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# 7. Removal of Heavy Metals and Dyes by Modified Graphene Oxide Nanoparticles

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## 7.1 Abstract:

Due to rapid industrialization and other anthropogenic activities the water is pervaded by heavy metals and dyes which makes water unfit for human use. Presence of heavy metals and dyes in water above the permissible range is a challenge for scientists, municipalities, engineers and environmentalists. Heavy metals and dyes are non-biodegradable and toxic in nature which leads to many health and environmental issues. Thus, from an environmental point of view, the removal of dyes and heavy metals is very important. In the same concern, modified graphene oxides had shown high adsorption ability in recent years. This chapter reveals the results of adsorption of heavy metals and dyes by graphene oxide nanoparticles. Various methods with few modifications were used in synthesis of Graphene oxide nanoparticles. The performance of modified graphene oxide nanoparticles with respect to adsorption of heavy metals and dyes was evaluated at different operational parameters such as contact time, dosage of GO, rpm, initial concentration and pH. Uptake and percentage of removal of heavy metals and dyes increased with increase in contact time, rpm and adsorbent dosage. This book chapter provides a method which is efficient, eco-friendly, less time consuming and reusable.

**Index terms**: Heavy metals, degradation, dyes, adsorption

## 7.2 Introduction:

With the rapid industrialization, dye and heavy metal pollution due to discharge from dyeing, tanneries, pulps, textile, petroleum and chemical industries has become the most serious environmental problem. Many dye pollutants are organic molecules containing polar functional groups, which are soluble in water, not easily degradable while heavy metals are inorganic molecules which are non-biodegradable and toxic in nature and could easily diffuse into the environment. Therefore, it is necessary to treat wastewater loaded with heavy metals and dyes before disposal to the water bodies. Various technologies have been studied for removal of dyes and heavy metals from wastewaters, including biodegradation, ultra-filtration, photo-catalytic degradation, oxidation and adsorption. Among these, carbon adsorbents and bio adsorbents are also used for this application [1].

The effectiveness of any adsorption process largely depends on the physicochemical properties of the used adsorbent. Nanotechnology is most emerging field of science and engineering in which nanostructures has being designed, engineered and fabricated by manipulation of matter in ranged from 1 to 100 nm [2]. Nanoparticles have significant properties which makes them apt for adsorption processes [3]. Nanoparticles can be metal based, polymer based and carbon based.

Graphene oxide (GO), a carbon based nanomaterial, presents a wide range of active oxygenized groups on its surface, can be used as an effective adsorbent to remove dyes and heavy metals from water [4]. It also possesses properties such as oxidation-reduction indicator and antiseptic. Among all the activated carbons and other nanocarbontubes, GO is the one of the most promising material to adsorbed heavy metals and dyes [5] due to its large theoretical surface area, hydrophilicity, and negative charge density.

### 7.2.1 Graphene Oxide as the Adorbent for Heavy Metals and Dyes:

This section shows various researches revealing the efficiency of differently synthesized Graphene oxide for adsorption of heavy metals and dyes from waste waters.

### 7.2.2 EDTA-Functionalized Magnetic Chitosan-Graphene Oxide Nano-composites (EDTA-MCS/GO):

Shahzad et al (2017) explored application of Graphene-based two-dimensional nanomaterials in treatment of heavy-metal-rich wastewater. EDTA-functionalized magnetic chitosan-graphene oxide nanocomposites (EDTA-MCS/GO) were prepared by using a reduction precipitation method and applied for the removal of Pb2+, Cu2+, and As3+, from aqueous solutions. FTIR, XRD, SEM, MPMS, zeta-potential and BET characterization of nanocomposites showed the composition of the formed nanoparticles. The various influencing operating parameters, like metal ion concentration, pH, temperature, and contact time on the removal of the metal ions, were investigated [6]. Owing to the functional moieties, large specific surface area, and hydrophilic behaviour the magnetic nanocomposite demonstrated excellent removal ability with a maximum adsorption capacity of 207.26 mg g-1, 42.75 mg g−1 and 206.52 mg g-1 for Cu2+, As3+ and Pb2+ respectively. The equilibrium data was tested by Freundlich isotherms and Langmuir, the result revealed that Pb2+ and Cu2+ followed Langmuir isotherm while As3+ followed Freundlich isotherms. Pseudo-second-order kinetic models was best fitted to the adsorption kinetics. The nanocomposite was reused in four successive adsorptions–desorption cycles, revealing a good regeneration capacity of the adsorbent.

### 7.2.3 Magnetic Graphene oxide:

The magnetic graphene oxide (MGO) were synthesized by fabricating the surface of graphene oxide (GO) with iron particles (Fe3+). The characterization of magnetic graphene oxide includes UV-VIS, FTIR, SEM, XRD and VSM analysis. Efficient removal of heavy metal ions like Pb2+, Cr3+, Cu2+, Zn2+ and Ni2+ were evaluated by using Atomic Absorption Spectroscopy (AAS). The various adsorption parameters for removal of heavy metals were pH (3-9), temperature (25-55°C), contact time (10-65 min) and adsorbent dose (0.002 – 0.016 g) [7].

The maximum adsorption capacities at pH 7 for $Zn^{2+}$, pH 5.0 for $Pb^{2+}$, pH 6 for $Cr^{3+}$, pH 6 for $Cu^{2+}$, and pH 8 for $Ni^{2+}$, ions were 200 mg $g^{-1}$, 62.89 mg $g^{-1}$, 63.69 mg $g^{-1}$ and 51.02 mg $g^{-1}$ respectively. The adsorption processes were endothermic and spontaneous; followed pseudo-second-order kinetics model and Langmuir adsorption isotherm. Additionally, magnetic graphene oxide revealed excellent antimicrobial properties with removal efficiency of 98.78%, 97.15% and 97.68% of Enterobacter agglomerans, E. coli, and Yersinia ruckeri, respectively. On this basis, magnetic graphene oxide has potential for removing the heavy metal ions and effective disinfection control of aqueous solution with economical reusability.

### 7.2.4 Graphene Oxide−Zirconium Phosphate (GO−Zr-P):

The surface of graphene oxide was functionalized by Zirconium (Zr) and Phosphate (P) to form graphene oxide−zirconium phosphate nanocomposite for the removal of heavy metals from aqueous medium. The GO−Zr-P nanocomposite was analysed by X-ray diffraction analysis, transmission electron microscopy, scanning electron microscopy, X-ray photoelectron spectroscopy, and zeta potential analysis [8]. The effects of initial concentrations, pH, and contact time were studied in the removal of heavy metal. The results indicated that, maximum adsorption capacity can be achieved at pH 6 for $Zn^{2+}$, $Pb^{2+}$, $Cd^{2+}$, and $Cu^{2+}$ as 251.58 mg $g^{-1}$, 363.42 mg $g^{-1}$, 232.36 mg $g^{-1}$, and 328.56 mg $g^{-1}$, respectively. After 20 min, removal efficiency was ~99%, through the dispersion of 150 mg of GO−Zr-P nanocomposite in 50 ppm of 100 mL heavy metals solution. The pseudo-second-order kinetic model and followed Langmuir and Freundlich isotherms. The XPS results demonstrated that the adsorption mechanism of zirconium (Zr) and phosphate (P) on the Graphene Oxide (GO), as well as adsorption of metal ions on the GO−Zr-P nanocomposite, were chemisorption, mainly through its surface complexation. The results confirmed that GO−Zr-P nanocomposite could be a promising sorbent for efficient and regenerable removal of heavy metals from aqueous medium.

### 7.2.5 Iron oxide-reduced graphene oxide nanocomposite:

The iron oxide-reduced graphene oxide nanocomposites were synthesized by a facile one-step process. The magnetic iron oxide is highly dispersive in rGO. The morphological makeup of iron oxide-reduced graphene oxide nanocomposites is of very fine spherical particles in Nano range. Fe304-rGO shows saturation magnetization approaching 59 emu $g^{-1}$ and super paramagnetic properties at room temperature. The adsorption of $As^{5+}$, $Pb^{2+}$, and $Ni^{2+}$, onto the Fe304-rGO showed pseudo-second-order kinetic model and followed both Freundlich and Langmuir isotherms, which indicates monolayer adsorption of the adsorbents and surface heterogeneity [9]. Fe304-rGO exhibits magnificent potential for heavy metals adsorption. The maximum monolayer adsorption capacities calculated by Langmuir equation are 65.79 mg $g^{-1}$ for $Pb^{2+}$, 76.34 mg $g^{-1}$ for $Ni^{2+}$, 58.48 mg $g^{-1}$ for $As^{5+}$. The Fe304-rGO nanocomposite demonstrated potential for adsorption of toxic metals ions from aqueous medium.

### 7.2.6 $Fe_3O_4/SiO_2$-GO:

A new approach is reported by Bao et al 2020 for synthesis of magnetic graphene oxide nanocomposite by using n-Propyltrimethoxysilane as cross coupling agent for connecting $Fe_3O_4/SiO_2$ and graphene oxide (GO). The synthesized GO was extracted by the solution with the help of permanent magnet and was used in the removal of cadmium and lead from the aqueous medium [10]. The various operational parameters were examined and the result came to be quite impressive as the adsorption capacity came to be 385.1 mg g-1 for lead (Pb) and 128.1 mg g-1 for cadmium (Cd) respectively. The presence of other metals like sodium (Na) and potassium (K) had little influence on the adsorption capacities of lead and cadmium. The adsorption followed pseudo-second order kinetics and Langmuir isotherms. The synthesized Fe3O4/SiO2-GO nanoadsorbents exhibited magnificent recyclability, reproducibility, and long-time stability. This study indicates that Fe3O4/SiO2-GO adsorbents can be opted as an effective sorbent and in rapid removal of heavy metal ions from aqueous medium.

## 7.3 Conclusion:

Based on researcher reports available, it was observed that graphene based nanoparticles are effective adsorbents for removal of heavy metals like cadmium, copper, chromium, mercury, lead and commercial dyes from water. The removal capacity of functionalized graphene oxide nanoparticles was found to be higher than traditional sorbents. In the study it was found that heavy metal loaded nanoparticles can be reused after desorption of heavy metal by treating them with suitable chemicals which makes them more useful for water treatment. Further, it was also observed that graphene based nanoparticles with treatment with other plant extracts or chemical can be efficiently used for removal of more than one heavy metal and dye from the water. By this it is concluded that graphene based nanoparticle can be used in the treatment of wastewater for removal of heavy metals and commercial dyes as these are environmental friendly, easy to use, effective and time saving process. Furthermore, with advancement of nanotechnology, Nano filters of graphene oxide can be prepared and effluent can pass through these filters before the discharge of effluent to water streams for efficient removal of toxic metals and dyes.

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