graphene and its modified forms are useful adsorbents for heavy metal removal because of their unique structure and surface characteristics. Therefore, the next focus will be more in-depth about adsorption by using graphene-based adsorbents to remove heavy metal ion and explore its superiority qualities for the excellent results.

6. Adsorption Using Graphene-Based Materials in Wastewater Treatment

Contamination of water resources by heavy metal and dyes from textile wastewater is a severe complication worldwide, metal ions like Cd, Pb, Cr, Zn, Cu, Co, Hg and As are the widespread contaminants in an aquatic environment. Due to the above corresponding pollutants' carcinogenicity, it is essential to treat this before discharging into the waterways. Among the diverse treatment methods, adsorption demonstrates the outstanding performance in removing heavy metal; the adsorption method is economical and productive on solid phase adsorbents for the heavy metal ions removal.^[131] Several low-cost adsorbents are available such as clays,^[132] bagasse fly ash,^[133] coal fly ash, silica gel, agricultural waste products, Jute,^[134,135] sawdust,^[136] industrial waste,^[137] neem leaf,^[138] red mud,^[139] activated carbon,^[140] zeolites^[141] and carbon nanotubes^[142] have been used for the adsorption of heavy metals and dyes from aqueous solutions. The above-mentioned

low-cost adsorbents achieved great attention in heavy metal removal. Some limitations limit their application in industrial sectors, including maintenance cost, energy requirement and a high volume of sludge production. Therefore, new low-cost adsorbent materials need to develop with the following features: high surface area, adjustable surface properties, easy regeneration, adequately scattering properties in the liquid phase, and recycling capabilities in a contaminated environment. The nanomaterials have a potential basis for the wastewater treatment processes due to their high surface area, surface adjustability and flexibility in adapting them for suitable usage. Nanotechnology has made it possible especially, carbon-based materials nanomaterials such as graphene and carbon nanotubes widely used in wastewater treatments.^[143] Nanomaterials are the smallest structures with a few nanometres,^[144] such as less than 100 nm [145] which developed in various forms, namely nanowires nanotubes, nanoflowers, nanofilms, nanoparticles, quantum dots and colloids.^[146] In this context, graphene-based nanocomposites play a predominant role in separation and purification technology due to their unique properties such as high surface area, minimal size, surface modification ability, and excellent conductivity, cost-effective synthesis and mainly biologically compatible.

6.1. Graphene and its Derivatives

Graphene is one of the allotropes of carbon, a single layer of two-dimensional thinnest material structure, incredibly strong, more than 40 times stronger than diamond and about 200 times stronger than steel the sp^2 -bonded hexagonal honeycomb structure of carbon atoms. It can even exist in a multilayer form, which means several sheets are stacked together to form the three-dimensional structure (3D). In contrast, the zero-dimensional structure is called,^[147] and a tube-like structure called one dimensional (1D) carbon nanotube was found in 1999, also known as cylindrical graphite sheets.^[148] Figure 7 illustrates the schematic diagram demonstrating that graphene is the main base of all other allotropes of graphitic forms. Since the discovery of 2-dimensional (2D) graphene in 2004, it has been treated as one of the precious materials in science and technology.^[149] Since then, graphene gained tremendous attention from researchers, academicians and industries because of its excellent thermal, electrical, mechanical and optical properties. Additionally, graphene has a high surface area, high in chemical stability, high impermeability to gases, high porosity, high optical transmittance, high elastically, tunable bandgap and biocompatibility.^[150,151] Graphene-based materials are extensively used infiltration due to the theoretical surface area of pristine graphene is $\sim 2600 \text{ m}^2 \cdot \text{g}^{-1}$ which is much higher than the surface area of carbon black ($850\text{--}900 \text{ m}^2 \cdot \text{g}^{-1}$) and carbon nanotubes (100--

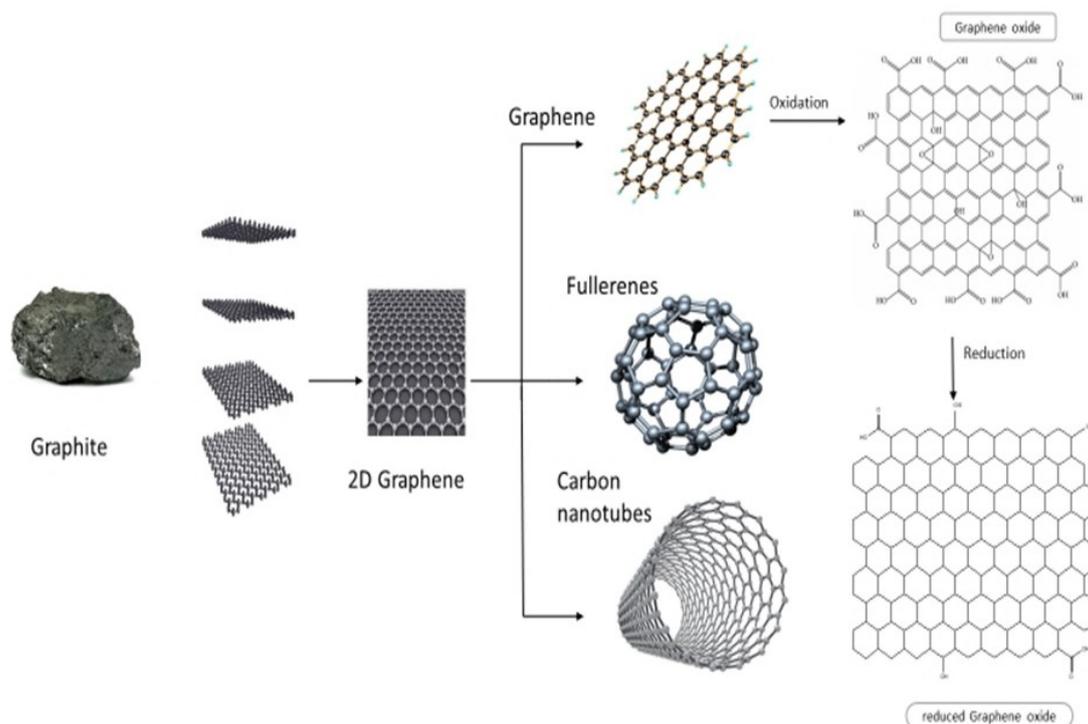


Figure 7. Illustrates the schematic diagram demonstrating the allotrope of graphitic forms and graphene's derivatives.

1000 $\text{m}^2 \cdot \text{g}^{-1}$) which tends to enhance the usage of graphene and its derivatives.^[149,152] Table 12. shows the characteristics of a single-layer graphene sheet.^[84] Graphene and its derivatives such as graphene oxide (GO) and reduced graphene oxide (rGO) have been demonstrated to be promising adsorbents for water treatment.^[153,154] Generally, graphene is insoluble and hard to disperse in all other solvents due to a robust Van der Waals interaction that can restrict sorption of metal ions. GO is considered as the oxidized form of graphene which is much more hydrophilic than the graphene and acquired greater

Table 12. The characteristic features of a single-layer graphene sheet.

Features	values
C–C bond length	$14.2 \times 10^{-2} \text{ nm}$
Optical transparency	97 %
Theoretical specific surface area	$2600 \text{ m}^2 \text{ g}^{-1}$
Thermal conductivity	$5000 \text{ W m}^{-1} \text{ K}^{-1}$
Density	0.77 mg m^{-3}
Density carrier	10^{12} cm^{-2}
Young's modulus	1100 G Pa
Fractural strength	125 G Pa
Resistivity	$10^{-6} \Omega \text{ cm}$
Rupture force	$\sim 42 \text{ Nm}^{-1}$
Electron mobility	$200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$

consideration in the heavy metal removal due to their large quantities of oxygen atoms on the surface GO in the forms of epoxy, hydroxyl and carboxyl groups that can efficiently bind a metal ion to form a metal complex through sharing an electron pair. Therefore, particularly GO nanosheets covalently bound with oxygen-containing groups such as carboxyl groups and phenolic hydroxyl groups suitable for the heavy metal removal.^[155] Besides the adsorption capacity of graphene-based composites depends upon a few variables such as the pore structures of graphene composites, functional oxygenated groups and pH of the aquatic environments. The microporosity structure is introduced to increase graphene composites' adsorption capacity, and magnetic functionality is introduced to recover and reuse graphene adsorbents. Graphene and its composites are applied in wastewater treatments, pollutants like heavy metals, dyes, pesticides, aromatic pollutants and antibiotics are removed through adsorption using graphene oxide composites^[156,157,158] which find out detection efficiency for Pb^{2+} , Cd^{2+} , Zn^{2+} , and Cu^{2+} at concentrations even as low as 0.1 ppb.^[159] Significantly, GO membranes have been demonstrated to be permselective, effective in removing salt ions, transforming seawater into potable water.

6.2. Production Techniques of Graphene and their Derivatives

Graphene has shown distinct differences from the other carbon nanomaterials. It is the thinnest and strongest material with exceptional electronic transport property and charge carrier. It is a single layer of graphite, as achieved by an exfoliated method. The properties of graphene immensely varied depending on its layer number and crystallinity. Graphene is categorized based on layer number as single-layer graphene, bilayer graphene and few layers (3-10) graphene.^[160,161] All the exciting graphene properties have been observed in single-layer graphene with good crystallinity. Thus, the primary challenge is to synthesize single-layer graphene without affecting the crystallinity. Graphene structure includes GO, rGO, graphene nanoplatelets (GNPs), graphene quantum dots (GQDs) and it has the ability in the form of graphene ink as well as graphene masterbatches. Production of graphene from graphite comes under two techniques: top-down technique and bottom-up technique. In the top-down method, the graphene layer is separated from natural graphite using mechanical exfoliation, chemical exfoliation, and chemical fabrication.

On the other hand, the bottom-up approach facilitates to utilise the carbonaceous gas to generate graphene by using pyrolysis, epitaxial growth, Chemical Vapor Deposition (CVD) and plasma synthesis. The CVD method is useful for a pure and single graphene production layer. The graphene layer defects can be controlled; moreover, the oxidation-reduction method is the most straightforward and low-cost method to produce graphene and their derivatives.^[162,163,164] The process

creates high-quality graphene, but the graphene is often damaged when it comes time to detach it from its substrate. Thus, the graphene obtained in this process contains several functional groups on its surface called GO. It is further reduced to eliminate these functional groups, though it's impossible to remove all the available groups altogether. It is subsequently known as rGO or chemically modified graphene (CMG). Due to oxygen functionalities, GO can quickly disperse in organic solvents, water, and different matrixes. This is a significant benefit when combining the material with polymer or ceramic matrixes to enhance their mechanical and electrical properties. Besides, activated carbon (AC) is one of the most common types of porous carbons and a typical form of disordered carbon with small pores and a high specific surface area obtained by thermal decomposition and partial oxidation (activation) organic compounds.^[165,166] Also, it is cheaper than graphene and related derivate compounds. However, due to the inert surface, amorphous and disordered characteristics, AC can agglomerate, further surpassing the materials' activity. Importance of graphene and its related compounds has been mentioned in Figure 8.

Advantages and disadvantages of graphene production methods are shown in Table 13.^[167] Graphene oxide is prepared by chemical oxidation and exfoliation of graphite with either the Brodie, Staudenmaier, or Hummers methods resulting in extended graphene sheets decorated with epoxy and hydroxyl functional groups and these functional groups on GO make a significant contribution to its hydrophilicity and high negative charge density.^[168] The properties of hydrophilicity characteristics of graphene oxide intensified due to

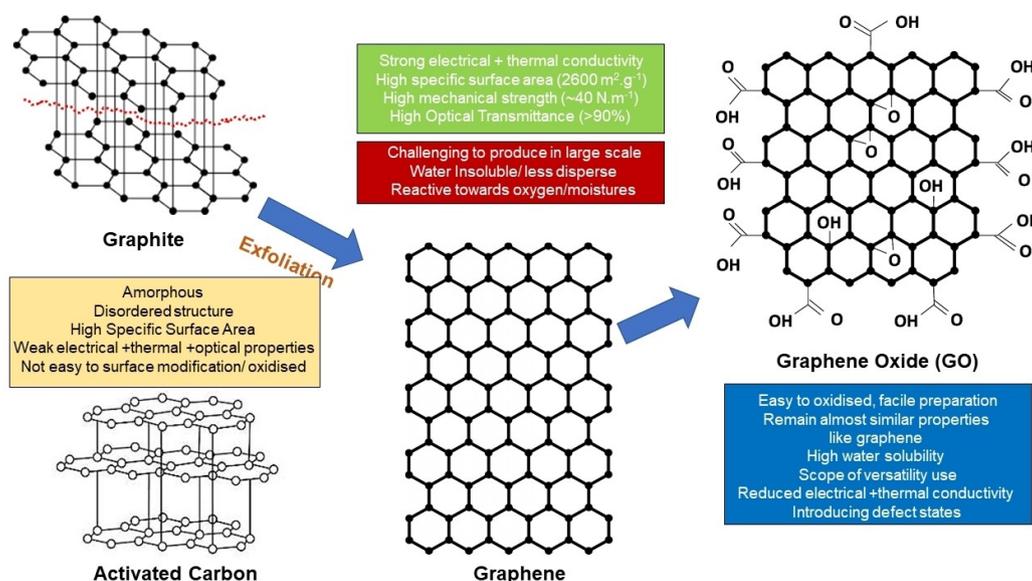


Figure 8. Highlights of graphene and graphene oxide properties compared to activated carbon.

Table 13. Advantages and disadvantages of graphene production methods.

Graphene synthesise methods	Advantages	Limitations
Mechanical utilization of too oriented pyrolytic graphite	Inexpensive, fewer defects, outstanding charge mobility and excellent chemical.	Little yield, the problem of large-scale manufacture
Chemical vapour deposition	High quality, mass manufacture, big size of graphene layers.	Expensive
Epitaxial growth on SiC	Good quality and big graphene layers size.	A costly method, high growth temperature.
Chemical reduction of exfoliated graphite oxide	Low cost, large-scale production.	Numerous defects, low purity, poor mechanical and electrical properties.
Liquid-phase exfoliation	Low cost, large-scale production.	Low yield, moderate quality and many impurities.
Carbon nanotubes unzipping	High yield, high quality, potentially low cost.	Moderate scalability.

oxygenated molecules that permit its application in an aquatic and biological environment. Graphene oxide and reduced graphene oxide obtained during oxidation and exfoliation of graphite-containing functional groups such as $-\text{COOH}$, $-\text{C}=\text{O}$ and $-\text{OH}$ which act as an energetic site for the binding of metal cation through electrostatic or coordinated interactions.^[169,170] Graphene can be modified or inserted into other materials such as polymers and metals, hence the obtaining nanocomposites enhanced the adsorption properties which achieve a more efficient result in the removal of heavy metal ions.^[171]

The liquid-phase exfoliation technique has a high potential for large-scale nanographene materials cost-effectively among these above-mentioned methods. Besides, the existing preparation methods, several other exfoliation methods assisted by microwave, intercalation, and ball mill, ultrasonic synthesis has emerged as a potentially low-cost, large scale production of single layers of graphene sheet/ flakes.^[172] Various synthesis routes employing the exfoliation method as described in Figure 9.

Removal of a pollutant metal-ion is employing by three basic mechanisms such as simple interaction, introducing magnetic nanomaterials and make a magnetic graphene-based composite, and composite with other nanostructure materials like core-shell, matrix-dispersed, mesoscale, lamellar, heterodimer, colloidal etc. as explained schematically in Figure 10. In case of the treatment, the viscous GO shows prominent interaction due to its negatively charged surface for COO^- and OH^- ions, which spread to produce a practical arrangement with the positive charge metal ions rapidly and thus removes the pollutant ions, this is the simplest way of interaction. Measurement of zeta potential and Raman spectroscopy will help understand the electrostatic interaction. Besides, the GO sheet interact strongly with metal ions are attracted to GO sheets via non-covalent bonds: hydrogen bonds, van der Waals forces, π - π stacking and hydrophobic interaction. However, allowing this mechanism restricts the

multiple GO sheet or related catalysts. Thus, to rectify the reuse cycle, the GO-sheets or related graphene-based material making composite with the magnetic nanomaterials is because if the GO-based material is magnetic it will be easy to separate them from the wastewater and the overall process is a quite facile, time-saving, and swift process. But the thing is, making such a magnetic composite is quite tricky, also after completing the composite, the magnetic nanomaterial loses its magnetic property even. Another mechanism establishes related to the surface modification of GO, maybe with a few ligands, polymers, or developing nanocomposite structures. All the mechanisms mentioned above are the primary way to attract the pollutant metal ion towards GO or its related materials. After interacting with the metal ions, the GO can undergo either photocatalytic or adsorption mechanism to remove the wastewater's metal-ion pollutant. Further, this review discusses various adsorption mechanisms and their related physical parameters in the next section.

6.3. Adsorption Mechanism of Graphene Oxide

Adsorption occurs when a liquid solute or adsorbate gets adsorbed on solid surface or adsorbent with the formation of an atomic or molecular film. The adsorption mechanisms of graphene oxide-based nanomaterials are categorized into three primary mechanisms: adsorption isotherms, adsorption kinetics and adsorption thermodynamic, which discussed following.

6.3.1. Adsorption Isotherm

Several isotherm equations are available few of them are namely Langmuir Isotherm, Freundlich Isotherm, Temkin Isotherm, Redlich-Peterson Isotherm and Dubinin-Radushkevich (D-R) Isotherms. Widely used adsorption Isotherms are Langmuir and Freundlich's models focused and applied to demonstrate the adsorption equilibrium between the adsorbent surface and the adsorbate. Adsorption of pollutants on

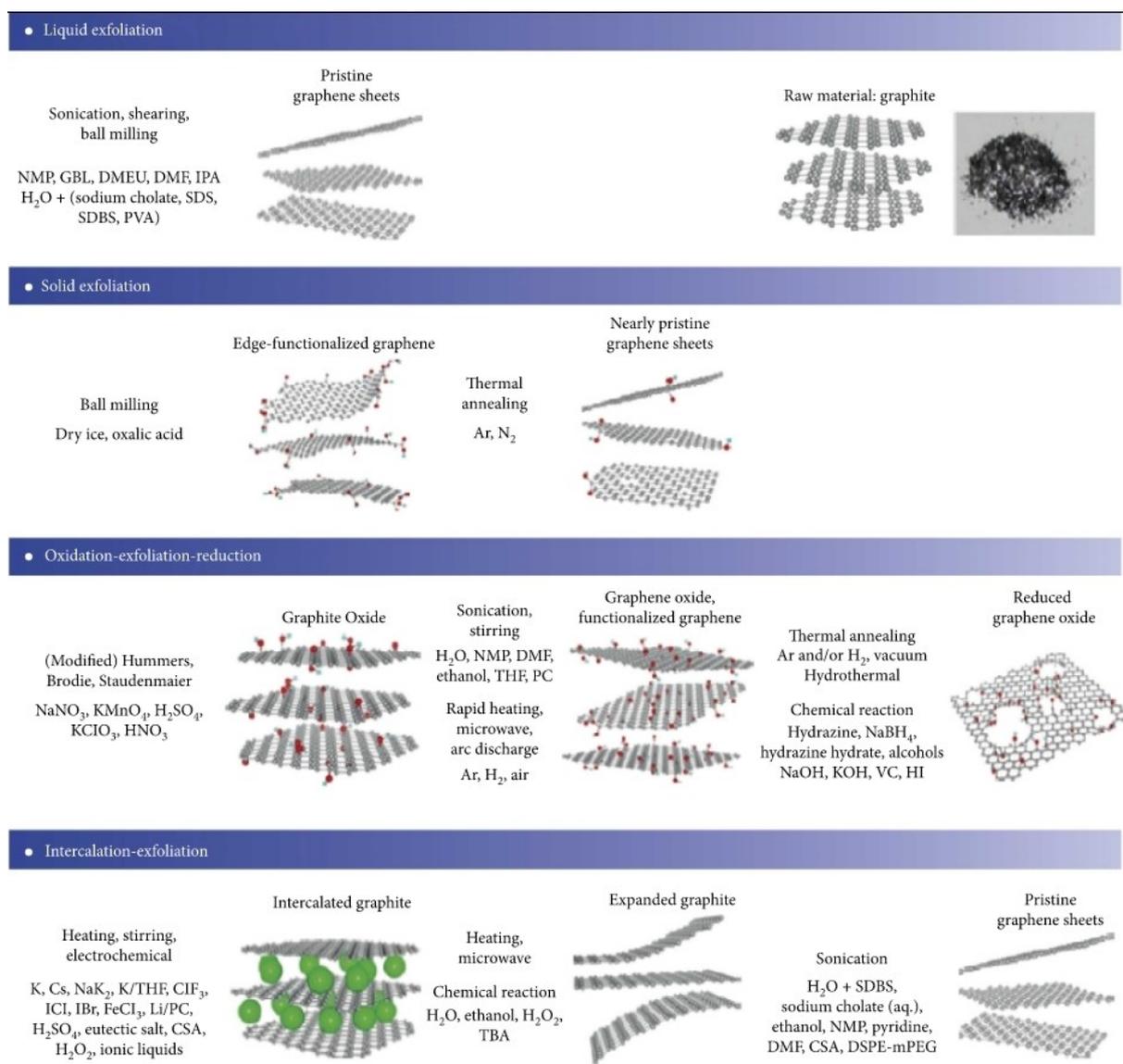


Figure 9. Various synthesis routes to prepare graphene sheet or flakes employed by exfoliation route.^[172]

adsorbents is usually studied through graphs known as adsorption isotherm which describe the equilibrium of the sorption of material on the surface of adsorbent at a constant temperature. For example, a single layer analysis on sorbent is assumed by the Langmuir model while multilayer adsorption on sorbent is allowed via an experimental model which is the Freundlich model.

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

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

where K_L is the constant in equilibrium ($L\text{mg}^{-1}$), q_{max} is the maximum adsorption capacity (mgg^{-1}) of sorbent, C is the concentration in equilibrium (mgL^{-1}), q is the number of adsorbed metals at equilibrium (mgg^{-1}).

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

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \quad (2)$$

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

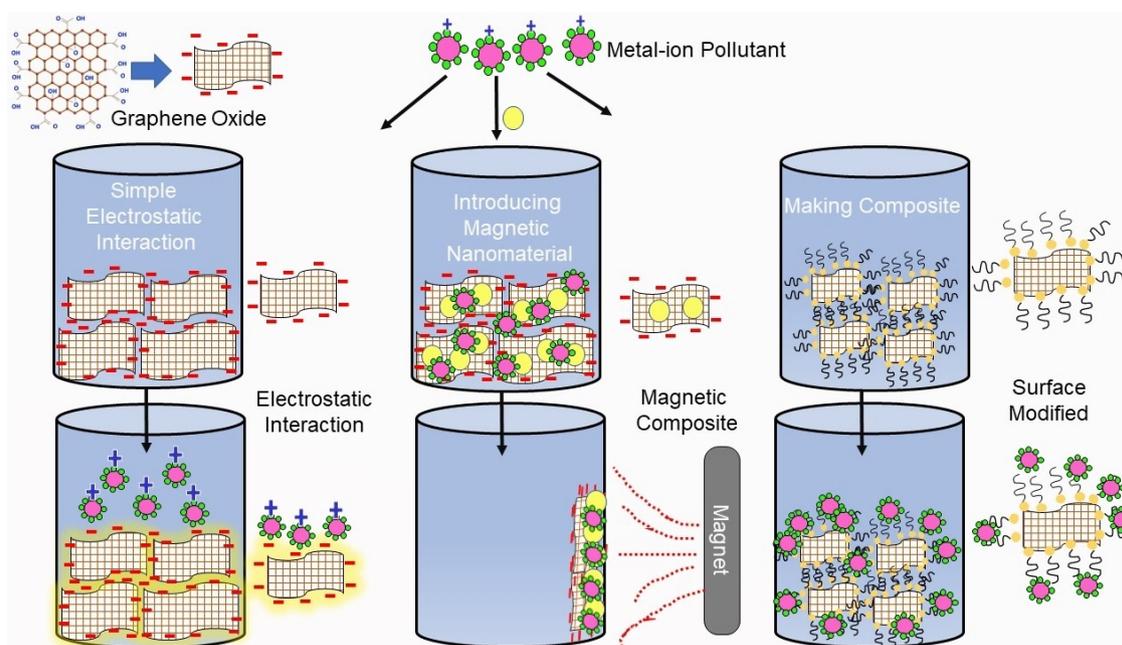


Figure 10. Different treatment mechanism of metal-ion pollutant with GO-based materials.

For the Freundlich isotherm, the non-linear and linear equations can be explained respectively as:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

$$\log q_e = \log k_F + \frac{\log C_e}{n} \quad (4)$$

where q_e is sorbate loading on sorbent at equilibrium (mg g^{-1}); K_F is a pointer of adsorption capacity ($\text{mg}^{1-n} \text{L}^n \text{g}^{-1}$), n is sorption energetics, and C_e is equilibrium liquid concentration of sorbate (mg L^{-1}).^[173]

6.3.2. Adsorption Kinetics

Several adsorption kinetics have been established to understand the adsorption kinetics and adsorption rate. Those include the pseudo-first-order, pseudo-second-order, the Weber and Morris sorption kinetic model, the Adam-Bohart-Thomas relation, the first order reversible reaction model, the external mass transfer model, the first-order equation of Bhattacharya and Venkobachar, intraparticle diffusion, Elovich's equations and Ritchie's equation. The kinetics prediction in the adsorption mechanism determines adsorption equilibrium time and adsorption rate. The pseudo-first-order and pseudo-second-order kinetics are most widely used to study the adsorption kinetics of pollutants and quantify the extent of uptake in adsorption kinetics. The pseudo-first-order is discovered which

is suitable for the first 20–30 min of interaction period and the adsorption rate of limiting step is physisorption.^[174] The adsorption may be physical or chemical, depending on the interaction between the adsorbate and adsorbents. Physisorption depends on the adsorbent's surface area, as the surface area of the adsorbent increases, the extent of adsorption also increases. The rise in sorbate amount at the interface is due to non-specific van der Waals forces in physical adsorption. In contrast, pseudo-second-order fixes the rate-limiting step as chemical adsorption, including the sharing of valence forces or electron exchanges between the adsorbate and adsorbent. Chemical adsorption is also known as Chemisorption. In chemisorption, adsorption occurs in adsorbed substances held by chemical bonds that create ionic bonds or covalent bonds. Chemisorption has a particular uniqueness, and it takes place only if there is a chemical bonding between adsorbent and adsorbate. These two kinetic models are well fitted with most heavy metal adsorption mechanisms because of the physisorption and chemisorption.

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

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

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).^[175]

For the pseudo-second-order model, it can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) represents the second-order rate constant for the adsorption process.

In addition, the rate of initial adsorption can be known as 'h', and the expression of 'h' is shown below^[176]

$$h = k_2 q_e^2 \quad (7)$$

6.3.3. Adsorption Thermodynamics

Thermodynamic parameters are Gibbs free energy (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS) which have been widely used to evaluate an adsorbate-adsorbent system. Negative ΔG points out the adsorption process's spontaneity, and (H) is used to identify adsorption's nature. A positive value of ΔH indicates the reaction is endothermic and the negative value of ΔH shows that the response is expressed as:

$$\Delta G = -RT \ln K_L \quad (8)$$

Enthalpy and entropy changes are related to the Langmuir equilibrium constant through the following expressions:

$$\ln K_L = \frac{\rho S}{R} - \frac{\rho H}{RT} \quad (9)$$

Therefore, a plot of $\ln K_L$ versus $1/T$ should be a straight line. ΔH and ΔS values could be obtained from the slope and intercept of this plot. The following equation determined the thermodynamic parameters such as changes in standard free energy (ΔG), enthalpy (ΔH) and entropy (ΔS):

$$\Delta G = \Delta H - T\Delta S \quad (10)$$

The slope and the intercept of the plot of ΔG versus T were used to determine the ΔS and ΔH values.^[1]

6.4. Graphene Oxide-Based Nanocomposites for the Removal of Heavy Metals

The exogenous functional groups on the surface of graphene oxide are responsible for the sorption of metal ions. Recently, graphene, its functionalised derivatives and composites are efficiently used for wastewater decontamination. Graphene and its functionalised compounds like GO extremely efficient for the removal of noxious heavy metals like Cd, Cu, Hg, Zn,

Sn, Pb, Mn, Fe, Cr, Ag, Ni, Co, Al and As etc., from wastewater due to high surface area, a large number of functional groups and high mobility charge carrier. Moreover, GO can offer low-cost wastewater technology compare to other treatment methods. Hence, it can be used for the purification of wastewater with organic effluents above the prescribed limits. GO can be the best replacement for the activated carbon-based water filter because these can be applied to remove all types of impurities in wastewater. The results are highly efficient in removing metal ions, organic contaminants and PAHs (Polycyclic aromatic hydrocarbons) etc.^[177] The past few decades, the synthesis and application of functionalised graphene modified with oxide containing, nitrogen-containing and sulphur containing functional groups have been increased, besides most of them have an excellent adsorption capacity for the removal of cationic and anionic heavy metals.

Adsorption capability of GO could be controlled by the total available surface area, which could be tailored by the microstructure. Sometimes, the coupling of the primary material with GO could enhance the adsorption reaction. Functionalisation plays a remarkable role in the interaction of removing heavy metals. Carbonaceous materials including activated carbon (AC), carbon nanotubes both single-walled and multi-walled (CNTs), and graphene oxide (GO) have been widely studied for adsorption of various environmental contaminants. Generally, the chemical and physical interactions between heavy metals and functional groups of adsorbents contribute significantly to heavy metals' adsorption. In addition, surface functionalization (surface modification) is essential to make the GO more soluble and stable in aqueous media (hydrophilicity). Sometimes lack of surface functional groups limits GO's application potential. Hence, surface modification of carbon materials enhances their surface properties of carbon adsorbents such as specific surface area, pore size distribution or pore volume, increasing functional groups' presence and enriching structural stability. Construction of functional groups on carbon surface is commonly occurring through three main techniques: oxidation, nitrogenation and sulfuration, which are utilised to introduce the oxygen, nitrogen, and sulphur heteroatoms on the sp^2 -carbon surface.^[178] Oxygen-containing functional groups, e.g., $-\text{OH}$, $-\text{COOH}$, $-\text{C}=\text{O}$ and $-\text{C}-\text{O}$ are generated using surface oxidation technique performed under refluxing condition in the presence of organic acids, e.g., such as HNO_3 and H_2SO_4 oxidising agents, e.g., H_2O_2 , KMnO_4 , and NaOCl .^[179] Among oxygen functional groups, hydroxyl and carboxyl have been widely contributed to the adsorption of heavy metals Pb(II), Cr(VI), Hg(II), Cd(II) and Ni(II) on various carbon adsorbents.^[180] Nitrogenation assists in generating nitrogen functional groups, e.g., $-\text{NH}_2$, $-\text{NH}$, $-\text{C}=\text{N}$ and $-\text{C}-\text{N}$ onto the surface of carbon materials which enhanced the adsorption of heavy metals.^[181] One of the nitrogen functional groups

such as amino (-NH₂) functionalisation of carbon nanotubes has recently gained attention due to its potential application of multi-purpose, including heavy metal removal. Sulfuration treatment is used to introduce sulfur-containing functional groups, e.g., C-S, C=S, or S=O onto the surface of carbon adsorbents. Production of sulfur on carbon achieved through utilising the sulfurizing agents such as S, SO₂, H₂S, Na₂S, K₂S, and dimethyl disulfide. During sulfuration treatment, the porous structure of carbon will increase or decrease the specific surface area and the pore volume depending on the treatment condition. The decrease in the surface area possibly caused by sulfur-containing particles.^[182,183] Often researchers combine different functionalization to obtain multifunctional and advanced GO-based nanomaterials having multiple properties in single nanosystem

BET (Brunauer-Emmett-Teller) surface area of carbonaceous materials also plays a predominant role in heavy metal removal. There are mainly two methods to measure specific surface area, namely, Langmuir isotherm and BET isotherm. Among these two methods, the multipoint BET is commonly used in material science to calculate solid powder's surface area by physical adsorption of gas molecules. The technique includes external area and pore area evaluations to determine the total specific surface area in m²·g⁻¹ yielding important information in studying the effects of surface porosity and particle size, and crucial for metal ion removal study. Table 14 presents the comparison of BET surface area of before and after functionalization of various carbonaceous materials, which helps identify the advantageous material for utilising metal ion removal from wastewater. Introduction of functionalization could also alter graphene's microstructure, resulting in graphene with various carbon to atomic oxygen ratio (C/O ratio), functional groups, electrical conductivity, and solubility solvents etc.

The synergistic effects between the nitrogen-containing and sulphur-containing materials, along with oxygen-containing compounds, have always had a favourable combination. The removal of cationic heavy metals most of the oxygen, nitrogen and sulphur containing GO compounds are acceptable as adsorbents. The removal of anionic heavy metals, oxygen, and nitrogen-containing GO-based compounds is more acceptable. The adsorption of heavy metals is directly influenced by the solubility of the contaminants in the solution.^[184] The self-assembled flower-like TiO₂ on exfoliated graphite oxide for heavy metal removal from aqueous solutions. The surface-attached and the oxygenated functional groups of exfoliated graphite oxide showed a high removal efficiency. The TiO₂ on GO significantly improved the removal efficiency of the heavy metals. The GO-TiO₂ hybrid adsorption capacities of heavy metals ions after 6 and 12 hours of hydrothermal treatment at 100 °C for Zn (II) removal were respectively 44.8 ± 3.4, and 88.9 ± 3.3 mg·g⁻¹, for Cd(II) removal was 65.1 ± 4.4 and 72.8 ± 1.6 mg·g⁻¹ and for Pb(II) removal 45.0 ± 3.8 and 65.6 ± 2.7 mg·g⁻¹ at pH 5.6. TiO₂ flower formed upon GO as the hydrothermal treatment time at 100 °C increase from 6 h to 12 h. Increased time resulted in an increase in the surface area of GO-TiO₂ hybrid, which then increased the removal capacity of heavy metal from aqueous solutions.^[185] The ordered porous chitosan-gelatin/GO (CGGO) monoliths with over 97% porosity by a unidirectional freeze-drying method and used as an adsorbent the heavy metal removal. The high porosity strengthened the CGGO porous monoliths effective adsorbents for the heavy metal ions such as Cu²⁺ and Pb²⁺. During adsorption, the influencing factors are pH, GO concentration, metal ion concentration together with the effect of EDTA (ethylenediaminetetraacetic acid) was examined. Employing EDTA groups on the GO surface through silanization could dramatically increase the active adsorption sites of EDTA-GO, facilitating

Table 14. Comparison of BET surface area before and after surface functionalization of various carbonaceous materials.

Type of carbon	BET surface area-before functionalisation (m ² ·g ⁻¹)	BET surface area-after functionalisation (m ² ·g ⁻¹)	References
Activated carbon from oil palm empty fruit bunch (EFB)	2.005	720	[188]
Activated carbon from sour cherry stones	41.54	1704	[189]
Activated carbon	515.94	871.67	[190]
Single wall carbon nanotube (SWCNT)	861	1587	[191]
Multi wall carbon nanotube (MWCNT)	16.21	336.37	[190]
Carbon nano tube (CNT)	122	154	[192]
Carbon nano tube (CNT)	272	200	[193]
Ordered mesoporous carbons (OMC)	523	886	[194]
Mesoporous carbon	184	600	[195]
Graphene	455.6	595.6	[196]
Graphene	77	1256	[197]
Polyaniline/Graphene oxide (PANI/GO)	42.5	65.3	[198]

interaction with the heavy metal ions, as shown in Figure 11. The combination of GO significantly increased the CGGO monoliths' strength in both wet and dry states and changed the porous structure. This material exhibited a too high adsorbing ability for the heavy metal ions, which then decreased at low pH and increased from 20% to 88% due to the addition of EDTA at low pH. The CGGO monoliths have high stability and can be recycled several times; additionally, they are biodegradable, non-toxic and regenerable efficient adsorbent. The adsorption of copper Cu^{2+} increased from 15.6 to 88.6% as the pH changed from 2 to 6. The CGGO monolith was doped with 0.5 wt% of GO, and the adsorption capacity of Pb^{2+} increased from 68.5 to 75.5 $\text{mg}\cdot\text{g}^{-1}$. The CGGO monoliths material can be a potential adsorbent for heavy metal ions from aqueous solutions.^[175]

Kong et al. (2020) recently studied the Langmuir adsorption capacities (q_{max}) of GO for various metal ions like metallic hard (Na^+ , Mg^{2+}), soft (Cd^{2+} and Pb^{2+}) and borderline ions (Ni^{2+} , Cu^{2+} , Zn^{2+} , Co^{2+}). They found the q_{max} in order of $\text{Na}^+ < \text{Mg}^{2+} < \text{Co}^{2+} < \text{Cd}^{2+} < \text{Zn}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} < \text{Pb}^{2+}$. Their studies presume to extend the prediction of adsorption behaviour of various metallic ions at adsorbents with known surface morphology (Figure 12).^[187]

Further, the adsorption capacity and application of GO and related composite materials for removing heavy metal ions from wastewater has been briefly summarized in Table 15 and Table 16, respectively.

The GO was synthesized via modified Hummers' method, studied the adsorption of Zn (II) on GO as a function of pH, adsorbent dosage, contact time and temperature from aqueous

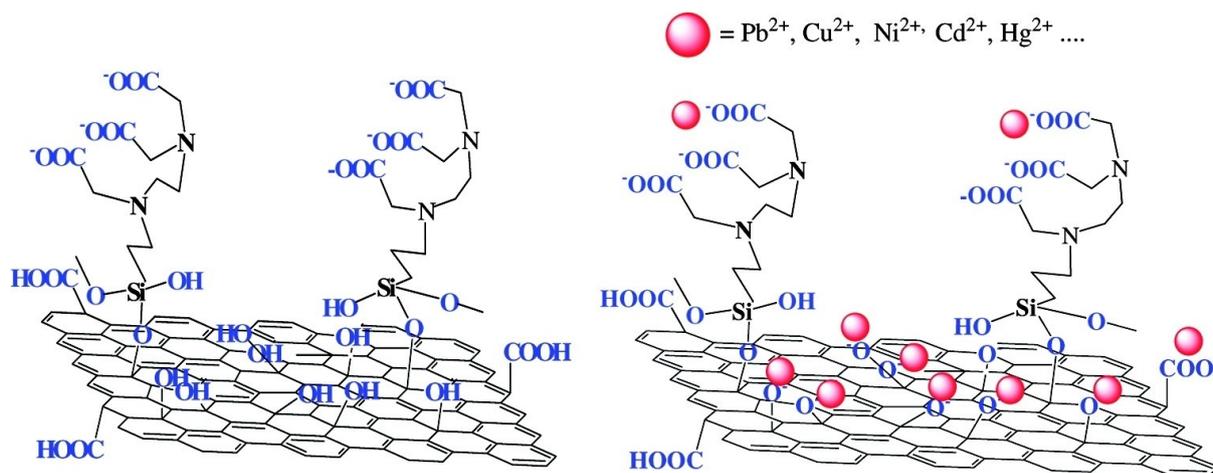


Figure 11. (a) Chemical structure of EDTA-GO and (b) its interaction with heavy metal cations. Reprinted with permission by American Chemical Society.^[186]

The adsorption capacity of graphene oxide (GO) towards metal ions

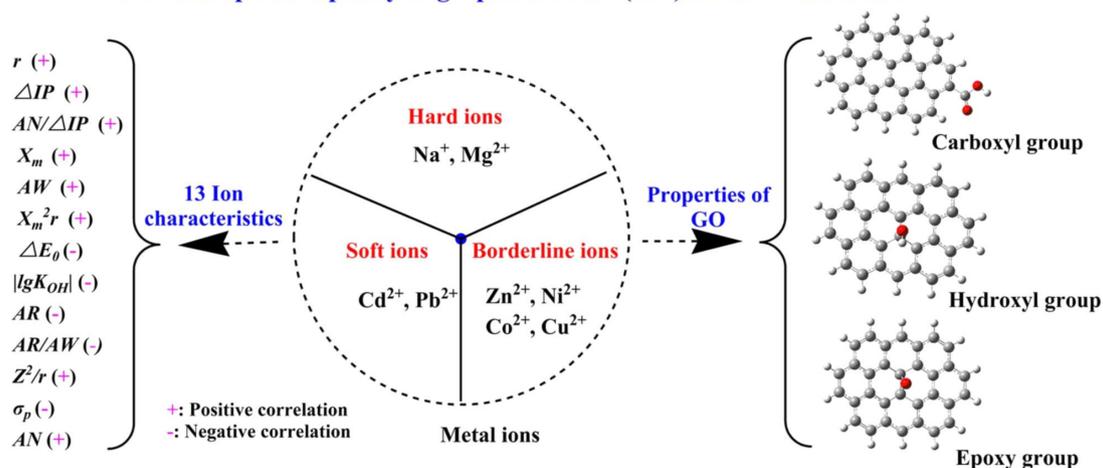


Figure 12. Schematic illustration of GO adsorption tendency towards various metal ions.^[187]

Table 15. Comparative study of GO and its related composite's adsorption capacity.

Adsorbents	Metal ion	Adsorption capacity Q (mg·g ⁻¹)	Conditions	Remarks	References
GO-TiO ₂	1. Pb (II) 2. Cd (II) 3. Zn (II)	65.6 ± 2.7 72.8 ± 1.6 88.9 ± 3.3	pH 5.6, 373.15 K	1. The enlargement of treatment period up to 12 h to remove more cadmium ions via the hydrothermal method. 2. Longer treatment times increased the surface area of GO-TiO ₂ hybrid, and the removal capacity of heavy metal increased. 3. The chemisorption of cadmium ions is taken place.	[185]
GO	Pb (II)	250	pH 6.0, 298 K	1. The equilibrium contact time is 60 min. 2. Well fitted with pseudo-second-order kinetics.	[199]
GO-DPA	1. Cd (II) 2. Pb (II)	257.20 369.75	pH 5 pH 5	1. The modified GO was influential in the enhancement of the functionality. 2. The combination of ultrasound power with adsorption method was very efficient short of time, enhancing the dispersion of adsorbent and metal ions.	[200]
GO membrane	Cd (II)	83.8	pH 5.8, 303 K	1. The equilibrium contact time is 15 min. 2. It is recommended to be used in industrial sites	[201]
CGGO	Pb (II)	~120	pH 6.0, 298 K	1. High porosity makes the CGGO porous monoliths effective adsorbents for metal ions. 2. The CGGO monoliths have good stability and can be recycled several times.	[175]
RGO/PAM	Pb (II)	1000	pH 6.0, 298 K	1. This material significantly enhances the dispersion property of rGO in aqueous solution and increases the adsorption capacity of rGO for heavy metal. 2. Well fitted with Langmuir isotherm and pseudo-second-order model.	[202]
GO-EDTA	Pb (II)	479 ± 46	pH 6.8	1. The adsorption process was completed within 20 min, which is faster than most of the carbon-based adsorbents. 2. The desorption behaviour of metals on the GO surface suggests that GO can be reused after treated with HCl solution	[203]
TGOCS	Cr (VI)	219.5	pH 2.0, 303 K	1. Adsorption followed the pseudo-second-order kinetic model and Langmuir isotherm. 2. The adsorption capacity increased as increasing temperature.	[204]
PAS-GO	Pb (II)	312.5	pH 4–5, 303 K	3. TGOCS for Cr (VI) removal was higher than that of the recently reported adsorbents. 1. The sorbent exhibited high adsorption capacity towards Pb (II). 2. Pb (II) sorption on PAS-GO is an endothermic process. 3. It is recommended for industries	[205]
SAGO aerogel	Pb (II)	267.4	pH 5.5, 303 K	1. Adsorption capacity of SAGO aerogel shows potentially promising material in wastewater treatment.	[206]
G-nZVI	Cr (VI)	162	pH 2–3, 293 K	1. The adsorption of Cr (VI) ions increases with an increase in temperature from 10 to 50°C. 2. The reduction of hexavalent chromium to trivalent chromium is higher for G-nZVI than for nZVI. 3. The adsorption data are fitted with Freundlich and Langmuir isotherm and kinetics fitted with pseudo-second-order kinetics.	[207]
GOMO	Pb (II)	190 mg·g ⁻¹	pH 6.5, 303.15 K	1. equilibrium contact in a brief period of 30 min. 2. Well fitted with the Langmuir isotherm model and pseudo-second-order kinetic model and the thermodynamic studies revealed that the adsorption was endothermic and spontaneous	[208]
DTC-GO	Pb (II)	132.10	pH 5.3, 298.15 K	1. The removal of Pb (II) ions from aqueous solution achieved in 60 min. 2. Nature of adsorption was exothermic and spontaneous and followed the Langmuir model.	[209]
MCGO	Pb (II)	76.94	5	1. The magnetic chitosan with GO sheets showed an increased surface area, enhancing the adsorption capacity. 2. This material helps to understand the fundamental properties of GO-based composites.	[210]

Table 15. continued

Adsorbents	Metal ion	Adsorption capacity Q ($\text{mg}\cdot\text{g}^{-1}$)	Conditions	Remarks	References
EDTA-GO	Pb (II)	454.6	3	3. Adsorption remained nearly 75% after 5 regeneration cycle, and MCGO with long term stability can be used as an excellent reusable adsorbent for Pb removal. 1. GO-EDTA can act as a multi-functional material.	[211]
GAHMs	Pb (II) Cr (III)	327.9 118.6	5 and 6 at room temperature	1. Adsorption for Cr (III) by GAHMs was endothermic and for Pb (II) was exothermic. 2. Well fitted with Langmuir isotherm	[212]
PoPD/RGO	Pb (II)	228	–	3. After five adsorption-desorption cycles, the GAHMs maintained high adsorption efficiency. 1. The adsorption processes were well fitted by the pseudo-second-order kinetic model and the Langmuir isotherm model.	[213]
GOCS	Pb (II)	383.4	pH 5.7, 298 K	2. This adsorbent exhibited a favourable performance for removing Pb ions. 1. Potentially economic adsorbent for the high-efficiency removal of Pb (II) from aqueous solutions.	[214]
CA-LDH + GO	Pb (II) Cr (VI)	221.2 64.4	5 5	2. Adsorption well fitted with pseudo-second-order and Langmuir Models. 1. Adsorbent was used as a secondary application in removing heavy metal ions from aqueous solutions that had high adsorption removal.	[215]
EDTA-mGO	Pb (II)	508.4 mg	4	2. The coagulation of GO on CA-LDH was mainly dominated by hydrogen bonds and electrostatic interaction. 1. The adsorption equilibrium time was 40 min. 2. The adsorption process well fitted with the pseudo-second-order kinetic model and the Freundlich and Temkin isotherm models.	[216]
GO-DPA	Pb (II) Cd (II)	369.79 257.201	5	3. EDTA-mGO can be recycled and exhibited good reproducibility, which reduces the cost and potential for particle application. 1. Adsorption equilibrium reached in 4 min.	[200]
PVK-GO	Pb (II)	887.98	pH 7 ± 0.5	2. The combination of ultrasound power with adsorption method was very efficient in shortening the time and enhancing adsorbent dispersion. 3. Adsorption mechanism well fitted with the Langmuir model and pseudo-second-order rate. 1. The results show that the oxygen-containing surface functional such as carboxylic acid and hydroxyl groups of PVK-GO insist on its adsorption capability. 2. The adsorption capacity of Pb (II) by the nanocomposite increased with an increasing amount of GO. This occurrence was attributed to the increasing concentration of oxygen-containing functional groups obtainable in the nanocomposite.	[217]
GO	Zn (II)	246	pH 7.0 ± 0.1 , 293 K	3. The adsorption of Pb (II) onto PVK-GO fits well with the Langmuir model and adsorption reached within 90 min. 1. Equilibrium studies indicated that adsorption capacity well fitted with Langmuir isotherm and pseudo-second-order kinetics. The main strength of the adsorption was chemical adsorption.	[218]
CTAB -GN	Cr (VI)	21.57	pH 2.0, 293 K	2. The thermodynamic parameters are exothermic and spontaneous process in nature. 1. The adsorption equilibrium state reached in about 40 min, which is faster than most of the carbon-based adsorbents and well fitted with the pseudo-second-order kinetic model.	[219]
GO-iron oxide	Pb (II)	588.24	pH 6.5 ± 0.1 , 303 K	2. The thermodynamic parameters indicated that Cr (VI) adsorption is an exothermic and spontaneous process. 1. This work highlighted the interaction of the organic and inorganic pollutants with GO-iron oxides and RGO-iron oxides composites.	[220]
PGOC	Pb (II)	99	Room temperature	2. The Langmuir model fits the adsorption isotherms better than the Freundlich model. 1. PGOC materials will be a potential effective adsorbent for metal ions in aqueous solution. 2. Excellent physical stability obtained even after 5 adsorption-desorption cycles.	[157]

Table 15. continued

Adsorbents	Metal ion	Adsorption capacity Q (mg·g ⁻¹)	Conditions	Remarks	References
AMGO	Cr (VI)	123.4	pH 2, T 298 K	3. PGOC materials established high mechanical strength in a wet state, which is critical for their usage. 1. Compared to the MGO, AMGO with amine groups, exhibited higher adsorption efficiency. 2. AMGO capable of playing a synergistic role in the Cr (VI) adsorption.	[221]
P(TA-TEPA)-PAM-RGO	Cr (VI)	397.5	pH 2, T 308 K	1. The adsorption process is endothermic and spontaneous; besides, the approach fits the Langmuir isotherm model and pseudo-second-order kinetic model. 2. This adsorbent is capable of synergistic contribution to the reduction and removal of Cr (VI).	[222]
TGOCS	Cr (VI)	219.5	pH 2, 303 K	1. The adsorbent prepared by microwave has higher yield and uptake. 2. Adsorption process was rapid, and 85% of adsorption uptake reached in 20 min.	[204]
PPy-GO NC	Cr (VI)	(i).606 (ii).625 (iii).666.67	pH 2, 25 °C pH 2, 35 °C pH 2, 45 °C	1. Regeneration studies revealed that the adsorbent could be reused up to 3 cycles. 2. The adsorption capacities increase with temperature increase. 3. The study showed no effect from co-existing ions on Cr removal. 4. The adsorption isotherms fitted well to the Langmuir isotherm model and pseudo-second-order kinetic model.	[223]
GFP	Cr (VI)	348.4	pH 2	1. The adsorption isotherms and kinetics well fitted with Langmuir isotherm and pseudo-second-order model. 2. This nanocomposite adsorbent is stable and recyclable through simple solvent regeneration method, maintaining about 72.2% of the removal efficiency after six adsorption-desorption cycles.	[224]
(i). GO-SO _x R (ii). GO-SO _x R @TiO ₂ (iii). GO-SO _x R @SiO ₂	Zn (II), Pb (II), Cd (II)	(i).1196,285,217 (ii).158,172,277 (iii).285,312,384	-	1. Parameters such as the initial concentration of metal ions and contact time strongly affect the adsorption. 2. The adsorption equilibrium process follows pseudo-second-order rate kinetics and the Langmuir and Redlich-Peterson isotherms.	[225]
PANI/GO	Cr (VI)	324.6	-	1. This material stable and environmentally friendly with a high adsorption capacity. 2. The high adsorption capacity of Cr (VI) on PANI/GO nanocomposites makes them excellent material for potential applications in industrial wastewater treatment.	[218]

GO-EDTA→Graphene oxide functionalized with ethylenediamine triacetic acid, PAS-GO→Amino siloxane oligomer-linked graphene oxide, SAGO→sodium alginate/graphene oxide, CCGO→chitosan-gelatin/graphene oxide, GAHMs→Graphene oxide/alginate hydrogel membranes, PoPD/rGO→poly o-phenylenediamine/reduced graphene oxide, GOCS→GO/Carbon Disulfide, CA-LDH + GO→Ca/Al layered double hydroxides Coagulated Graphene oxide, EDTA-mGO→EDTA functionalized magnetic graphene oxide, GO-DPA→graphene oxide modified with 2,2'-dipyridylamine, PVK-GO→Poly N-vinylcarbazole *with* GO, CTAB-GM graphene modified with cetyltrimethylammonium bromide, PGOC→Porous GO/chitosan, AMGO→amino functionalized graphene oxide, P(TA-TEPA)-PAM-RGO→poly(tannin-tetraethylenepentamine)-polyacrylamide-reduced graphene oxide, TGOCS→trithylenetetramine modified graphene oxide/chitosan composite, Ppy-GO→polypyrrole graphene oxide nanocomposite, GFP→Graphene/Fe₃O₄@polypyrrole nanocomposites, GO-SO_xR→Sulfur functionalized graphene oxide, PANI/GO→Polyaniline/graphene oxide.

Table 16. Removal of the heavy metal ion related to textile waste using graphene and GO-based adsorbents.

Adsorbent	Metal ion	Adsorption capacity Q (mg/g)	Comments	References
GO-SF (Graphene oxide/silk fibroin aerogel)	Ag (I)	161.5	(i). This material removes cationic dyes and heavy metals ions effectively.	[226]
	Zn (II)	72.1		
	Ni (II)	13.9		
	Cu (II)	83.4		
Lignin-PNMA-rGO	Pb (II)	753.5	(i). This material shows removal ability for both organic dye and metal ion. (ii). Potentially low-cost adsorbent and ideal for both organic dye and metal ion removal.	[227]
Three-dimensional porous graphene carbon hydrogel (3D-PGCH)	Ag(I)	234.32	(i). Efficient material for both organic dye and metal ion removal. (ii). Adsorption capacity remained at a high level after four-cycle experiments	[228]
Sulfonated graphene oxide (SGO)	Pb (II)	415	(i). Showed superior adsorption capacity toward metal ions and dyes	[229]
D-GSH (Date syrup-based graphene sand hybrid)	Pb (II)	781	(i). D-GSH adsorbent showed remarkable efficiency in simultaneously removing both dye and heavy metals. (ii). Cost-effective and recyclability up to 3 cycles for all the contaminants.	[230]
	Cd (II)	793		

solution batch technique. The suitable pH for removing Zn (II) was about 7, and the optimal dosage was 2 mg. The adsorption equilibrium of Zn (II) onto GO increased within 20 min time, which was well fitted with pseudo-second-order kinetic rate and Langmuir adsorption isotherms with maximum adsorption capacity $246 \text{ mg} \cdot \text{g}^{-1}$ at 293 K. The thermodynamic parameters suggested that the Zn (II) sorption on GO was a spontaneous and exothermic. The maximum recovery of Zn (II) achieved with hydrochloric acid.^[212] Deng et al., the author estimated the adsorption properties of Pb (II) and Cd (II) on functionalised graphene prepared by the electrolysis method. The adsorption capacities were $406.6 \text{ mg} \cdot \text{g}^{-1}$ at pH 5.1 for Pb (II) and $73.42 \text{ mg} \cdot \text{g}^{-1}$ for Cd (II) at pH 6.2 respectively and further, the adsorption capacities fitted with Pseudo second order kinetics^[156] The adsorption properties of GO towards metal ions such as zinc, cadmium, copper and lead have been investigated and GO maximum adsorption capacities towards heavy metal ions 345,530 and $1119 \text{ mg} \cdot \text{g}^{-1}$ for Zn (II), Cd (II), Pb (II) and Cu (II) respectively. The adsorption affinity in the single metal system followed the sequence Pb (II) > Cd (II) > Zn (II) > Cu (II) and in binary metal systems the sequence was Pb (II) > Cu (II) > Cd (II) > Zn (II). The kinetic study indicates the adsorption of heavy metal ions onto GO nanosheets was monolayer coverage and controlled by chemical adsorption involving strong surface complexation of metal ions with oxygen-containing groups surface of GO. The author mentioned that the dispersibility of GO and the strong tendency of GO–Me (II) to precipitate enlarge the new direction to the removal of heavy metal ions from aqueous solutions, furthermore, GO is one of the potential materials which

resulted in the maximum adsorption capacities when compared with previous results with various adsorbents.^[231]

7. Conclusion and Outlook

In this review, the heavy metal-based dyes and their potential impact on the environment, human and aquatic life were explored. The socio-economic analysis of the different textile wastewater treatment methods was investigated, and graphene-based adsorbents related remediation methods were reviewed. The study of GO adsorbents for heavy metal ion and its related pollutant dyes removal is still in the laboratory research stage. GO as an adsorbent still consists of many difficulties like complicated synthesis process; high-quality yield production; inadequate selectivity of heavy metal ion; unable to ensure its quality and supply; separation and purification after each cycle. However, the progress of commercial applications of graphene or GO-based adsorbents is still at its beginning, and there are tremendous, and new approaches are constantly being explored.^[232,233,234] Preliminary, GO, and its composite nano-structured derivate adsorbents showed excellent adsorption potential for removing metal ions from the textile wastewater. Further, it is necessary to address the current challenges as follows:

- Investigated different types of dyes elaborately from that addressed the heavy metal ion contamination entryway, which then explored the impact on the environment and human health and reviewed the applicable conventional treatment methods to treat these effluents.

- Graphene and its functionalized composites play a significant role in heavy metal removal such as Cr, Pb, As, Zn, Cu, Hg, Cd etc., from wastewater figured out from the extensive literature of this review.
- Graphene and its functionalized composites are predominantly used in wastewater decontamination process due to its surface area, many highly efficient functional groups, and high mobility charge carriers.
- Graphene-based materials are the best replacement for the other carbon-based water filter because graphene can be applied for all types of impurities in wastewater treatment and which also provide highly potentially efficient results in heavy metal removal, organic pollutants etc.; hence, it can be used as the potential substitute in industries for the purification of wastewater with organic effluents above the prescribed limits.
- The obstacles which need to be overcome are things such as mass production and graphene quality. To thrive metal-ion removal capacity requires a large area, defect-free, grain boundary-free, monocrystalline graphene to be readily available and unfortunately, to date that has not been achieved. It is debatable that it exhibits some toxic qualities.
- Production of high-quality graphene is expensive, containing a complex fabrication process, involving toxic chemicals, and restricted chemical reactions. Besides, it requires a high temperature during the growth process and at the same time susceptible to the oxidative atmosphere.
- To overcome the costly synthesis process of graphene, it is required to make graphene from natural resources or modify the physicochemical properties of GO or rGO to get a high-quality performance similar to graphene. GO, or rGO is readily and cheaply scalable for industrial production, but suffers from the lesser surface area, and degraded thermo-electrical quality.
- Therefore, GO's challenges in retaining the favourable adsorbent properties in terms of porosity, crystallinity, and ease of processing. As such, future avenues of graphene-based adsorbent research to achieve natural environmental friendliness and cost-effective will undoubtedly stem from the interplay between laboratory scale to industrial scale experimental discoveries.
- Nevertheless, considering the optimization of reaction procedures and environmentally friendly synthetic routes, graphene and graphene oxide will achieve more cost-effective industrialization acceptance. Also, few functional modifications methods should be developed, such as non-alkali carbonylation and carbon-carbon multi-bond addition reactions, which are rarely reported in GO and further its adsorption characteristics.
- There are still many open issues and opportunities for further research efforts. Accordingly, more studies are also

needed to make full use of the outstanding structural and electronic properties of GO in the composite adsorbent.

- Purifying water using today's technology is expensive and energy-intensive; there is a pressing need for new research to identify novel approaches to purify water at a lower cost, use less energy, and significantly minimise the impact on the environment. Water treatment processes employ several membranes based on their pore sizes: reverse osmosis, nanofiltration, ultrafiltration, microfiltration, and particle filtration.

Notes

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