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Graphene-based nanocomposites: An efficient detoxification agent for heavy metal removal from wastewater

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Numerous scientific and technological developments in wastewater treatment procedures are brought on by the shortage of clean water supplies. Heavy metals' recalcitrance in wastewater has been shown to be a difficult issue. Further, drinking water quality must be at its highest for human health to be at its best; nevertheless, a number of human activities are continuously degrading it, which has an effect on human health either directly or indirectly. Because heavy metals are the primary causes of many chronic illnesses and have a tendency to bio accumulate, they are giving rise to a lot of worries. Technologies from all over the world are being developed to address the demand for clean drinking water. The objective of the current study is to raise awareness of the need to remove dangerous dense metals from various types of wastewater and the application of modified graphene nanocomposite for their adsorption-based removal. Graphene-based nanocomposite materials have been picked for this application due to their large surface area, superior mechanical strength, and reactivity towards polar and nonpolar contaminants for the electrostatic emission of the heavy metal ions arsenic (As), chromium (Cr), copper (Cu), and lead (Pb).

Keywords: Graphene nanocomposite, Decontamination, Pollutants, Heavy metals, Adsorption

Heavy metals like arsenic (As), chromium (Cr), copper (Cu), and lead (Pb) have been introduced into water and soil as a result of anthropogenic activities. Heavy metals are neither biologically degraded nor break into harmless end products; they are permanently added to our environment in elemental or ionic form. Therefore, their high concentration rises above the allowed limit[1,2]. They enter in water, soil and cause fouling thus increasing the toxicity level in the successive food chain[3]. The lungs, kidney, liver, skin, and other organs are all damaged by the hazardous concentration of these dense metal ions, in addition to the peripheral nervous system. They even cause cancer when present in larger concentrations[4]. They typically come from industrial, agricultural, natural resource and traffic discharge operations. The continuous increase in their toxicity levels in water and soil, demand new methodologies for the decontamination with special features in the water purifier industry[5]. Arsenic, chromium, copper, and lead have respective upper limits of 0.05 parts per million (ppm), 0.05 ppm, 2 ppm, and 0.01 ppm in India[6]. Above these levels, all water contaminants have a negative impact on people.

Water treatment mainly involves the processes which make the water more suitable and contamination-free for the direct use of living beings. Idealised cycle for water uses is shown in Fig. 1. Adsorption[7], precipitation, membrane separation[8], amalgamation, ion-exchange[9,10], reverse osmosis, nanofiltration[11], electrodialysis[12], advanced oxidation technologies[13], chemical precipitation[14] and flotation process[15] are some of the technologies used to remove these hazardous dense metals from waste aqueous phases. Among these processes, adsorption is emerging as potentially favoured in view of its high selectivity, more efficient, cost-effectively, design flexibility & regeneration[16]. Magnetic separation revealed that the endothermic & spontaneous chemisorption reactions of these dangerous heavy metallic ions were recyclable[17]. The most pressing need for humanity is the investigation of methods for heavy metal removal that are both affordable and energy efficient.

Graphene is the form of carbon that is sp^2 hybridized and has a honeycomb-like structure with conjugated π- bonds, which gives mechanical as well as thermal strength to their sheets[18]. It contains an

Fig. 1 — Idealized cycle for water uses

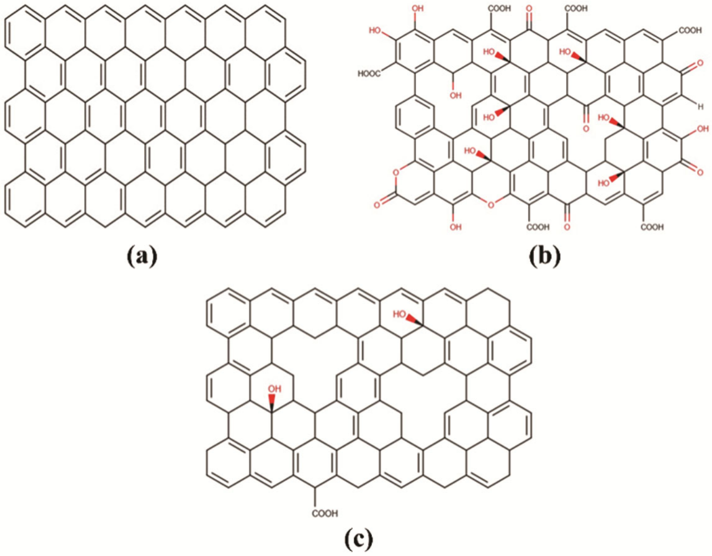

Fig. 2 — Arrangement of (a) graphene, (b) graphene oxide (GO) and (c) reduced-graphene oxide (r-GO) sheet

enormous aerial surface (2300 m^2/g) which exhibits efficient adsorption capacity and adsorbent affinity on toxic metals[7]. Its 2D structure enhances its suitability. The preparation of graphene can be done both top-down and bottom-up. Bottom-up preparation is used when organic and tiny molecules undergo chemical reactions, whereas top-down preparation is used for preparations resulting from chemical derivations. Since preparation of graphene is not very easy, use of reduced-graphene oxide is more popular, which requires oxidation of graphene (GO), usually by Hummer's method, followed by reduction in suitable environment (Fig. 2). Modifications in the oxidant of Hummer's method and proper control of temperature can lead to formation of single-layered GO[19]. The drying step followed by oxidation is yet another important step, as direct drying may lead to stacked layers, which would not allow diffusion of pollutants and create restriction in adsorption. Instead, lyophilization, produces a porous structure removing water molecules by sublimation[20]. The large numbers of oxygen functional groups at the surface sites leads to huge active sites for the electrostatic attraction with the heavy metals (Fig. 3). Reduced graphene oxide (RGO) has lesser oxygen atoms. The positively charged heavy metals are bound by the negatively charged oxygen atoms and groups. Through the adsorption process, this attraction plays a significant role in the decontamination operations of contaminated water[21]. In the present scenario, increasing the active sites via functionalization of graphene enhance the utility and efficiency of decontamination[22-24]. For adsorption application, covalent functionalization is mostly adopted as non-

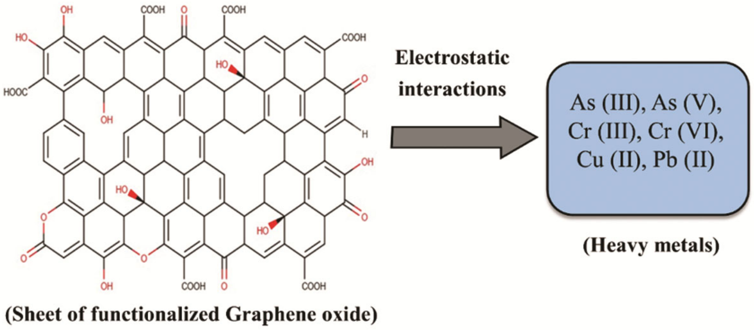

Fig. 3 — Feasible schematic interaction profile between functionalized graphene oxide and heavy metals

covalent functionalization may produce graphene-polyphenols[25]. Graphene can also be used in the form of sponge. The sponge structure can easily diffuse the pollutants and enhance the adsorption activity[26]. Lyophization can be used for the fabrication of graphene sponge. Because of their promising and intrinsic properties, the continuous modification of graphene as membrane, composite, and nano-materials have exhibited much attention in the application part (chemical, biochemical and different biological field)[27].

Over the years, modified graphene in different forms have played important roles in water purification and given more attention to improving the purification capacity of water[28]. Modified graphene-like graphene nanomembrane, graphene nanocomposite has been proven to be most promising candidate for the purification processes of water[29]. It takes a remarkable action in the purification of water with higher efficiency and long-term durability[30]. The presence of different functional groups in graphene-based nanocomposites with respect to cationic and anionic heavy metals is the primary mechanism for the removal of heavy metal ions from wastewater.

The structure of graphene and its forms and the functional groups play an important role in governing the adsorption phenomena[31]. The oxygen rich structure of GO attracts the positive charged heavy metals, cationic dyes and other positively charged contaminants. The performance of GO is affected by pH variation; for example, if GO is placed in an alkaline environment, the carboxylic groups become deprotonated, enhancing its adsorption activity. However, GO is not suitable for negatively charged pollutants on account of electrostatic repulsion, π-π interaction, hydrophobic interaction, H-bonding are the other interactions responsible for graphene and its forms to act as adsorbent, however, they are not of much importance for positively charged heavy metals[32]. Adsorbent properties, its chemistry, the pH of the solution, the presence of foreign ions, and temperature are some of the variables that might affect the adsorption process. An adsorbent with good affinity adsorbs a large number of metal ions. Similarly, low temperature and fewer foreign ions, enhance the adsorption process.

In this review, we have discussed systematically the role of modified graphene nanocomposite to extract the heavy metals (i.e. arsenic, chromium, copper, and lead) to improve the water quality for living beings. The chemical and structural properties of graphene-based nanocomposites have shown excellent adsorption capacity and can be used like new adsorbent materials for water treatment. The valid chemical variation on the surface of graphene has exhibited enhancement in the adsorption power of the materials.

Basic kinetics models associated with adsorption

First, second, pseudo-first, and pseudo-second order models have been used to simulate the kinetics of metal ion adsorption on the desired adsorbent in order to identify the governing mechanism of adsorption processes[33].

Simple first and second order rate equations

A basic first and second order equation that takes into account the effects of the system's initial metal ions concentration and various adsorbent dosages may be used to explain the metal ion's adsorption kinetics.

$$\frac{-\mathrm{dCt}}{\mathrm{dt}} = \mathrm{K}_1 * \mathrm{C}_0 \qquad \text{... (1)}$$

$$\frac{\mathrm{dCt}}{\mathrm{dt}} = \mathrm{K}_2 * (\mathrm{C}_t)^2 \qquad \text{... (2)}$$

C_t = Metal ion concentration at time t, C_0 = Initial metal ion concentration, K_1 = First order rate constant, and K_2 = Second order rate constant.

Pseudo-first-order and pseudo-second-order rate equations

Pseudo-first and second order, have been also used for the capacity of the solid adsorbent applied for the liquid/solid system.

$$\frac{dqt}{dt} = K_1 * (q_e - q_t) \quad \dots (3)$$

$$\frac{dqt}{dt} = K_2 * (q_e - q_t)^2 \quad \dots (4)$$

q_e = Adsorption capacity at equilibrium, q_t = adsorption capacity after time t, K_1 = pseudo-first order rate constant, and K_2 = pseudo-second order rate constant.

Arsenic (As)

Arsenic exists in the form of oxides in the soil as well as in water with various oxidation state (-3, +3, 0, and +5)[34]. Variability in an oxidation state of arsenic comes under the pH of the medium[35]. As(III) oxidation state exists when pH is lower than 9.2 while As(V) oxidation state is predominant at different pH (6-9) range. Because of the high mobility of As(III) oxidation state, these are more toxic in comparison to As(V)[36]. So, oxidizing agents like chlorine, hydrogen peroxide (H_2O_2), permanganate, ozone (O_3), and per sulfate-doped systems were usually imposed to oxidize As(III) to As(V) oxidation state[37]. The penetration of arsenic into groundwater as As(III) and As(V) via different routes like industrial effluents, deposition of rocks, volcanic radiation, bioscience sources, and geothermal responses occur. The primary path of arsenic intake for living things is portable water. Continuous exposure of arsenic to the body affects the central nervous system, kidney, skin, liver, heart, and lungs in living organisms[38,39]. Long term contact with arsenic leads to skin problems. To standardize the condition, World Health Organization (WHO) has fixed the current yardstick for the maximum concentration range for arsenic ions in water to be 10 µg/L, by Community of European is 0.01 mg/L and by regulation of water quality of India is 0.05 mg/L (Table 1)[40,41]. Therefore, the fabrication of powerful and efficient filters is the necessity to assure the new path for arsenic extraction.

Modified graphene oxide nanocomposite for the extraction of arsenic ions from water

Graphene oxide composite can play a vital role in the water treatment sector for the removal of arsenic from water. Mishra and Ramaprabhu (2011) explored hydrogen exfoliated graphene sheets (HEG) with concentrated HNO_3 to impart hydrophilic functionalized groups at the surfaces of HEG sheets. With these functional groups, the capturing power of metals in water was higher. The calculated specific surface area for this composite was 442.87 m^2/g with removal efficiency approximately 65% (As)[42]. Zhu *et al.* (2012) synthesized magnetic graphene nanocomposite based on Fe_2O_3 nanoparticles (NPs) by thermal decomposition technique in order to the separation of arsenic ions. Grafted NPs of graphene nanoplatelet enhanced the adsorption active sites applying magnetic field externally. The maximum capacity of adsorption of this nanocomposite was approximately 11.34 mg/g[43]. Sheng *et al.* (2012) synthesized a magnetic graphene oxide (MGO) composite by using co-precipitation process using $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ solution to dope Fe_3O_4 on the GO nanosheets. The maximal adsorption was 59.6 mg/g for MGO composite in comparison to pure GO (80.1 mg/g)[44]. Vadahanambi *et al.* (2013) synthesized 3-D graphene-carbon nanotube-iron oxide nanocomposite and found that the vertical standing of carbon nanotube (CNT) on graphene sheets and iron oxide nanoparticle increased the adsorbing power. The highest adsorption was found at approximately 6.5 mg/g for arsenic[45]. Wen *et al.* (2013) synthesized an easy and well-planned method to develop a nanocomposite based on double-layered hydroxides by the hydrothermal process by varying the composition of graphene oxide (LDHs/GO). The LDHs solution made from the mixture of $MgCl_2-AlCl_3-$HMT (hexamethylenetetramine) showed optimum adsorption of 183.11 mg/g with 6.0% of GO with a maximal area of 35.4 m^2/g[46]. Paul *et al.* (2015) outlined that the grafting of humic acid in Fe_3O_4-GO nanocomposite

Table 1 — The MPL norm for various dangerous heavy metals[6]

Heavy metals	Affecting areas of human body	Maximum permissible limit
Arsenic	Central Nervous System, Kidney, Skin, Liver, Heart, Lungs	0.05 mg/L
Chromium	Liver, Spleen, Kidney, Human Eyes, Reproductive organs	0.05 mg/L
Copper	Nervous System, Reproductive System, Connecting Tissues, Circulatory System	2.0 mg/L
Lead	Brain Growth, Genetic Disorder	0.01 mg/L

Table 2 — Adsorption capacity for Arsenic ions by different modified graphene-based adsorbents

Adsorbent	Process/Technique	Adsorption capacity	References
Functional based HEGs (Hydrogen exfoiled graphene sheets) based on con. HNO_3	Thermal exfoliation	139 mg/g	42
Fe_2O_3 doped Graphene nanocomposite	Thermal decomposition	11.34 mg/g	43
Magnetic graphene oxide (MGO prepared by using $FeCl_3.H_2O$ and $FeCl_2.H_2O$ solution doping on the graphene oxide nanosheets)	Co-Precipitation	59.6 mg/g	44
3-D graphene-carbon nanotube-iron oxide nanostructures	Microwave process	6.5 mg/g	45
Double layered hydroxides [$MgCl_2$−$AlCl_3$−HMT(hexamethylenetetramine)] and varying composition of graphene oxide	Hydrothermal process	183.11 mg/g	46
Fe_3O_4 doped graphene oxide with coating of humic acid (HA)	Co-Precipitation	61.73 mg/g	47
Magnetite (Fe_3O_4)-graphene oxide (M-GO) and magnetite-reduced graphene oxide (M-rGO)	Chemical reduction	85 mg/g from M-GO 57 mg/g from M-rGO	48
Eu-MGO/Au@MWCNT	Electrochemical Technique	320 mg/g for arsenite and 298 mg/g for arsenate	49
Fe_3O_4/RGO/Cu-ZEA	Solid state dispersion (SSD) method	50.51 mg/g	50
Magnetite/non-oxidative graphene (M-nOG)	Thermal treatment physical exfoliation	38 mg/g for arsenite and 14 mg/g for arsenate	51
Iron oxide-graphene oxide (GO)	Co-Precipitation	147 mg/g and 113 mg/g for arsenite and arsenate	52
Graphene oxide-manganese ferrite (GMF)	Co-Precipitation	102 mg/g for arsenate	53
Graphene oxide/ copper ferrite foam (GCFF)	Hydrothermal method	51.64 mg/g for arsenite and 124.69 mg/g for arsenate	54
Fe_3O_4@CuO&GO	Co-Precipitation	70.36 mg/g and 62.60 mg/g for arsenite and arsenate	55
SGO@LDH	Spray assisted deep frying	149.3 mg/g for As(III)	56

enhanced the removal efficiency by almost two times at pH 7 and reached the maximum capacity of 61.73 mg/g[47]. Yoon *et al* .(2016) synthesized MGO as well as magnetite-reduced graphene oxide (M-rGO) using hydrazine for arsenite and arsenate extraction. The active sites present in MGO were more in comparison to M-rGO, resulting in the higher removal efficiency[48]. Roy *et al.* (2016) fabricated magnetic graphene oxide doped with europium along with gold NPs functionalized multi-walled carbon nanotube (Eu-MGO/Au@MW CNT) hybrid adsorbent. The adsorption capacity for arsenate and arsenite was 320 mg/g and 298 mg/g[49]. Khatamian *et al.* (2017) prepared a hybrid by using Cu-exchanged zeolite with reduced graphene oxide (rGO) that had only 50.51 mg/g of adsorption[50]. Yoon *et al.* (2017) incorporated magnetite/non-oxidative graphene (M-nOG) complex from scale-up manufacturing procedure. The maximal adsorption was located to be 38 mg/g and 14 mg/g for arsenite and arsenate sequentially[51]. Su *et al.* (2017) fabricated iron oxide with GO nanocomposite adsorbent with varying amounts of iron oxide from 36-80 wt%. The maximal adsorption was spotted around 147 mg/g and 113 mg/g for 80% iron loading for arsenite and arsenate[52]. The greatest adsorption was reported to be 102 mg/g when Shahrin *et al.* (2018) created a graphene oxide-manganese ferrite (GMF) nanohybrid using the co-precipitation method to detoxify water from arsenate ions[53]. Wu *et al.* (2018) fabricated graphene oxide (GO) and copper ferrite hybrid on Fe-Ni foam via hydrothermal method for the arsenite and arsenate extraction. The capacity of adsorption for arsenite and arsenate was 51.64 mg/g and 124.69 mg/g respectively[54]. Wu *et al.* (2019) synthesized magnetic hybrid using Fe_3O_4 and CuO on graphene oxide (GO) layers by co-precipitation technique also found 70.36 mg/g and 62.60 mg/g as the adsorption capacity for arsenite and arsenate, sequentially (Table 2)[55]. Kamali *et al.* (2022) synthesized nano spherical graphene modified with layered double hydroxide (SGO@LDH) using spray assisted deep frying process and shown optimum capacity of 149.3 mg/g for As(III) ions[56].

Chromium (Cr)

Chromium metal is the most common metal on the earth's surface. It consists of various oxidation forms from -2 to +6 however too popular are +3 and +6[57].

These oxidation states are mainly existent in the form of halides, sulfides, and oxides[58]. Chromium(VI) is much virulent from chromium(III) as it exhibits high mobility in water, soil, and plants and gets readily absorbed by cells[59,60]. These oxidation states of chromium are generated mainly by industrial effluents, fertilizers, sewage, etc. These effluents cause Cr to enter the food chain through the agriculture system[61]. Mostly liver, spleen, and kidney are affected by chromium. Chromium(VI) easily penetrates the RBCs and gets converted into Cr(III), which form a complex with RBCs; thus, affecting the lung and heart functions[62]. Human eyes and reproductive functions are impacted by the increasing concentration of Cr. Consumption over time reduces the immune system's effectiveness and serves as a major contributor to the development of many diseases, including cancer[63]. By the Environment Protection Agency, the maximum concentration limit standardized for both oxidation states (+3 and +6) of Cr is 0.1 mg/L, in the European countries that value is 0.5 mg/L and by the regulation of water quality India MCL is 0.1 mg/L (Table 1)[40,41].

Modified graphene oxide composite for the decontamination of water from chromium ions

Yuan *et al.* (2013) developed Mg-Al doped graphene double hydroxides nanocomposite to achieve adsorption of Cr (VI) ions with potent efficiency. The maximum capacity of adsorption was nearly 172.55 mg/g with a 1.0 g/L dose of Mg-Al-graphene[64]. Li *et al.* (2014) synthesized magnetic chitosan GO-ionic liquid (MCGO-IL) composite adsorbent for chromium ions sorption. The resulted composite displays maximal adsorption of 145.35 mg/g[65]. Chauke *et al.* (2015) developed GO-alpha cyclodextrin-polypyrrole hybrid nano composite for the harmful chromium ions emission from wastewater. GO was functionalized with alpha-cyclodextrin followed by treatment with polypyrrole to form the composite. The supreme adsorption limits were from 606.06 to 666.67 mg/g[66]. Ge and Ma (2015) synthesized a novel triethylenetetramine graphene oxide/chitosan (TGOCS) hybrid adsorbent by the microwave irradiation system for chromium ions emission. The optimum competency of adsorption was 219.5 mg/g at pH 2 in 20 min. The huge capacity observed was because of the high reactivity of chromium ions on TGOCS composite not only because of surface area, specific surface area[67]. Guo *et al.* (2015) formed a magnetic composite via doping of 1, 2-diamino cyclohexane tetraacetic acid into magnetic graphene oxide (DCTA/E/MGO) and found the maximum capacity of adsorption to be approximately 80 mg/g at low pH[68]. Zhao *et al.* (2016) developed a magnetic ternary compound amino-functionalized graphene oxide supported with Fe_3O_4 nanoparticles (AMGO) for the hexavalent chromium sorption and reduction of chromium (VI) to chromium (III) atoms from waste aqueous. The capability of adsorption based on Langmuir isotherm was predicted around 123.4 mg/g[69]. He *et al.* (2017) synthesized 3-aminopropyl triethoxysilane-functionalized GO (AS-GO) nanocomposite for the chromium ions detoxification. In this nanocomposite, 3-aminopropyltriethoxysilane plays an important role. When it reacts with heavy metals like chromium, the organosilane forms stable chelates. The optimum capacity of adsorption was estimated at 215.2 mg/g at 328 K[70]. Al nafiey *et al.* (2017) fabricated rGO-cobalt oxide (rGO-Co_3O_4) nanocomposite adsorbent for the hexavalent chromium ions extraction from contaminated water. The optimum adsorption of this magnetic nanocomposite was reported to be 208.8 mg/g[71]. Fang *et al.* (2018) synthesized nanocomposite based on polypyrrole supported on graphene/silica nanosheets by sol-gel method for chromium ions extraction. The maximum capacity of adsorption was outlined to be 429.2 mg/g at pH 2 and room temperature[72]. Zhang *et al.* (2018) created rGO /Ni-O nanocomposite at room temperature for the removal of hexavalent chromium ions from industrial water. The optimal adsorption was found to be 198 mg/g at pH 4 at room temperature, indicating that the adsorption behaviour relied on pH, not temperature[73]. Samuel *et al.* (2019) prepared a nanocomposite of chitosan supported GO (CS-GO) in batch operation from ultrasonic irradiation technique for the detoxification of water from chromium ions. Based on the Langmuir isotherm the adsorption capability was reported as 104.16 mg/g[74]. Wang *et al.* (2019) fabricated Fe_3O_4/graphene nanocomposite obtained from potassium humate, it contains a number of functional groups having oxygen and shows excellent adsorbent properties for the decontamination of water. The sorption capability for chromium ions was 280.6 mg/g (Table 3)[75]. Pan *et al.* (2022) synthesized amino functionalized magnetic graphene based composite (TEPA-GO/$CoFe_2O_4$) by one step hydrothermal reaction and shown 114.81 mg/g adsorption capacity for Cr(VI) ions[76].

Table 3 — Adsorption capacity of Chromium ions by different modified graphene planted adsorbents

Adsorbent	Process/Technique	Adsorption capacity	References
Mg-Al doped graphene double hydroxides	Hydrothermal reaction	172.55 mg/g	64
Magnetic chitosan graphene oxide-ionic liquid (MCGO-IL) composite	Ultrasonication	145.35 mg/g	65
Graphene oxide-alpha cyclodextrin-polypyrrole hybrid nanocomposites	Polymerization	606.06 mg/g to 666.67 mg/g	66
Triethylenetetramine modified graphene oxide/chitosan (TGOCS)	Microwave irradiation method	219.5 mg/g	67
1,2-diaminocyclohexanetetraacetic acid into magnetic graphene oxide (DCTA/E/MGO)	Chemical reaction	80 mg/g	68
Amino functionalized graphene oxide supported with Fe_3O_4 nanoparticles (AMGO)	Hydrothermal method	123.4 mg/g	69
3-aminopropyltriethoxysilane-functionalized graphene oxide (AS-GO)	Refluxing method	215.2 mg/g	70
rGO-Co_3O_4	Chemical reduction	208.8 mg/g	71
GS-PPy (polypyrrole-graphene/silica)	Polymerization	429.2 mg/g	72
Graphene oxide/NiO	Chemical reduction	198 mg/g	73
chitosan supported graphene oxide (CS-GO)	Ultrasonic and Solvothermal	104.16 mg/g	74
Fe_3O_4/graphene nanocomposite obtain from potassium humate	Co-Precipitation/Calcination	280.6 mg/g	75
TEPA-GO/CoFe2O4	One-step hydrothermal	114.81 mg/g	76

Table 4 — Adsorption capacity of Copper ions by different modified graphene-based adsorbents

Adsorbent	Process/Technique	Adsorption capacity	Reference
Graphene oxide	Redox method	117.5 mg/g	89
Polyvinyl alcohol/chitosan hydrogel compounded with graphene oxide	Instantaneous gelation method	162 mg/g	90
Magnetic graphene oxide-supported with β-cyclodextrin	Wet chemical	65 mg/g	91
Poly allyl amine hydrochloride (PAH)-graphene oxide (GO)	Chemical reaction	349.03 mg/g	92
Magnetic polyaniline/graphene oxide (MPANI/GO)	Polymerization/Calcination	101.94 mg/g	93
Carboxyl functionalized graphene oxide (GO-COOH)	Chemical reaction	357.14 mg/g	94
Magnetic chitosan-graphene oxide (MCGON) nanocomposite	Co-precipitation	217.4 mg/g	95
SA/PVA/GO (SPG)	Encapsulation	247.16 mg/g	96
Fe_3O_4@GO/MnO_x	Hydrothermal	62.65 mg/g	97
Functionalized graphene nano sheets (FGNs)	Oxidation method	103.22 mg/g	98
GO-EDTA-CS	Covalent binding and electrostatic interaction	130 ± 2.80 mg/g	99

Copper (Cu)

In general, copper is a crucial component in the human body to maintain the catalytic activity of enzymes[77-79]. It mainly exists as a +2-oxidation state and plays an important role as both nutrient and toxicant in a small amount. However, some salt of copper is poisonous. The higher concentration of Cu affects gastrointestinal function then consecutively nervous system, reproductive system, connective tissues, and circulatory system[80-83]. Disruption of Cu absorption and excretion in the human body causes Menkes and Wilson's disease[84-87]. Acute toxicity, chronic toxicity, genotoxicity, mutagenicity, and carcinogenicity, all rise in water due to heavy metal ions[88]. The maximum concentration level of copper ions in the human body fixed by the Environmental Protection Agency is 1.0 mg/L, by the European community is 3.0 mg/L, and by regulation of water quality of India 0.01 mg/L[40,41]. To resolve this copper toxicity level to the living beings various modified graphene composite were synthesized and has been reviewed.

Modified graphene oxide composite for Copper ions detoxification from muddy water

Wu *et al.* (2013) applied GO adsorbent like removing agent of Cu(II) from dense water and studied the effect of the pH, adsorption time as well as the initial dosage of GO. As we increase the pH values from 1.0 to 5.3, the capacity of adsorption increases up to 39, 62.5, and 79.5 mg/g by taking 50, 100, and 150 mg/L of preliminary copper ion concentration, due to affect the surface charge by pH (Table 4)[89]. Li *et al.*

(2015) synthesized a unique graphene oxide bio-adsorbent based on polyvinyl alcohol/chitosan hydrogel. The maximum capacity of adsorption for copper ions containing water was 162 mg/g at 30°C. The regeneration of the adsorbent was possible with the help of an HNO_3 solution[90]. Hu *et al.* (2015) designed the magnetic GO-carried with β-cyclodextrin for copper ions detoxification from industrial wastewater. The appearance of $LiNO_3$, NaCl, KNO_3, $NaNO_3$, $NaClO_4$, and citric acid in an aqueous solution enhanced the extraction of Cu ions from water and the rate of adsorption was controlled by the film diffusion method[91]. Xing *et al.* (2015) fabricated composite based upon GO nanolayers supported to polyallylamine hydrochloride (PAH), a water-soluble polymer with large density, by cross-linking reaction for the detoxification of different Cu ions forms and showed a strong dependency on pH and temperature while weak dependency on ionic strength. The optimum value of adsorption reported was 349.03 mg/g[92]. Liu *et al.* (2016) synthesized a magnetic polyaniline/graphene oxide (MPANI/GO) composite for the copper ions emission. Polyaniline contains an amino imide group that was responsible for the detoxification of heavy metals like copper. The optimum adsorption capacity under the batch mode operation reported for MPANI/GO composite was 101.94 mg/g[93]. White *et al.* (2018) prepared GO with carboxyl functional groups (GO-COOH) nanocomposite adsorbent using chloroacetic acid (Cl-CH2-COOH) & graphene. In the carboxylation process, the –OH group changes into –COOH groups which enhance the adsorption of copper ions. The optimum adsorption capacity according to Langmuir isotherm was reported to be 357.14 mg/g[94]. Similarly, Hosseinzadeh and Ramin (2018) prepared magnetic chitosan-graphene oxide (MCGON) nanocomposite adsorbent. This nanocomposite consists of GO supported with ethylenediamine (ED), Fe_3O_4 NPs, and chitosan-g-poly (acrylic acid-co-2-acrylamido-2-methylpropane sulfonic acid) copolymer with various branches of -C=O, –COOH, $-SO_3H$, -OH, -C-O-C, $-NH_2$ which indicate the novel adsorbent for the adsorption of copper dense metal atoms[95]. Yi *et al.* (2018) formed a hydrogel adsorbent based on sodium alginate (SA)/polyvinyl alcohol (PVA) supported on graphene oxide for the separation of copper ions from wastewater. Sodium alginate has various carboxyl and hydroxyl groups, which are responsible for effective copper ions adsorption[96]. Zhang *et al.* (2018) fabricated Fe_3O_4@GO/MnO_x nanocomposite using hydrothermal reaction which contains $KMnO_4$ as a MnO_x source. MnO_x showed a very high activity because of the existence of oxygen functional groups. Magnetic graphene oxide further enhanced copper adsorption. The optimum capacity of adsorption estimated for copper ions was 62.65 mg/g at 303.15 K according to Langmuir adsorption isotherm under batch operation[97]. Cao *et al.* (2019) developed an adsorbent based on functionalized graphene nanosheets (FGNs) by oxidation process containing many functional groups for the copper ions detoxification from waste effluents. The optimum adsorption capacity was reported 103.22 mg/g using Freundlich isotherm[98]. Verma *et al.* (2022) synthesized GO-EDTA-CS composite by using covalent binding followed by electrostatic interaction process. The optimum capacity was 130 ± 2.80 mg/g for copper ions from waste water[99].

Lead (Pb)

Lead is counted as one of the most poisonous xenobiotic heavy metals[100]. It mainly occurs in the +2-oxidation state in oxide and carbonate form. A trace amount of lead can cause various health risks[101]. Non-biodegradability properties of this metal are the major cause of their toxicity as it continuously persists in soil, water, and successive food chain[102-105]. The lead toxin affects the development of the brain, with children being more affected than adults. It also has an ongoing influence on subsequent generations and has the potential to lead to hereditary problems[106-108]. The primary roots of lead in water are industrial activities, dust, paint, and various anthropogenic activities in water, soil, and food. Lead poisoning is also known as plumbism[109]. The neurological system, hematopoietic system, nephrological system, gastrointestinal tract, and cardiovascular system are all impacted by the toxic concentration of lead, in addition to the immune system[110-112]. The maximum concentration limit fixed by Environment Protection Agency is 0.1 mg/L, by European Community is 0.5 mg/L and by regulation of water quality in India is 0.1 mg/L for the living beings[40,41]. Continuous increase in the toxic degree of lead in successive food chain leads to serious concern for the researchers and motivates in searching new methodology to resolve this problem. Out of various technologies, one of them is modified graphene. It plays a crucial role to detoxify the water from heavy metals.

Table 5 — Adsorption capacity of lead ions by different modified graphene-based adsorbents.

Adsorbent	Process/Technique	Adsorption capacity	Reference
EDTA-GO	Silanization process	525 mg/g	113
EDTA-magnetic graphene oxide (EDTA-mGO)	Mechanical ribbling	508.4 mg/g	114
Graphene oxide-cysteamine (GO-SH_3)	Chemical bonding	243 mg/g	115
HMO@GO	Chemical bonding	553.6 mg/g	116
HPA-GO	Chemical reaction	819.7 mg/g	117
GO-mβCD	Sonication	312.5 mg/g	118
Magnetic chitosan-functionalized 3D graphene (MCF3DG)	Hydrothermal	957.28 mg/g	119
Nickel ferrite-reduced graphene oxide (NFRGO)	Co-precipitation	33.418 mg/g	120
Attapulgite (ATP)-graphene oxide	Hydrothermal reaction	450.9 mg/g	121
Graphene oxide	Modified Hummers method	11.57 mg/g	122
rGO-Mn_3O_4	Hydrothermal reduction	130.28 mg/g	123

Modified composite of graphene oxide for the detoxification of water from lead ions

Various modified graphene which was used to decontaminate the water from lead by the researchers have reviewed as follows (Table 5): Madadrang *et al.* (2012) formed an EDTA (Ethylene diamine tetraacetic acid) based graphene oxide composites for lead adsorption. The specific surface area of EDTA-GO was found 623 m^2/g and the highest capacity of sorption was 525 mg/g at 6.8 pH[113]. Cui *et al.* (2015) prepared an adsorbent based on magnetic GO functionalized along with EDTA (EDTA-mGO) and obtained adsorption of 508.4 mg/g[114]. Yari*et al.* (2015) prepared a composite of graphene oxide-based on thiol functional groups by the variable cysteamine concentration like 60 mg (GO-SH1), 80 mg (GO-SH2), and 100 mg (GO-SH3) for the Pb ions. The effects of various parameter like contact time, temperature, pH and cysteamine dosage on desorption. As we increase these parameters, the adsorption rate also increases. The capability was 217 mg/g for GO-SH1, 222 mg/g for GO-SH2, and 243 mg/g for GO-SH3, respectively for pseudo-second-order reaction[115]. Wan *et al.* (2016) proceed nanocomposite based on hydrated manganese oxide supported on GO (HMO@GO). HMO@GO plays a crucial role in enhancing activity as well as selectivity against lead metal ions. The optimum adsorption capacity reported approximately 553.6 mg/g for the Pb ion[116]. Hu *et al.* (2016) synthesized multifunctional hyperbranched polyamine GO (HPA-GO) nucleophilic ring-opening reaction of poly (ethylene glycol) di epoxy and amine monomer then supported on graphene oxide. The optimum adsorption capacity for lead ions was 819.7 mg/g based on Langmuir isotherm[117]. Nyairo *et al.* (2017) fabricated nanocomposite based on GO along with methyl-β-cyclodextrin (GO-mβCD). The optimum capacity of adsorption of this composite was displayed around 312.5 mg/g at 298 K and pH 6, following pseudo-second-order and Langmuir isotherm[118]. Nasiri *et al.* (2018) made magnetic chitosan-functionalized 3D graphene nanocomposite furnished with the $NiFe_2O_4$ NPs (MCF3DG) using a hydrothermal process. The maximal sorption for Pb ions was located to be 957.28 mg/g at pH 8.5 and that was almost 98% lead ions eliminated from waste solutions[119]. Lingamdinne *et al.* (2018) formed nanocomposite based on nickel ferrite-rGO (NF-rGO) as lead ions weapon in industrial effluent. The optimum adsorption capacity was reported 33.418 mg/g when taken 18.38 mg/L initial concentration and 0.55 g/L adsorbent dose at contact time within 83 min[120]. Wei *et al.* (2019) synthesized a material based on attapulgite (ATP)-GO by using the simply hydrothermal process for lead ions removal. Attapulgite is water containing magnesium aluminum phyllosilicate salt showing large cation exchange capacity as well as rapid ecofriendly hydration. The optimum adsorption was reported to be 450.9 mg/g at room temperature according to Langmuir isotherm[121]. Futalan*et al.* (2019) prepared an adsorbent based on graphene oxide by the modified hummer's technique for the extraction of lead. The optimum adsorption was estimated to be 11.57 mg/g at 313 K for lead ions from the Freundlich adsorption isotherm[122]. Lingamdinne *et al.* (2022) synthesized rGO-Mn_3O_4 nanocomposite from hydrothermal reduction approach and shown maximum 130.28 mg/g adsorption capacity for lead ions[123].

The absorption capacity can be enhanced with the addition of carbon materials (such as biomass-derived carbon), polymers, and metal oxide in graphene and its derivative to form the desired composite[124,125]. Further combination of these materials with new generation moving carriers such as PP (polypropylene), LDPE-PP (low-density polyethylene- polypropylene), and PUF-PP (polyurethane foam-polypropylene) might prove to be more effective in the removal of carcinogenic heavy metals[126].

Future perspectives

Water is a crucial natural resource for all living things. Therefore, maintaining their integrity and purity is a major job for researchers. Different innovative technologies are available to convert contaminated water into its decontaminated state. In this direction, nanotechnology plays a significant role as adsorbents in water treatment technology in addition to graphene-based nanohybrid. Graphene is suitable for water treatment due to its variety of features.

- High porosity and larger surface area
- Many functional groups on surface for capture heavy metals
- Eco friendly nature

These characteristics of graphene attract more interest in the area of surface modification to improve the surface area, porosity, and surface functional group for the water purification business. Bi-composite and ternary graphene nanocomposites will receive more attention in the future because of their high reusability, rapid adsorption process, and long durability.

Conclusion

In this study, we examined several synthesized modified graphene that was utilized to purify water of various heavy metals, including arsenic, chromium, copper, and lead. The highest potential adsorption removal capacity with europium-doped magnetic graphene oxide gold nanoparticle composite was reported to be 320 mg/g in the instance of an arsenic metal's most damaging form, arsenite [As (III)]. Similar to the instance of chromium metal, graphene oxide-alpha cyclodextrin-polypyrrole nanocomposite has been found to have a maximum adsorption range of 606.06 to 666.67 mg/g. The highest recorded adsorption capacity (357.14 mg/g) for copper ions was found in a nanocomposite of carboxyl functionalized graphene oxide (GO-COOH). In the case of lead ions, a magnetic chitosan-functionalized 3D graphene nanocomposite outfitted with $NiFe_2O_4$ nanoparticles (MCF3DG) has been reported to have the greatest sorption capacity of 957.28 mg/g. In the description above, the water treatment method has utilized the modified graphene nanocomposite in a series of steps. In order to boost their adsorption capability and produce healthy, disease-free living, our main focus will be on developing functionalized graphene nanocomposites in the future.

Declaration of Competing Interest

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

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